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THERMODYNAMICS OF HYDROTHERMAL SYSTEMS AT ELEVATED TEMPERATURES AND PRESSURES

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ABSTRACT. Chemical relations in hydrothermal systems can be described in terms of the thermodynamic properties of minerals, aqueous species, gases, and concentrated sodium chloride solutions. Sufficient thermodynamic data are available to permit calculation of equilibrium constants for a large number of hydrothermal reactions at high temperatures and pressures. Where these data are incomplete, the calculations involve entropy estimates, application of average heat capacities, and/or assumptions concerning the temperature dependence of thermodynamic variables and the relative importance of electrostatic and non-electrostatic interaction among the aqueous species in hydrothermal solutions. High temperature stoichiometric activity coefficients for individual ions can be calculated using deviation functions computed from osmotic coefficients for concentrated sodium chloride solutions. The results of such calculations, together with computed heat capacities, enthalpies, entropies, and equilibrium constants for many hydrothermal species and reactions at high temperatures are presented in tables and diagrams. The methods, assumptions, and equations employed in the calculations are summarized in general notation. The numerical information contained in the tables permits calculation of the solubilities of silicates, sulfides, carbonates, sulfates, and oxides in multicomponent hydrothermal solutions containing high concentrations of sodium chloride at elevated temperatures, and evaluation of the mass transfer accompanying irreversible reactions responsible for metasomatism and ore deposition in hydrothermal systems.

INTRODUCTION

The chemistry of electrolyte solutions at high temperatures has received considerable attention in recent years, and it is now possible to predict with confidence the thermodynamic characteristics of hydrothermal solutions to $>$ 300°C (Criss and Cobble, 1964a and b; Cobble, 1964, 1966a and b; Helgeson, 1967a). It is the purpose of this paper to summarize the equations and methods involved in applying such predictions to hydrothermal equilibria and to compute an internally consistent set of values for the thermodynamic properties of hydrothermal systems at high temperatures. The results of the calculations are presented in tables as well as diagrams to facilitate extrapolation to the supercritical region and to enable the reader to use the numerical values in his own investigations.

Most of the species and reactions considered below are important in hydrothermal processes involving "acid" aqueous solutions containing high sodium chloride concentrations. Electrolyte solutions of this kind occur in the Salton Sea geothermal system (White, Anderson, and Grubbs, 1963; Helgeson, 1968a), and they are commonly found in fluid inclusions in vein minerals (Roedder, 1963, 1965, 1967). Chloride-rich acid solutions are responsible for high temperature metasomatism (Orville, 1963; Helgeson, 1967b) and hydrothermal rock alteration (Hemley, 1959; Hem-

ley, Meyer, and Richter, 1961; Hemley and Jones, 1964; Meyer and Hemley, 1967). In addition, both experimental (Barnard and Christopher, 1966; Hemley and others, 1967; Cloke, 1969) and theoretical (Helgeson, 1964, 1967c; Helgeson and Garrels, 1968; Helgeson, Garrels, and MacKenzie, 1969) evidence indicates that these solutions are capable of transporting and precipitating metals and sulfides in ore-forming concentrations at elevated temperatures.

Aqueous species contributing to hydrothermal processes involving acid chloride-rich solutions include HCO_3^-, HSO_4^-, HS^-, H_2CO_3 and $CO_{2(aq)}$, $H_2S_{(aq)}$, KCl, NaCl, HCl, $CaSO_4$, $MgSO_4$, H_4SiO_4, and chloride and sulfate complexes of the ore forming metals. There is little evidence that polynuclear metal ion complexes are important, or that chloride complexes of ferrous iron, calcium, magnesium, or aluminum form to significant degrees below $\sim$ 300°C (Sillén and Martell, 1964; Helgeson, 1964). Bicarbonate and bisulfate metal ion complexes and carbonate, bicarbonate, sulfate, and bisulfate complexes of sodium and potassium exhibit minor association below this temperature (Quist and others, 1963; Quist and Marshall, 1966; Helgeson, 1967a; Lafon, ms). Aluminum ion forms stable complexes with fluoride and (to a much lesser extent) sulfate ions in aqueous solutions. However, thermodynamic calculations indicate that fluoride and sulfate complexes probably contribute only slightly to the transport of aluminum in hydrothermal solutions at high temperatures, even where the pH of the solution is low. At low temperatures, aluminum fluoride complexes may be important in acid solutions (Hem, 1968). Aluminum hydroxide complexes appear to be the primary agents of aluminum transport in "acid" as well as "alkaline" hydrothermal solutions at high temperatures. Hydroxide complexes of calcium, sodium, potassium, magnesium, and most other metal ions are important only in alkaline solutions below 300°C, but ferrous hydroxide may associate to a significant extent in acid solutions above 200°C. Of the several oxidation states of gold, iron, and copper that form, aurous, ferrous, and cuprous ions and complexes predominate in hydrothermal solutions. Zn^{++}, Pb^{++}, Cu^+, Cu^{++}, Fe^{+++}, Ag^+, Au^+, and Au^{+++} ions associate primarily with Cl^- in chloride-rich solutions. Although concentrations of metal-carbonate, sulfide, bisulfide, and polysulfide complexes are negligible in acid low-sulfide solutions, metal-sulfate complexes may be important contributors to mineral solubilities in such solutions at temperatures below $\sim$ 200°C.

For temperatures below 300°C, the standard state adopted for the aqueous phase is an hypothetical 1 molal solution at 1 atm and any specified temperature. For gases and solids the standard state is unit activity for the ideal gas and the pure solid, respectively, at 1 atm and any specified temperature. The pressure dependence of hydrothermal equilibria are slight (considered negligible in this contribution) below 300°C. For this reason, pressure is regarded as a variable only where higher temperatures are considered. In these instances, the standard states apply to any specified temperature and pressure.

LIST OF SYMBOLS

A – molal Debye-Hückel parameter defined by equation (39).
a – coefficient in equations (16) and (17), equal to 0.01875.
$\mathring{a}$ – coefficient (in the Debye-Hückel equation) assumed to represent the distance of closest approach of ions in an electrolyte solution.
a_1, a_2 – coefficients in equation (26).
a' – coefficient in equations (28) and (31).
a'' – coefficient in equations (10), (11), and (12).
a_i – activity of the ith species.
a_w – activity of H_2O.
α – degree of association defined by equations (33), (34), and (54).
α' – coefficient in equation (17).
α'' – coefficient in equation (5).
B – molal Debye-Hückel parameter defined by equation (40).
$B^{\cdot}$ – deviation function describing the departure of the mean ionic activity coefficient of an electrolyte from that predicted by the Debye-Hückel expression.
b – coefficient in equations (16) and (17), equal to −12.741.
b_1, b_2 – coefficients in equation (4).
b' – coefficient in equations (28) and (31).
b'' – coefficient in equations (10), (11), and (12).
β – overall dissociation constant for complexes, or equilibrium constant for gas-aqueous reactions.
β' – coefficient in equation (17).
β'' – coefficient in equation (5).
$\mathfrak{C}$ – representation of cations.
$\mathfrak{C}L_y$ – representation of a mononuclear complex involving cation $\mathfrak{C}$ and y moles of anion L.
c – coefficient in equations (16) and (17), equal to 7.84×10^{-4}.
$\check{c}$ – integer index for complexes in equations (18), (20), (21), (24), (36), and (54).
c' – coefficient in equations (28) and (31).
c'' – coefficient in equations (10), (11), and (12).
$C^\circ_{P,i}$ – standard heat capacity of the ith species.
$\left.C^\circ_{P,i}\right|_{T_r}^{T}$ – average standard heat capacity of the ith species from temperature T_r to temperature T.
$\Delta C^\circ_{P,r}$ – standard heat capacity of reaction.
$\left.\Delta C^\circ_{P,r}\right|_{T_r}^{T}$ – average standard heat capacity of reaction from temperature T_r to temperature T.
$\gamma_{\check{c}}$ – activity coefficient in the $\check{c}$th complex.

$\dot{\gamma}_i$ — stoichiometric individual ion activity coefficient of the ith ion in a multicomponent electrolyte solution containing a predominant concentration of a given salt (defined by eq 45).
γ^*_i — individual ion activity coefficient of the ith ion.
$\gamma_\pm$ — stoichiometric mean activity coefficient.
$\gamma^*_\pm$ — mean ionic activity coefficient.
γ^*_+ — individual ion activity coefficient of a cation.
γ^*_- — individual ion activity coefficient of an anion.
$\dot{d}$ — integer index for the difference expressed by equation (20).
d' — coefficient in equations (28) and (31).
$\hat{e}$ — integer index for anions in equations (21), (22), (25), (26), (50), (51), and (52).
ε — dielectric constant.
f_i — fugacity of the ith species.
$\Delta G^\circ_{f,i}$ — standard Gibbs free energy of formation from the elements of the ith species.
ΔG°_r — standard Gibbs free energy of reaction.
h — average number of water molecules associated with ν ions.
H°_i — standard enthalpy of the ith species.
ΔH°_i — standard enthalpy of formation from the elements of the ith species at the reference temperature plus the enthalpy change for the ith species associated with an increase in temperature from T_r to T.
$\Delta H^\circ_{f,i}$ — standard enthalpy of formation from the elements of the ith species.
ΔH°_r — standard enthalpy of reaction.
θ — coefficient in equations (16) and (17), equal to 219.0.
I — stoichiometric ionic strength.
$\bar{I}$ — true ionic strength.
i — integer index for chemical species.
$\hat{i}$ — integer index for cations in equations (19), (20), (21), (24), (26), and (27).
j — integer index for reaction products.
K — equilibrium constant.
k — Henry's law coefficient.
K_{sp} — activity product constant.
L — representation of anions.
l — integer index for reactants.
λ' — coefficient in equation (17).
M_i — molarity of the ith species.
m_i — molality of the ith species.
$m_{t,i}$ — total molality of the ith ion or salt.
n — number of moles of a given cation in a mineral.
$\tilde{n}$ — sum of the exponents in the Law of Mass Action equation.
ν — number of moles of ions in 1 mole of a given salt.
ν_+ — number of moles of the cation in 1 mole of a given salt.
ν_- — number of moles of the anion in 1 mole of a given salt.

P — pressure in atmospheres.
P_r — reference pressure in atmospheres (1 atm).
q — integer index for mononuclear complexes involving a common ligand in equations (26) and (27).
R — gas constant, equal to 1.9872 cal $mole^{-1}$ deg^{-1} or 82.0575 cm^3 atm $mole^{-1}$ deg^{-1}.
$r_{\hat{e}}$ — ion radius of the êth anion.
$r_{\hat{\imath}}$ — ion radius of the îth cation.
ρ — density.
S^* — sum of the entropies of 1 mole of an aqueous species and its coordinated water molecules.
S°_i — standard conventional third law entropy of the ith species.
$S^{\circ(abs)}_i$ — standard absolute third law entropy of the ith species.
$S^*_{\dot{d}}$ — difference in the sum of the entropies of 1 mole of an aqueous complex and its coordinated water molecules and the sum of the entropies of the free cation and its coordinated water molecules.
ΔS°_e — standard electrostatic entropy of dissociation.
ΔS°_r — standard entropy of reaction.
S_ψ — solubility of the ψth mineral (in molality units) defined by equation (51).
σ — exponential coefficient in equation (36).
T — temperature in degrees Kelvin.
T_r — reference temperature in degrees Kelvin (298.15°K).
u — integer index in equation (48).
$\bar{u}$ — number of water molecules coordinated to a cation.
ΔV°_r — standard volume of reaction.
ϕ — stoichiometric osmotic coefficient.
x — number of water molecules coordinated to a complex.
y — number of moles of ligand L coordinated in a mononuclear complex of the form ϵL_y.
v — number of moles of a given anion in a mineral.
ψ — integer index for minerals.
$\dot{z}$ — limit of the range of integer index y in equations (46), (47), and (49).
Z_i — charge on the ith species.
ω — coefficient in equations (16) and (17), equal to 1.00322.

PREDICTIVE METHODS

In the present state of knowledge, limitations imposed by the amounts and kinds of data available for hydrothermal reactions dictate the "best" methods for predicting thermodynamic properties of hydrothermal systems at elevated temperatures. A variety of approximations, each with its own uncertainties, can be used for this purpose. Because the reliability of numerical values obtained from such approximations reflects the method as well as the data used in the calculations, the computational methods applicable under various circumstances are summarized below.

Equilibrium Constants

The basic thermodynamic equation describing the temperature dependence of the equilibrium constant is

$$\log K(T) = \log K(T_r) - \frac{\Delta H^\circ_r(T_r)}{2.303R}\left(\frac{1}{T} - \frac{1}{T_r}\right) - \frac{1}{2.303RT}\int_{T_r}^{T} \Delta C^\circ_{P,r}(T)dT + \frac{1}{2.303R}\int_{T_r}^{T} \Delta C^\circ_{P,r}(T)d \ln T \quad (1)$$

in which ΔH°_r and $\Delta C^\circ_{P,r}$ are, respectively, the standard enthalpy and heat capacity of reaction, R is the gas constant, K the equilibrium constant, T the temperature of interest (in °K), and T_r the reference temperature (298.15°K in this commun.). For most reactions involving aqueous solutions, the integrals in equation (1) cannot be evaluated rigorously because the required heat capacity functions are not available. To integrate the last two terms in equation (1), the assumption is frequently made that $\Delta C^\circ_{P,r}(T)$ is zero or constant, but this practice often leads to serious errors in computed log K(T) values at elevated temperatures (Cobble, 1964; Helgeson, 1964, 1967a). In many cases, ambiguities and uncertainties resulting from these assumptions can be avoided by adopting one or another of the alternate approaches summarized below.

Calculation from average heat capacities.—Average heat capacities $\left(C^\circ_P\right]_{T_r}^{T}\right)$ for ions can be computed from absolute entropies by evaluating

$$C^\circ_{P,i}\Big]_{T_r}^{T} = \frac{S^\circ_i{}^{(abs)}(T) - S^\circ_i{}^{(abs)}(T_r)}{\ln T/T_r} \quad (2)$$

where $S^\circ_i{}^{(abs)}$ is the absolute entropy of the ith species. The absolute entropy is related to the conventional entropy (S°) by

$$S^\circ_i{}^{(abs)}(T) = S^\circ_i(T) + Z_i S^\circ_{H^+}{}^{(abs)}(T) \quad (3)$$

where Z_i represents the charge on the ith species and $S^\circ_{H^+}{}^{(abs)}(T)$ is the absolute entropy of the hydrogen ion at temperature T. Criss and Cobble (1964a) have shown that the absolute entropies of ions at high temperatures can be calculated from

$$S^\circ_i{}^{(abs)}(T) = b_1(T) + b_2(T)\, S^\circ_i{}^{(abs)}(T_r) \quad (4)$$

where b_1 and b_2 are temperature dependent coefficients characteristic of simple cations, simple anions, oxy-anions, or acid oxy-anions. The relation expressed in equation (4) was obtained by assigning absolute entropies to the hydrogen ion at various specified temperatures. Equation

(4) can be combined with equation (2) to define a similar relation for average heat capacities. This expression appears as

$$\left.\begin{matrix} T \\ C^\circ_{P,i} \\ T_r \end{matrix}\right] = \alpha''(T) + \beta''(T)\, S^\circ_i{}^{(abs)}(T_r) \tag{5}$$

where $\alpha''(T) = b_1(T)/\ln(T/T_r)$ and $\beta''(T) = (b_2(T)-1)/\ln(T/T_r)$. Values of b_1, b_2, α'', and β'' have been computed by Criss and Cobble (1964a and b) for 60°, 100°, 150°, 200°, 250°, and 300°C. These coefficients allow absolute entropies and average heat capacities to be calculated for a large number of aqueous species at elevated temperatures.

When average heat capacities can be computed for all reactants and products in a given reaction, the equilibrium constant at temperature T can be predicted directly from

$$\log K(T) = \log K(T_r) - \frac{\Delta H^\circ_r(T_r)}{2.303R}\left(\frac{1}{T} - \frac{1}{T_r}\right) - \frac{\left.\begin{matrix} T \\ \Delta C^\circ_{P,r} \\ T_r \end{matrix}\right] (T-T_r)}{2.303RT} + \frac{\left.\begin{matrix} T \\ \Delta C^\circ_{P,r} \\ T_r \end{matrix}\right] \ln T/T_r}{2.303R} \tag{6}$$

in which

$$\left.\begin{matrix} T \\ \Delta C^\circ_{P,r} \\ T_r \end{matrix}\right] = \sum_j \left.\begin{matrix} T \\ C^\circ_{P,j} \\ T_r \end{matrix}\right] - \sum_l \left.\begin{matrix} T \\ C^\circ_{P,l} \\ T_r \end{matrix}\right] \tag{7}$$

where j and l represent the products and reactants, respectively.

Calculation from a combination of average and actual heat capacities.—In cases where the actual heat capacities for some (but not all) of the reactants or products in a given reaction are defined by empirical power functions of temperature, equilibrium constants can be computed by first evaluating (for those species)

$$\Delta H^\circ_i(T) = \Delta H^\circ_{f,i}(T_r) + \int_{T_r}^{T} C^\circ_{P,i}(T)\, dT \tag{8}$$

and

$$S^\circ_i(T) = S^\circ_i(T_r) + \int_{T_r}^{T} C^\circ_{P,i}(T)\, d \ln T \tag{9}$$

in which $\Delta H^\circ_i(T)$ is the standard enthalpy of formation from the elements of the ith species at the reference temperature $[\Delta H^\circ_{f,i}(T_r)]$ plus the enthalpy change for the ith species associated with an increase in

temperature from T_r to temperature T. Heat capacities of solids and gases are usually described by power functions of the form

$$C^\circ_{P,i}(T) = a'' + b''T + c''/T^2 \tag{10}$$

so that equations (8) and (9) will normally appear as

$$\Delta H^\circ_i(T) = \Delta H^\circ_{f,i}(T_r) + a''(T-T_r) + \frac{b''}{2}(T^2-T_r^2) - c''\left(\frac{1}{T} - \frac{1}{T_r}\right) \tag{11}$$

and

$$S^\circ_i(T) = S^\circ_i(T_r) + a'' \ln T/T_r + b''(T-T_r) - \frac{c''}{2}\left(\frac{1}{T^2} - \frac{1}{T_r^2}\right) \tag{12}$$

Where average heat capacities are known for the remaining reactants and products, standard enthalpies and entropies at a given temperature can be calculated by evaluating

$$\Delta H^\circ_i(T) = \Delta H^\circ_{f,i}(T_r) + C^\circ_{P,i}\Big]_{T_r}^{T}(T-T_r) \tag{13}$$

and

$$S^\circ_i(T) = S^\circ_i(T_r) + C^\circ_{P,i}\Big]_{T_r}^{T} \ln T/T_r\,. \tag{14}$$

High temperature equilibrium constants for the reaction can then be computed from

$$\log K(T) = \frac{T\left(\sum_j S^\circ_j(T) - \sum_l S^\circ_l(T)\right) - \sum_j \Delta H^\circ_j(T) + \sum_l \Delta H^\circ_l(T)}{2.303RT} \tag{15}$$

where j and l again refer to the products and reactants, respectively. When equation (15) is employed, care must be exercised to avoid confusion between relative and absolute entropies in the summation terms of the equation. If heat capacity power functions are known for all reactants and products, high temperature equilibrium constants can be computed simply by combining equations (11), (12), and (15).

Prediction of dissociation constants.— In geochemical problems it is quite common to find that no heat capacity data of any kind are available for one or more of the reactants or products in a given reaction. This is particularly true for complexes in aqueous solution. Despite this handicap, dissociation constants often can be closely approximated to $\sim$ 200°C by evaluating (Helgeson, 1967a)

$$\log K(T) = \frac{\Delta S^\circ_r(T_r)}{2.303RT}\left[T_r - \frac{\theta}{\omega}\left(1 - \exp[\exp(b+aT) - c + (T-T_r)/\theta]\right)\right] - \frac{\Delta H^\circ_r(T_r)}{2.303RT} \tag{16}$$

where θ, ω, a, b, and c are temperature independent constants characteristic of the solvent. For aqueous solutions these coefficients have the values 219.0, 1.00322, 0.01875, −12.741, and 7.84×10^{-4}, respectively (Helgeson, 1967a). The method of approximation afforded by equation (16) involves the assumption that $\Delta C^\circ_{P,r}(T)$ changes monotonically but nonlinearly with temperature; $\Delta C^\circ_{P,r}(T)$ is implicitly defined in terms of $\Delta S^\circ_r(T_r)$ in the equation. Dissociation constants computed from equation (16) are often much closer approximations of actual dissociation constants at high temperatures than those computed by assuming $\Delta C^\circ_{P,r}(T) = 0$ or $\Delta C^\circ_{P,r}(T) =$ a constant. Equation (16) is an approximation modified from equation (17) below.

Where dissociation constants are known over a restricted temperature range, experimental log K(T) values can be fit by the method of least squares to

$$\log K(T) = \frac{\Delta S^\circ_e(T_r)}{2.303RT}\left[T_r - T - \frac{\theta}{\omega}\left(1 - \exp[\exp(b+aT) - c + (T-T_r)/\theta]\right)\right] - \frac{\Delta H^\circ_r(T_r)}{2.303RT} + \frac{\Delta S^\circ_r(T_r)}{2.303R} + \frac{\alpha'}{2.303R}(\ln T/T_r - 1 + T_r/T) + \frac{\beta'(T-T_r)^2}{4.606RT} + \frac{\lambda'}{4.606RT}(T^3/3 - T_r^3/3 - T_r^2T + T_r^3) \quad (17)$$

where θ, ω, a, b, and c are constants with the values given above, $\Delta S^\circ_e(T_r)$ is the electrostatic entropy of dissociation at the reference temperature (T_r), and α', β', and λ' are temperature independent coefficients characteristic of the reaction (Helgeson, 1967a). Values of the reaction-dependent parameters defined by the low temperature fits can then be used to predict log K values at higher temperatures. However, care must be exercised to avoid overfitting. Where only a few experimental values are available, or the data are highly uncertain, all of the reaction-dependent coefficients should not be included in the least squares fit routine; that is, λ', or λ' and β' should be set to zero.

Entropy and Heat Capacity Estimates

For many reactions in aqueous solution, equilibrium constants are known only at 25°C. In such cases it is common to find that insufficient entropy or enthalpy data are available for the species involved in the reaction to permit calculation of high temperature equilibrium constants using the approaches described above. This problem often can be overcome in a first approximation by estimating entropies of dissociation or the entropies and heat capacities of reactant or product species.

Dissociational reactions in aqueous solution.—Entropies of dissociation for complexes in aqueous solution at 25°C can be estimated from entropy correlation plots. These entropies can then be used in conjunction with equation (16) to approximate dissociation constants at higher temperatures. The approach summarized below for making such esti-

mates is a modification of that employed by Cobble (1953b) for estimating the entropies of complex ions.

For convenience, let us define the sum of the entropies of 1 mole of an aqueous species and its coordinated water molecules as S*; that is, for a given temperature,

$$S^*_{[\text{€L}_y(H_2O)_x^{z_č}]} \equiv S^\circ_{[\text{€L}_y^{z_č}]} + xS^\circ_{[H_2O]} \tag{18}$$

and

$$S^*_{[\text{€}(H_2O)_{ū}^{z_î}]} \equiv S^\circ_{[\text{€}^{z_î}]} + ūS^\circ_{[H_2O]} \tag{19}$$

in which S° is the conventional third law entropy, €L_y is a mononuclear complex involving cation € and y moles of anion L, x and ū represent the number of water molecules coordinated to the complex and cation, respectively, and $Z_č$ and $Z_î$ are the respective charges on the complex and the cation. Subtracting equation (19) from equation (18) gives

$$S^*_{[\text{€L}_y(H_2O)_x^{z_č}]} - S^*_{[\text{€}(H_2O)_{ū}^{z_î}]} = \Delta S^*_{ḍ} = S^\circ_{[\text{€L}_y^{z_č}]} - S^\circ_{[\text{€}^{z_î}]} + (x - ū)S^\circ_{[H_2O]} \tag{20}$$

where $\Delta S^*_{ḍ}$ is the difference in the sums of the entropies expressed in equations (18) and (19). Equation (20) can now be combined with the expression for the entropy of dissociation of the complex written as

$$\Delta S^\circ_r = S^\circ_{[\text{€}^{z_î}]} + yS^\circ_{[L^{z_ê}]} - S^\circ_{[\text{€L}_y^{z_č}]} \tag{21}$$

to give

$$\Delta S^\circ_r = yS^\circ_{[L^{z_ê}]} + (x - ū)\,S^\circ_{[H_2O]} - \Delta S^*_{ḍ} \tag{22}$$

where $Z_ê$ is the charge on the anion. If as a first approximation we assume,

$$x = ū - y \tag{23}$$

then equations (20) and (22) reduce, respectively, to

$$\Delta S^*_{ḍ} = S^\circ_{[\text{€L}_y^{z_č}]} - S^\circ_{[\text{€}^{z_î}]} - yS^\circ_{[H_2O]} \tag{24}$$

and

$$\Delta S^\circ_r = y\left(S^\circ_{[L^{z_ê}]} - S^\circ_{[H_2O]}\right) - \Delta S^*_{ḍ} \tag{25}$$

For complexes involving a common ligand at 25°C, empirical considerations indicate that $\Delta S^*_{ḍ}$ can be described by

$$\Delta S^*_{ḍ(q)} = \hat{a}_1 + \hat{a}_2/(r_{î(q)} + r_{ê(q)}) \tag{26}$$

in which $\hat{a}_1$ and $\hat{a}_2$ are coefficients characteristic of the group of complexes, and $r_{î(q)}$ and $r_{ê(q)}$ are the radii of the cation and ligand, respectively, in the qth complex. The validity of equation (26) can be

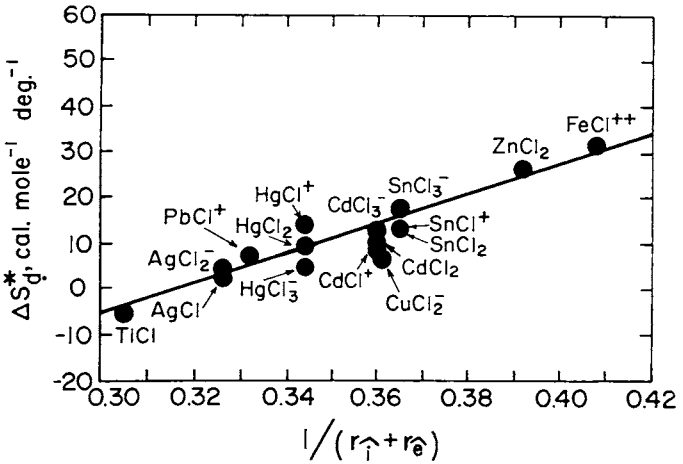

Fig. 1. Correlation plot of ΔS^*_d (see text—eqs 20 and 24) for metal chloride complexes at 25°C and 1 atm against the reciprocal of the sum of the radii of the ions in the complex. The plotted values of ΔS^*_d and the sources of data from which they were calculated (see text) are given in table 1. The curve shown above is consistent with equation (27).

assessed for chloride complexes in figure 1. The data used in computing the ΔS^*_d values plotted in figure 1 are given in table 1 along with the sources from which they were obtained. The maximum deviation from the linear curve of the points in figure 1 is 8 cal mole^{-1} deg^{-1} (for $CuCl_2^-$), but the average deviation is only 3 cal mole^{-1} deg^{-1}, which is well within the experimental uncertainty of the data. The specific statement of equation (26) for the curve in figure 1 is

$$\Delta S^*_{d(q)} = -102.5 + 325/(r_{i(q)} + 1.81) \qquad (27)$$

where 1.81 is the radius of the chloride ion (Sienko and Plane, 1963). Values of ΔS°_r computed from equations (25) and (27) for the species shown in figure 1 are given in table 1 to afford a numerical comparison with those based on experimental data.

The procedure summarized above for estimating dissociational entropies is of general applicability; that is, expressions similar to equations (26) and (27) can be developed for various groups of dissociational reactions for which data are incomplete. Entropy estimates obtained in this manner permit approximations of high temperature dissociation constants for a large number of complexes of interest in geochemistry. For many of these, only experimental dissociation constants at 25°C are available, but estimates of $\Delta S^\circ_r(T_r)$ allow approximations of $\Delta H^\circ_r(T_r)$ [from $\Delta H^\circ_r(T_r) = T_r \Delta S^\circ_r(T_r) - 2.303RT_r \log K(T_r)$] and thus estimation of high temperature dissociation constants from equation (16). In cases where sufficient data are not available to estimate dissociational

entropies from correlation plots, it may be possible to estimate directly the entropy of a particular complex, neutral species, or ion, which will then permit calculation of dissociational entropies at 25°C. A number of techniques for making such estimates have been summarized by Latimer (1952), Cobble (1953a and b), and others.

TABLE 1

Entropies of dissociation for chloride complexes in aqueous solution at 25°C and 1 atm

Reaction	Cation radius[a] (Å)	Experimental $\Delta S°_r$ (cal mole^{-1} deg^{-1})	Calculated[b] ΔS^*_d (cal mole^{-1} deg^{-1})	Calculated[c] $\Delta S°_r$ (cal mole^{-1} deg^{-1})
$AgCl \rightleftharpoons Ag^+ + Cl^-$	1.26	−6[d]	2.6	−6.6
$AgCl_2^- \rightleftharpoons Ag^+ + 2Cl^-$	1.26	−11[d]	4.4	−9.8
$CuCl_2^- \rightleftharpoons Cu^+ + 2Cl^-$	0.96	−13.0[e]	6.6	−21.2
$PbCl^+ \rightleftharpoons Pb^{++} + Cl^-$	1.20	−11.6[f]	7.4	−8.6
$ZnCl_2 \rightleftharpoons Zn^{++} + 2Cl^-$	0.74	−32.7[g]	26.3	−31.3
$HgCl^+ \rightleftharpoons Hg^{++} + Cl^-$	1.10	−17[h]	13.8	−12.5
$HgCl_2 \rightleftharpoons Hg^{++} + 2Cl^-$	1.10	−16[i]	9.6	−15.7
$HgCl_3^- \rightleftharpoons Hg^{++} + 3Cl^-$	1.10	−13.7[i]	4.1	−18.9
$CdCl^+ \rightleftharpoons Cd^{++} + Cl^-$	0.97	−11.4[j]	8.2	−17.6
$CdCl_2 \rightleftharpoons Cd^{++} + 2Cl^-$	0.97	−16.4[j]	10.0	−20.8
$CdCl_3^- \rightleftharpoons Cd^{++} + 3Cl^-$	0.97	−22.3[k]	12.7	−24.0
$SnCl^+ \rightleftharpoons Sn^{++} + Cl^-$	0.93	−15.4[l, n]	12.2	−19.3
$SnCl_2 \rightleftharpoons Sn^{++} + 2Cl^-$	0.93	−18.9[l, n]	12.5	−22.5
$SnCl_3^- \rightleftharpoons Sn^{++} + 3Cl^-$	0.93	−27.4[l, n]	17.8	−25.7
$FeCl^{++} \rightleftharpoons Fe^{+++} + Cl^-$	0.64	−35[m]	31.8	−33 3
$TlCl \rightleftharpoons Tl^+ + Cl^-$	1.74	2.2[l]	5.4	0.2
$AuCl_2^- \rightleftharpoons Au^+ + 2Cl^-$	1.37			−6.0
$AuCl_4^- \rightleftharpoons Au^{+++} + 4Cl^-$	0.9			−30.2
$SnCl_4^- \rightleftharpoons Sn^{++++} + 4Cl^-$	0.71			−39.2

[a] Sienko and Plane (1963). [b] Computed from equation (25) using the experimental entropies shown above together with 16.7 cal mole^{-1} deg^{-1} for $S°_{H_2O}$ (Wagman and others, 1968) and 13.51 for $S°_{Cl^-}$ (Ahluwalia and Cobble, 1964). [c] Calculated from equations (25) and (27). [d] Jonte and Martin (1952). [e] Calculated from $S°_{CuCl_2^-}$ (Latimer 1952) and the ionic entropies in table 3. [f] Austin, Matheson, and Parton (1959). [g] Based on least squares fits of log K(T) values at 150° and 115°C (Kraus and Raridon, 1960) and 25°C (Marcus and Mayden, 1963) using equation (16). [h] Malcolm, Parton, and Watson (1961). [i] Williams (1954). [j] Helgeson (1967a). [k] Vanderzee and Dawson (1953). [l] Wagman and others (1966). [m] Rabinowitch and Stockmayer (1942). [n] Latimer (1952).

Minerals.—Although thermodynamic data are now available for a large number of minerals (Robie, 1966; Robie and Waldbaum, 1968), only free energy data (derived from solubility studies) at 25°C exist for many minerals of interest in hydrothermal and metamorphic studies. Approximation of the standard enthalpies of formation of these minerals at 25°C permits calculation of provisional equilibrium constants for high temperature hydrothermal reactions that could not otherwise be evaluated in the present state of knowledge. As a rule, direct estimation of the standard enthalpies of formation of minerals involves prohibitive uncertainties owing to the lack of adequate general models for calculating bond energies in minerals. In contrast, third law entropies of minerals can be approximated closely by direct estimation, which permits calculation of $\Delta H^\circ_f(T_r)$ from $\Delta H^\circ_f(T_r) = \Delta G^\circ_f(T_r) + T_r\Delta S^\circ_f(T_r)$, where $\Delta S^\circ_f(T_r)$ is the standard entropy of formation of the mineral from its elements.

Entropies of silicates, sulfates, and carbonates can be approximated by summing the entropies of the oxide components of the minerals (Latimer, 1952; Fyfe and others, 1958). Although such a summation does not provide for all of the configurational entropy contribution, the uncertainty attending this procedure rarely exceeds 10 percent and more often than not is less than a few cal $mole^{-1}$ deg^{-1}. Close estimates can be made for clay minerals if the entropy of H_2O is taken to be that of ice at 25°C (10.68 cal $mole^{-1}$ deg^{-1}, Robie and Waldbaum, 1968) or assigned a value of 9.4 cal $mole^{-1}$ deg^{-1} (Latimer, 1952). For example, the entropy of muscovite obtained from the sum of the entropies of its oxide components at 25°C is 69.8 cal $mole^{-1}$ deg^{-1} if H_2O is represented by ice, and 68.5 cal $mole^{-1}$ deg^{-1} if Latimer's value for the entropy of hydrate water is used; the experimental entropy of muscovite is 69.0 cal $mole^{-1}$ deg^{-1} (Robie and Waldbaum, 1968). An error of a few cal $mole^{-1}$ deg^{-1} in the entropy of a mineral rarely introduces significant error in high temperature calculations of mineral equilibria. In contrast to summing the entropies of oxide components, entropies of minerals can also be estimated with confidence by summing the values tabulated by Latimer (1952) for the entropy contributions of elements and ions in solid compounds. This procedure is particularly useful for estimating the entropies of multicomponent sulfides.

As in the case of entropy, heat capacities of minerals can be approximated closely by summing the heat capacities of the components of the minerals. This is true also for heat capacities of minerals expressed by power functions of temperature (eq 10). For example, the heat capacity power function for muscovite obtained by summing the power functions for its oxide components is $89.95 + 33.23 \times 10^{-3}T - 20.67 \times 10^{5}T^{-2}$ when ice (9.0 cal $mole^{-1}$ deg^{-1}) is used to represent H_2O (see footnote n, table 8). The experimentally derived function is $97.56 + 26.38 \times 10^{-3}T - 25.44 \times 10^{5}T^{-2}$ (Kelley, 1960). At 25°C, the estimated heat capacity defined by the first of these power functions is 77 cal $mole^{-1}$ deg^{-1} compared to the experimental value of 77 cal $mole^{-1}$ deg^{-1}. At

300°C the corresponding values are 103 cal mole^{-1} deg^{-1} compared to 105 cal mole^{-1} deg^{-1}. Discrepancies of this order of magnitude are insignificant with respect to calculated equilibrium constants at high temperature.

Estimates of entropies and heat capacity power functions of temperature make it possible to compute standard enthalpies of formation for minerals at 25°C from high temperature phase equilibrium data. For example, the $\Delta H^\circ_f(T_r)$ value for annite used to compute the high temperature hydrolytic equilibrium constants for this mineral in table 12 were calculated from the high temperature equilibrium P_{H_2O} and f_{O_2} for sanidine + magnetite + $H_2O_{(g)} \rightleftarrows$ annite + $\frac{1}{2}O_{2(g)}$ (Eugster and Wones, 1962) at 500°C and 2070 atm. An estimated entropy (table 12) and heat capacity power function (table 8) for annite permitted calculation of the high temperature values for the entropy of annite (eq 9). The same calculations for the other species in the assemblage (for which thermodynamic data are known) permitted calculation of $\Delta S^\circ_r(T)$ for the equilibrium assemblage at 500°C. From the values of f_{O_2} and P_{H_2O} given by Eugster and Wones, and fugacity coefficients for H_2O[1] (Anderson, 1967), $\Delta G^\circ_r(T)$ could also be computed, which made it possible to calculate $\Delta H^\circ_r(T)$, and hence, $\Delta H^\circ_{annite}(T)$. Application of the estimated heat capacity power function resulted in the value of $\Delta H^\circ_f(T_r)$ for annite given in table 12.[2]

Activity Coefficients in Sodium Chloride Solutions

Because the solute in many hydrothermal solutions is composed largely of sodium chloride, the thermodynamic properties of aqueous solutions of this salt can be used to compute activity coefficients in concentrated hydrothermal solutions at elevated temperatures. Thermodynamic properties of concentrated sodium chloride solutions are summarized in table 2. The methods used in computing the values shown in the table are outlined briefly below.

[1] Fugacity coefficients for other gases involved in similar calculations can be computed from data given by Garrels and Christ (1965).

[2] The effects of pressure were disregarded in the calculation of the enthalpy of formation of annite described above. The volume changes for reactions used in such calculations are commonly small, and the pressure corrections are thus often smaller than the uncertainty in the experimental data. Where this is not true the experimental equilibrium constants should first be corrected for pressure by evaluating

$$\log K(T,P_r) = \log K(T,P) - \frac{1}{2.303RT}\int_{P_r}^{P} \Delta V^\circ_r\,(T,P)dP$$

where P_r refers to the reference pressure (1 atm in this commun.), ΔV°_r is the standard change in volume for the reaction in cm^3 mole^{-1}, and R is the gas constant expressed as 82.0575 cm^3 atm mole^{-1} deg^{-1}. In many instances this equation can be approximated closely by

$$\log K(T,P_r) = \log K(T,P) - \frac{\Delta V^\circ_r\,(T_rP_r)(P - P_r)}{2.303RT}\,.$$

Analysis of vapor pressure data.—Stoichiometric osmotic coefficients for sodium chloride solutions from 25° to 270°C have been fit (Helgeson, 1967b; Helgeson and James, 1968) with a least squares computer routine employing a Debye-Hückel power function for activity coefficients suggested by Lietzke and Stoughton (1961). The activity coefficient power function is

$$\ln \gamma_{\pm}(T,I) = \frac{-2.303\ A(T)\ |Z_1Z_2|\ I^{1/2}}{1 + a'(T)I^{1/2}} + b'(T)I + c'(T)I^2 + d'(T)I^3 \quad (28)$$

where $\gamma_{\pm}(T,I)$ represents the stoichiometric mean activity coefficient at temperature T and stoichiometric ionic strength I, $a'(T)$, $b'(T)$, $c'(T)$, and $d'(T)$ are temperature-dependent coefficients, Z is the charge on the subscripted cation (1) and anion (2), and A(T) is the Debye-Hückel parameter defined below by equation (39).

The stoichiometric mean activity coefficient of NaCl is related to the stoichiometric osmotic coefficient (ϕ) by

$$\phi(T,I) = 1 + \frac{1}{I}\int_0^I I\ d \ln \gamma_{\pm}(T,I). \quad (29)$$

Equation (29) can also be written as

$$\phi(T,I) = 1 + \ln \gamma_{\pm}(T,I) - \frac{1}{I}\int_0^I \ln \gamma_{\pm}(T,I)\ dI, \quad (30)$$

and integrated with the aid of equation (28) to give the following power function for the stoichiometric osmotic coefficient:

$$\phi(T,I) = 1 - \frac{2.303\ A(T)\ |Z_1Z_2|}{a'^3(T)I}\left[(1 + a'(T)I^{1/2}) - 2\ln(1 + a'(T)I^{1/2}) - \frac{1}{1 + a'(T)I^{1/2}}\right] + \frac{b'(T)I}{2} + \frac{2c'(T)I^2}{3} + \frac{3d'(T)I^3}{4} \quad (31)$$

The values of the power series coefficients defined by the fits of the osmotic coefficients of NaCl with equation (31) were used in equation (28) to calculate the stoichiometric mean activity coefficients shown in table 2. Because experimental osmotic coeffcients are available for NaCl at only three concentrations above 100°C (table 2), the d' coefficient was set to zero in the least squares fits.[3]

Calculations providing for complexing.—The stoichiometric mean activity coefficient of sodium chloride at a given temperature is related to the mean ionic activity coefficient ($\gamma^*_{\pm}$) by

$$\gamma_{\pm NaCl} = (1 - \alpha_{NaCl})\ \gamma^*_{\pm NaCl} \quad (32)$$

[3] Since these calculations were carried out, Lindsay and Liu (1968) have presented osmotic coefficient data for NaCl at concentration intervals of 0.1 *m* from 0.05 to 3.50 *m* and temperatures from 125° to 300°C. Least squares fits of their data yield activity coefficients in close agreement with those computed above.

in which α_{NaCl} is the degree of association of the solute, defined by

$$\alpha_{NaCl} = \frac{m_{NaCl}}{m_{t,NaCl}} \tag{33}$$

where m_{NaCl} is the molality of the complex and $m_{t,NaCl}$ is the stoichiometric (total) molality of the salt. Combining equation (33) with the Law of Mass Action for the dissociation of NaCl leads to

$$\alpha_{NaCl} = \frac{\gamma_{\pm}^{2} m_{t,NaCl}}{K_{NaCl}\,\gamma_{NaCl}} \tag{34}$$

where K_{NaCl} and γ_{NaCl} are, respectively, the dissociation constant and activity coefficient of the complex. Equation (34) can be used to compute values of α_{NaCl} (and consequently values of $\gamma^{*}_{\pm NaCl}$—eq 32) from stoichiometric mean activity coefficients if dissociation constants and activity coefficients for the complex are known.

Although sodium chloride solutions are essentially completely dissociated at low temperatures, above ~200°C this is no longer true. Experi-

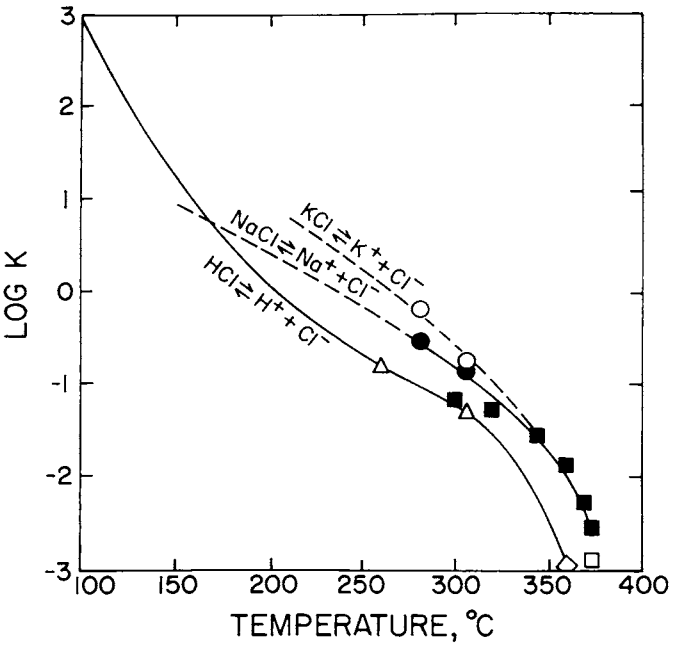

Fig. 2. Dissociation constants for NaCl, KCl, and HCl at high temperatures (see table 4). Open circle = KCl—Wright, Lindsay, and Druga (1961) after Noyes (1907); filled circle = NaCl—Wright, Lindsay, and Druga (1961) after Noyes (1907); triangle = HCl—Wright, Lindsay, and Druga (1961) after Noyes (1907); open square = KCl—extrapolated from supercritical data (Franck, 1961); filled square = NaCl—Pearson, Copeland, and Benson (1963a); diamond = HCl—Pearson, Copeland, and Benson (1963b). The smooth curve for HCl is based on a least squares fit of low and high temperature log K(T) values (Helgeson, 1967a) using equation (17), but those for KCl and NaCl are based on simple interpolation. The dissociation constants plotted above are consistent with molal units of concentration.

mental dissociation constants for aqueous NaCl below 281°C are not available; those reported in the literature for higher (but subcritical)[4] temperatures are plotted together with comparative values of log K(T) for KCl and HCl in figure 2. Calculated degrees of association and mean ionic activity coefficients for sodium chloride at elevated temperatures are given in table 2. The values shown in table 2 for these parameters were computed from equations (32) and (34) using extrapolated values of K_{NaCl} (table 2)[5]. The extrapolated dissociation constants are those corresponding to the dashed curve for NaCl in figure 2. The activity coefficient of the complex was represented in the calculations by γ_{CO_2} in NaCl solutions (table 2). Values of γ_{CO_2} were computed from Henry's law coefficients (Ellis and Golding, 1963) by evaluating (for each temperature and molality of sodium chloride)

$$\gamma_{CO_2} = k_{m_t}/k \tag{35}$$

where k and k_{m_t} are the Henry's law coefficients in pure water and in a sodium chloride solution of total molality, m_t. Because Henry's law coefficients are not available for concentrations of NaCl over 2 molal at high temperatures, extrapolations of γ_{CO_2} were also necessary. These extrapolations were accomplished for each temperature with the aid of an empirical equation, which can be written in general notation as

$$\gamma_{\overset{\circ}{C}} = 10^{\sigma \bar{I}} \tag{36}$$

where $\gamma_{\overset{\circ}{C}}$ is the activity coefficient of a neutral complex, σ is the slope constant on semi-logarithmic coordinates, and $\bar{I}$ is the true ionic strength of the solution. The true ionic strength of a sodium chloride solution is given by

$$\bar{I} = \tfrac{1}{2} \sum_i Z_i^2 m_i = (1 - \alpha_{NaCl})I \tag{37}$$

where i designates the charged species in solution and I is the stoichiometric ionic strength (equiv. to $m_{t,NaCl}$).

Equation (36) closely approximates the activity coefficients of a large number of molecular species in aqueous electrolyte solutions at 25°C (Randall and Failey, 1927a-c), and it also describes γ_{CO_2} in NaCl solutions up to 2 m at high temperatures (Helgeson, 1967b; Helgeson and James, 1968). Because the activity coefficients of different molecular species in a given salt solution are similiar (Randall and Failey, 1927a-c),

[4] Supercritical dissociation constants for NaCl over a wide range of temperature and pressure are also now available (Quist and Marshall, 1968a).

[5] At present, there is little alternative to graphic extrapolation of high temperature log K(T) data to obtain estimates below 281°C. The uncertainties in the high temperature data are sufficiently large to preclude definitive least squares fits using theoretical log K(T) expressions (Helgeson, 1967a). Attempts to obtain values of log K_{NaCl} and γ_{NaCl} from least squares fits of the stoichiometric activity coefficients using equations providing for complexing have been only partly successful owing to the limited data available for the temperature range where NaCl associates to a significant degree (Helgeson and James, 1968).

TABLE 2

Thermodynamic properties of concentrated sodium chloride solutions at elevated temperatures[1]

	$m_{t,\,NaCl}$	Temperature, °C							
		25°	50°	100°	150°	200°	250°	270°	300°
Osmotic coefficient (ϕ_{NaCl})[a]	1.0	0.935	0.940	0.935	0.900	0.855	0.797	0.769[n]	
	2.0	0.983	0.996	0.986	0.953	0.900	0.824	0.786	
	3.0	1.045	1.059	1.048	0.991	0.920	0.832	0.784[n]	
Stoichiometric mean activity coefficient ($\gamma_{\pm NaCl}$)[b]	1.0	0.656	0.656	0.622	0.532	0.443	0.356	0.318	0.25[p]
	2.0	0.670	0.678	0.641	0.532	0.425	0.320	0.277	0.22[p]
	3.0	0.719	0.728	0.687	0.546	0.419	0.301	0.254	0.20[p]
Standard state dissociation constant (K_{NaCl})					9.4[e]	2.63[e]	0.71[e]	0.40[e]	0.15[m]
Degree of association (α_{NaCl})[d]	1.0	0.00	0.00	0.00	0.025	0.061	0.133	0.178	0.29[p]
	2.0	0.00	0.00	0.00	0.043	0.093	0.173	0.209	0.32[p]
	3.0	0.00	0.00	0.00	0.056	0.115	0.206	0.238	0.34[p]
True ionic strength ($\bar{I}_{NaCl}$)[o]	1.0	1.0	1.0	1.0	0.975	0.939	0.867	0.822	0.71
	2.0	2.0	2.0	2.0	1.914	1.814	1.654	1.582	1.36
	3.0	3.0	3.0	3.0	2.832	2.655	2.382	2.286	1.98
Mean ionic activity coefficient ($\gamma^*_{\pm NaCl}$)[f]	1.0	0.656	0.656	0.622	0.546	0.472	0.410	0.387	0.36[n]
	2.0	0.670	0.678	0.641	0.556	0.468	0.387	0.349	0.32[n]
	3.0	0.719	0.728	0.687	0.578	0.473	0.379	0.333	0.30[n]
Debye-Hückel activity coefficient ($\gamma_{\pm NaCl,D.-H.}$)[g]	1.0	0.599	0.598	0.566	0.497	0.429	0.384	0.388	0.36
	2.0	0.556	0.556	0.524	0.449	0.378	0.335	0.330	0.32
	3.0	0.534	0.535	0.503	0.425	0.352	0.311	0.308	0.30
Deviation function ($B\cdot$)[h]		0.041	0.043_5	0.046	0.047_5	0.047	0.034	0.015	0.0[n]
Activity coefficient of carbon dioxide in NaCl solutions (γ_{CO_2})[i]	1.0	1.27	1.24	1.20	1.19	1.23	1.34	1.42[m]	1.50
	2.0	1.57	1.50	1.44	1.40	1.47	1.67	1.83[m]	2.00
	3.0	1.93	1.80	1.74[n]	1.70[n]	1.74[n]	1.86[n]	2.03[n]	2.29[n]

Activity of water $(a_w)^j$	1.0	0.9669[l]	0.9667	0.9669	0.968	0.970	0.972	0.973	
	2.0	0.9316[l]	0.9308	0.9315	0.934	0.937	0.942	0.945	
	3.0	0.8932[l]	0.8919	0.8930	0.898	0.905	0.914	0.919	
A (Debye-Hückel)[k]		0.5095	0.5354	0.6019	0.6915	0.8127	0.9907	1.0905	1.2979
B (Debye-Hückel) $\times 10^{-8}$[k]		0.3284	0.3329	0.3425	0.3536	0.3659	0.3807	0.3879	0.4010
å (Debye-Hückel term in the Stokes-Robinson expression—eq 41)		3.94[r]	4.19[r]						
		3.89[q]	4.20[q]	4.19[q]	3.58[q]	3.22[q]	3.43[q]	3.79[q]	4.4[s]
h (hydration parameter—eq 41)		3.61[r]	3.70[r]						
		3.67[q]	3.69[q]	3.90[m]	4.01[q]	4.22[q]	3.61[q]	2.22[q]	1.2[s]

[a] Values at 25° and 100° are from Robinson and Stokes (1959), at 50° from Harned (1961), and at 150° and above from Gardner, Jones, and de Nordwall (1963). [b] The values at 25°, 50°, and 100° were taken from Harned and Owen (1958); for 150° to 270°, the values were computed from equation (28) after performing least squares fits of the osmotic coefficients using equation (31). [c] Extrapolated from higher temperature data (fig. 2). The values of K are consistent with molal units of concentration. [d] Computed from the stoichiometric activity coefficients, dissociation constants, and values of γ_{CO_2} in NaCl solutions (to represent γ_{NaCl}) using equation (34). [e] Computed from the degrees of association using equation (37). [f] Computed from the degrees of association and the stoichiometric activity coefficients using equation (32). [g] Computed from $\log \gamma_{\pm,\ D.-H.}\ (T,\bar{I} = -A(T) \mid Z_1Z_2 \mid \bar{I}^{1/2}/(1 + å(T)B(T)\bar{I}^{1/2})$ using the values of å(T), A(T), B(T), and $\bar{I}$ given above. [h] Smoothed (fig. 3) values computed (using eq 38) from the mean ionic activity coefficients and those calculated from the Debye-Hückel equation[g]. [i] Computed (using eq 35) from Henry's Law coefficients for CO_2 in water and NaCl solutions at elevated temperatures (Ellis and Golding, 1963). [j] Computed from the osmotic coefficients using equation (42). [k] Computed (Helgeson, 1967b) from equations (39) and (40) using density and dielectric constant data for water taken, respectively, from Keenan and Keyes (1936) and Akerlof and Oshry (1950). [l] Robinson and Stokes (1959). [m] Interpolated. [n] Extrapolated. [p] Computed from the values of K_{NaCl}, γ_{CO_2} in NaCl solutions (to represent γ_{NaCl}), and extrapolated values of the mean ionic activity coefficient (eqs 32 and 34). [q] Calculated from least squares fits of the mean ionic activity coefficients in the concentration range 1.0 to 3.0 m using the Stokes-Robinson equation (eq 41). [r] Obtained from least squares fits (eq 41) in the concentration range 0.1 to 3.0 m. [s] Computed from the Stokes-Robinson equation (eq 41) using the values of A(T), B(T), $\bar{I}$, B(T), and the extrapolated mean ionic activity coefficients shown above. [t] All values given in this table are consistent with molal units of concentration.

the assumption that $\gamma_{NaCl} \approx \gamma_{CO_2}$ in NaCl solutions probably introduces negligible error into mean ionic activity coefficient calculations.

Deviation function.—The departure of the log of the mean ionic activity coefficient from that predicted by the Debye-Hückel expression at 25°C has been described by Scatchard (1936) and others with a deviation function. Pitzer and Brewer (1961) designate this function with the symbol B˙ to distinguish it from the limiting function at zero concentration. The deviation function at a given temperature can be defined by writing

$$B^{\cdot}(\bar{I}) = \frac{\log \gamma^{*}_{\pm} + A|Z_1Z_2|\bar{I}^{1/2}/(1 + \text{å}B\bar{I}^{1/2})}{\bar{I}} \tag{38}$$

in which å is the "distance of closest approach" of the ions in solution, and A and B are the molal Debye-Hückel coefficients given by

$$A(T) = \frac{1.8246 \times 10^{6}(\rho_{H_2O}(T))^{1/2}}{(\varepsilon_{H_2O}(T)T)^{3/2}} \tag{39}$$

and

$$B(T) = \frac{50.29 \times 10^{8}(\rho_{H_2O}(T))^{1/2}}{(\varepsilon_{H_2O}(T)T)^{1/2}} \tag{40}$$

where ρ_{H_2O} is the density, and ε_{H_2O} the dielectric constant of water at temperature T. Values of the A and B coefficients in equation (38) at 10 degree intervals from 25° to 350°C have been presented elsewhere (Helgeson, 1967b).

The definition of the deviation function expressed by equation (38) differs somewhat from that used previously by Scatchard (1936), Pitzer and Brewer (1961), and others to analyze the behavior of electrolyte solutions at low temperatures. The function employed by these investigators is defined by an expression of equation (38) in which stoichiometric ionic strength is used, and the product åB is set to unity. Although this simplification is useful for considering the behavior of electrolyte solutions at low temperatures, it is desirable to include explicit provision for å and true ionic strength in calculations of B˙ at high temperatures.

The deviation function, B˙, is essentially independent of concentration at ionic strengths of $\sim$ 0.5 or more in most electrolyte solutions at 25°C. Cobble (1964) assumed this function to be temperature independent as well, and he employed 25°C values of B˙ to calculate high temperature activity coefficients. It is shown below that Cobble's assumption is invalid for concentrated sodium chloride solutions at elevated temperatures.

Prediction of the deviation function for high temperature sodium chloride solutions requires values of the Debye-Hückel å parameter at each temperature. Because of the high sensitivity of the deviation function to small errors in the å values used in the equation, this parameter

must be known accurately in order to define adequately the temperature dependence of the deviation function. The required values of å were obtained by fitting the mean ionic activity coefficients in table 2 with a least squares computer routine involving the Stokes-Robinson equation (Stokes and Robinson, 1948; Robinson and Stokes, 1959).

The Stokes-Robinson equation closely describes the concentration dependence of the mean ionic activity coefficients of a large number of strong electrolytes to high concentrations at 25°C. For a given electrolyte at temperature T and true ionic strength $\bar{I}$, this expression appears as

$$\log \gamma^*_{\pm}(T,\bar{I}) = -\frac{A(T)\,|Z_1Z_2|\bar{I}^{1/2}}{1 + å(T)B(T)\bar{I}^{1/2}} - \frac{h(T)}{\nu}\log a_w(T,\bar{I}) - \log\,[1 - 0.018m(\nu - h(T))] \qquad (41)$$

in which a_w is the activity of H_2O, m is the molality of the completely dissociated solute (equivalent to $\bar{I}$ in the case of NaCl), å is the "distance of closest approach" of the ions in solution, ν is the number of ions per mole of solute, and h is the *average* number of water molecules coordinated to ν ions in solution. The Stokes-Robinson equation provides for the effects of ion hydration on the activity coefficient of the solute. It can be derived rigorously from equations describing the Gibbs free energy of the solution in terms of the chemical potentials of H_2O and the hydrated and unhydrated solute. Two assumptions are involved in the derivation: (1) that the coefficient h is independent of concentration, and (2) that the Debye-Hückel term in the equation accurately describes the part of the departure of activity from molality due to electrostatic interaction of the *solvated* ions. The excellent fits obtained by Stokes and Robinson (1948) of observed activity coefficients in a large number of concentrated electrolytes at 25°C suggest that these assumptions are valid.

Equation (41) was used to compute least squares fits of the mean ionic activity coefficients for sodium chloride solutions shown in table 2 (Helgeson and James, 1968). The values of $\bar{I}$ in equation (41) were computed from equation (37) using the degrees of association (α_{NaCl}) given in table 2. The activities of water employed in the calculation were computed from the stoichiometric osmotic coefficient (ϕ) for each temperature and total concentration of NaCl (m_t) by evaluating

$$\ln a_w = -\frac{\nu m_t \phi}{55.55}. \qquad (42)$$

The osmotic coefficients and computed activities of water are given in table 2 along with the values of å(T) and h(T) for NaCl obtained from the least squares fits. The deviation functions calculated (eq 38) from the å and $\gamma^*_{\pm}$ values are also shown in table 2.

It can be seen in figure 3 that B'_{NaCl} passes through a maximum with increasing temperature, but that at each temperature B'_{NaCl} is only slightly dependent on concentration at molalities of NaCl between one and three. The maximum variation in B'_{NaCl} with concentration in the

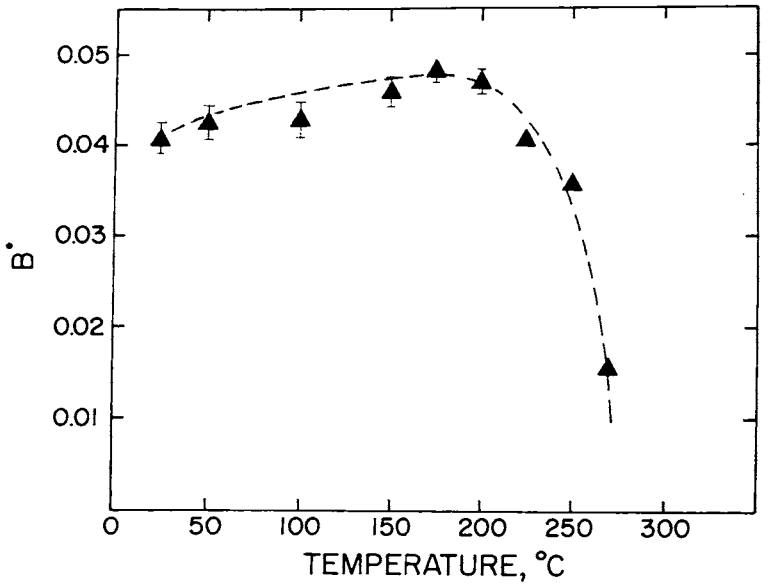

Fig. 3. Plot of the deviation function, B', against temperature for 1, 2, and 3 molal NaCl solutions. The symbols represent the mean values of B' at each temperature computed from equation (38); the vertical bars on the symbols depict the maximum variation in B' in 1 to 3 molal solutions. Where no vertical bar is shown, the maximum variation is within the limits of the symbol.

range 1.0 to 3.0 $m_{t,\mathrm{NaCl}}$ from 25° to 270°C is ± 0.002 from the values represented by the symbols in figure 3; this variation represents a slight increase in B' with increasing concentration. However, it can be seen in figure 3 that the uncertainty in the data from which the B' values were calculated exceeds the extent of this variation. Although mean ionic activity coefficients for NaCl are not available above 270°C (see footnote 3, p. 743), it appears likely that B' approaches zero in the region of 300°C. B' also becomes small in HCl solutions at high temperatures (Helgeson and James, 1968). The behavior of B' in figure 3 suggests that the simple Debye-Hückel expression in the Stokes-Robinson equation for $\gamma^*_{\pm}$ (eq 41) is sufficient to describe the mean ionic activity coefficient of NaCl in 1 to 3 molal solutions in the region of 300°C. This is not surprising because the hydrational entropies of ions at 25°C are relatively large negative numbers that would be expected to become substantially less negative with increasing temperature, and the bulk of the solute in sodium chloride solutions is associated above 300°C.

From a practical standpoint, the fact that the Debye-Hückel expression can be used to predict accurately mean ionic activity coefficients in concentrated electrolytes at high temperatures is extremely useful. Note, however, that such calculations are valid only when true (and not stoichiometric) ionic strength is used in the equation. It can be demonstrated that the product åB (where B is the Debye-Hückel co-

efficient) for NaCl solutions is essentially independent of temperature from 25° to 270°C. Also, B˙ is closely related to γ_{CO_2} in NaCl solutions, which is reflected by the relative success of the Delta approximation (Helgeson, 1964) in predicting activity coefficients at elevated temperatures. Various theoretical implications of the behavior of γ_{CO_2}, $\gamma_{\pm}$, $\gamma^*_{\pm}$, å, *h*, and B˙ for NaCl solutions and other electrolytes at elevated temperatures together with empirical correlations of these parameters with thermodynamic variables have been considered in detail elsewhere (Helgeson and James, 1968).

True individual ion activity coefficients.—In the derivation of the Stokes-Robinson equation (eq 41), the departure of activity from molality for the completely dissociated solute over and above that described by the Debye-Hückel term for the solvated ions is attributed to ion hydration; that is, as the concentration of the solute increases at a given temperature, the product $B\bar{I}$, which is numerically equivalent to the sum of the second and third terms on the right side of the Stokes-Robinson equation, is a function only of the decrease in the number of uncoordinated solvent molecules per 1000 g of water. At constant concentration in sodium chloride solutions of 1 to 3 molal, the number of uncoordinated water molecules apparently first decreases and then increases with increasing temperature above 25°C.

In a concentrated multicomponent electrolyte solution consisting predominantly of sodium chloride, ions present in small concentrations (compared to that of the sodium chloride) should contribute negligibly to the ionic strength and total coordination of water molecules in the solution. In such an electrolyte, close approximations of individual ion activity coefficients for the species present in small concentrations can be calculated from

$$\log \gamma^*_i(T,\bar{I}) = \frac{-A(T)Z_i^2\bar{I}^{1/2}}{1 + å_i(T)B(T)\bar{I}^{1/2}} + B\dot{}(T)\bar{I} \qquad (43)$$

where γ^*_i is the activity coefficient of the *i*th ion present in small concentrations in the solution, $\bar{I}$ and B˙ are the true ionic strength and deviation functions, respectively, for pure solutions of the supporting electrolyte, and $å_i$ refers to the "distance of closest approach" of the *i*th ion. Equation (43) can also be written for mean ionic activity coefficients of salts present in small concentrations in a sodium chloride solution. This requires only that the relation

$$\gamma^*_{\pm} = \left({\gamma^*_+}^{\nu_+} {\gamma^*_-}^{\nu_-} \right)^{1/\nu} \qquad (44)$$

be satisfied for the dissociated part of the salt in question.

Provided appropriate å values are known for each temperature, equation (43) and the data in table 2 permit calculation of activity coefficients of ions present in small concentrations in sodium chloride solutions at high temperatures and concentrations of NaCl. Unfortunately, values of å for most ions at high temperatures are not available, nor

can they be calculated with confidence. It appears that the best approximation that can be made in the present state of knowledge is to assume that å coefficients for ions are independent of temperature and employ the values at 25°C in calculations of high temperature activity coefficients from equation (43). It can be seen in table 2 that å for NaCl solutions from 25° to 300°C varies between −0.7 and 0.5 angstroms from its value at 25°C. If the å values for other salts behave in a similar fashion, the error involved in calculating high temperature activity coefficients by assuming å values at 25°C to be constant should be negligible compared to other uncertainties attending geochemical calculations. On the other hand, if the temperature variation of å coefficients for other salts is similar to that exhibited by the å for HCl, the error may be substantial at high temperatures. The å coefficient for HCl is essentially constant from 25° to 150°C, but it increases rapidly with increasing temperature between 150° and 275°C (Helgeson and James, 1968). Nevertheless, it appears likely that the temperature dependence of å coefficients for metal ions and metal ion complexes will prove to be more like NaCl than HCl.

Because å coefficients tend to increase at high temperatures, high temperature activity coefficients computed from equation (43) assuming constant å values equal to their values at 25°C should be minimal approximations. Where such approximations render individual ion activity coefficients less than ~0.1, the effect of small errors in the activity coefficients on calculations of solution equilibria may be large. For this reason, approximations of individual ion activity coefficients at high temperatures and concentrations of sodium chloride should be confined to monovalent and possibly divalent species. Predictions of high temperature activity coefficients in concentrated solutions of mixed electrolytes in which more than ~20 percent of the solute is not sodium chloride requires use of Harned's rule coefficients or coefficients for a similar but higher order power function (Lietzke, Hupf, and Stoughton, 1965; Helgeson, 1967b).

Stoichiometric individual ion activity coefficients.—Calculations of high temperature mineral solubilities in concentrated hydrothermal solutions in which the solute is predominately sodium chloride can be simplified considerably by first computing stoichiometric individual ion activity coefficients for the solution. The stoichiometric individual ion activity coefficient, $\dot{\gamma}_i$, is defined as

$$\dot{\gamma}_i = \frac{a_i}{m_{t,i}} \tag{45}$$

where a_i and $m_{t,i}$ designate the activity and total molality of the ith ion present in small concentrations in the sodium chloride solution. Garrels and Thompson (1962) used the symbol γ_T for stoichiometric individual ion activity coefficients. The γ_T used by Garrels and Thompson differs from the $\dot{\gamma}_i$ in equation (45) only to the extent that the latter specifically refers to the presence of the ith ion in an electrolyte solution containing a predominant concentration of some other salt.

Values of $\dot{\gamma}_i$ can be calculated for a given temperature and concentration of sodium chloride (or some other supporting electrolyte) by evaluating one of several possible mass balance relations that can be written for the ith ion, depending on its identity. For example, if $\mathbb{C}$ represents a cation associated in a series of z mononuclear complexes involving y moles of anion L ($y = 1, 2, 3, \ldots, z$), we can write

$$m_{t,\mathbb{C}} = m_{\mathbb{C}} + \sum_{y}^{z} m_y \tag{46}$$

where $m_{\mathbb{C}}$ and m_y are the molalities, respectively, of cation $\mathbb{C}$ and the yth complex, which has the form $\mathbb{C}L_y$. Expressing equation (46) in terms of activities leads to

$$m_{t,\mathbb{C}} = \frac{a_{\mathbb{C}}}{\gamma^*_{\mathbb{C}}} + \sum_{y}^{z} \frac{a_{\mathbb{C}} a_L{}^y}{\beta_y \gamma_y} = a_{\mathbb{C}} \left(\frac{1}{\gamma^*_{\mathbb{C}}} + \sum_{y}^{z} \frac{a_L{}^y}{\beta_y \gamma_y} \right) \tag{47}$$

where γ_y is the activity coefficient of the yth complex, $a_{\mathbb{C}}$ and a_L are the activities of the cation and anion, respectively, γ^* represents the true individual ion activity coefficient of the subscripted species, and β_y is the overall dissociation constant for the yth complex defined as

$$\beta_y = \prod_{u}^{y} K_u \tag{48}$$

where u is an integer index ($u = 1, 2, 3, \ldots, y$) and K_u represents the stepwise dissociation constant for the uth complex. Combining equations (45) and (47) leads to

$$\dot{\gamma}_{\mathbb{C}} = \frac{1}{\dfrac{1}{\gamma^*_{\mathbb{C}}} + \displaystyle\sum_{y}^{z} \frac{a_L{}^y}{\beta_y \gamma_y}} = \frac{1}{\dfrac{1}{\gamma^*_{\mathbb{C}}} + \displaystyle\sum_{y}^{z} \frac{m_L{}^y \gamma^*_L{}^y}{\beta_y \gamma_y}} \tag{49}$$

If the total molality (m_t) of cation $\mathbb{C}$ is small compared to that of sodium chloride, the values of $\gamma^*_{\mathbb{C}}$ and γ^*_L (and γ_y when the yth complex is a charged species) in equation (49) can be calculated from equation (43). The values of $\bar{I}$ and B' used in the calculations are those obtained from equations (37) and (38) for the supporting electrolyte; the β values in equation (49) can be predicted from the thermodynamic relations discussed above. If the yth complex is a nonpolar neutral species, γ_y can be approximated as γ_{CO_2}; if it is more like H_4SiO_4, γ_y can be regarded as unity (Helgeson, 1964; 1967b). Where the ligand involved is chloride in a concentrated sodium chloride solution containing small concentrations of other species, the mean ionic activity of sodium chloride in a pure sodium chloride solution can be used as a close approximation of a_L. In such cases, $m_L{}^y \gamma^*_L{}^y$ in equation (49) can be replaced by $m_{t,NaCl}\, \gamma_{\pm NaCl}$ and (because $\gamma_{\pm NaCl}$ is known—table 2) $\dot{\gamma}_{\mathbb{C}}$ can then be computed as

a function of $m_{t,\mathrm{NaCl}}$. Where L does not correspond to Cl^-, $\dot{\gamma}_{\mathbf{C}}$ can be calculated as a function of m_{L}. In many cases m_{L} in hydrothermal solutions can be approximated as $m_{t,\mathrm{L}}$.

Expressions analogous to equations (46) to (49) can be derived to calculate values of $\dot{\gamma}_{\mathrm{L}}$. Such expressions are particularly useful where the anion L is associated predominantly with the hydrogen ion. Under these conditions, $\dot{\gamma}_{\mathrm{L}}$ can be computed as a function of pH. By rearranging equation (45), precomputed values of $\dot{\gamma}_{\mathbf{C}}$ and $\dot{\gamma}_{\mathrm{L}}$ permit calculation of the activities of the free C and L ions in concentrated hydrothermal solutions directly from analytical data. Consequently, hydrothermal mineral solubilities can be predicted without further consideration of complexes in solution; that is, provided all important complexes are included in the calculations of the $\dot{\gamma}_{\mathbf{C}}$ and $\dot{\gamma}_{\mathrm{L}}$ values.

Solubility Calculations

By specifying values for such variables as pH and the total molality of NaCl in concentrated sodium chloride solutions at a particular temperature, values of $\dot{\gamma}$ for S^{--}, SO_4^{--}, CO_3^{--}, Ag^+, Fe^{+++}, Cu^{++}, and other ions that may be present in small concentrations in hydrothermal solutions can be calculated from expressions of equation (49) or the corresponding equation for anions. Provided these calculations include provision for a realistic distribution of aqueous species, the solubility of a given mineral in the solution can then be computed from the activity product relation,

$$m_{t,i}^{\,n}\, m_{t,\hat{e}}^{\,\nu}\, \dot{\gamma}_i^{\,n}\, \dot{\gamma}_{\hat{e}}^{\,\nu} = \mathrm{K}_{\mathrm{sp}_\psi} \tag{50}$$

where $\mathrm{K}_{\mathrm{sp}_\psi}$ is the activity product constant of the ψth mineral, which consists of n moles of the ith cation and v moles of the êth anion in the system. The stoichiometric solubility (where $\nu m_{t,i} = n m_{t,\hat{e}}$) is then given by

$$\mathrm{S}_\psi = \frac{m_{t,i}}{n} = \frac{1}{n}\left(\frac{n^{\nu}\mathrm{K}_{\mathrm{sp}_\psi}}{\nu^{\nu}\dot{\gamma}_i^{\,n}\dot{\gamma}_{\hat{e}}^{\,\nu}}\right)^{1/(n+\nu)} \tag{51}$$

in which S_ψ is the solubility (in molality units) of the ψth phase. If $m_{t,\hat{e}}$ (the total molality of the êth anion) is specified, non stoichiometric solubilities can be computed from

$$\mathrm{S}_\psi = \frac{m_{t,i}}{n} = \frac{1}{n}\left(\frac{\mathrm{K}_{\mathrm{sp}_\psi}}{m_{t,\hat{e}}^{\,\nu}\dot{\gamma}_i^{\,n}\dot{\gamma}_{\hat{e}}^{\,\nu}}\right)^{1/n} \tag{52}$$

If more than one solid phase is in equilibrium with the solution, expressions analogous to equations (51) and (52) can be derived by combining statements of equation (50) for each solid and writing a mass balance expression relating the total molalities of each cation in solution. The mutual solubilities of the minerals in the solution can then be computed from these equations.

Pressure as a Variable

As indicated earlier, the pressure dependence of equilibrium constants for most hydrothermal reactions is slight (considered negligible in this discussion) at temperatures below ~300°C. This is true for solid phase equilibria even at much higher temperatures, but for dissociational reactions in aqueous solution, pressure effects become significant as temperature increases above ~300°C.

The need for a general method of computing equilibrium constants at high pressures and temperatures has become more acute in recent years. Experimental data for hydrothermal systems are frequently obtained at temperatures and pressures greater than 300°C and 1000 atm. The dependence of equilibrium constants on pressure is a volume function, but few ionic volumes are known for aqueous electrolytes at high temperatures and pressures, and those data that exist (Owen and Brinkley, 1941; Couture and Laidler, 1956; Zen, 1957; Hepler, 1965; Ellis, 1966, 1967, 1968) are rarely definitive with respect to the volumes of individual ions and complexes. Despite this handicap, the effect of pressure on dissociation constants in aqueous solutions of electrolytes can be closely approximated from the temperature and pressure dependence of the dielectric constant of water.

Consideration of the thermodynamic characteristics of dissociational reactions as a function of temperature suggests that the dielectric constant of water essentially controls the stabilities of complexes in aqueous solutions of electrolytes at high temperatures (Helgeson, 1967a). It can be shown that the conventional molal[6] dissociation constant for a neutral complex in the supercritical pressure-temperature region for water can be described within the uncertainty of the experimental data by a monotonic function of the dielectric constant of the solvent; that is, the molal log K(T,P) for a given neutral complex is essentially a constant for all pressure-temperature combinations that result in the same value of the dielectric constant of water in the supercritical region. Data are not available to determine whether the same relation exists for charged complexes in the supercritical region, but theoretical considerations suggest that the stabilities of these species should also vary monotonically with the dielectric constant of the solvent.

[6] The conventional dissociation constant does not provide explicitly for the participation of the solvent in the dissociational reaction. If the reaction is written to include the correct degree of participation by the solvent, then the *isothermal* dissociation constant becomes independent of the dielectric constant of the medium (Quist and Marshall, 1968b). Most supercritical dissociation constants reported in the literature are consistent with molar units of concentration (for example, Franck, 1961; Quist and Marshall, 1966, 1968a and c). These data can be converted to be consistent with molal units of concentration by solving $\log K_m = \log K_M - (\tilde{n} - 1) \log \rho_{H_2O}$, where K_m and K_M are the molal and molar dissociation constants, respectively, ρ_{H_2O} represents the density of water, and $\tilde{n}$ is equal to the sum of the exponents in the Law of Mass Action equation for the dissociational reaction. Despite recent arguments to the contrary (Quist and Marshall, 1968a) dissociation constants consistent with molal units of concentration and the molal scale of concentration itself are perfectly appropriate for calculations pertaining to the supercritical region. Molal units of concentration are commonly more useful than molar units in geochemical calculations.

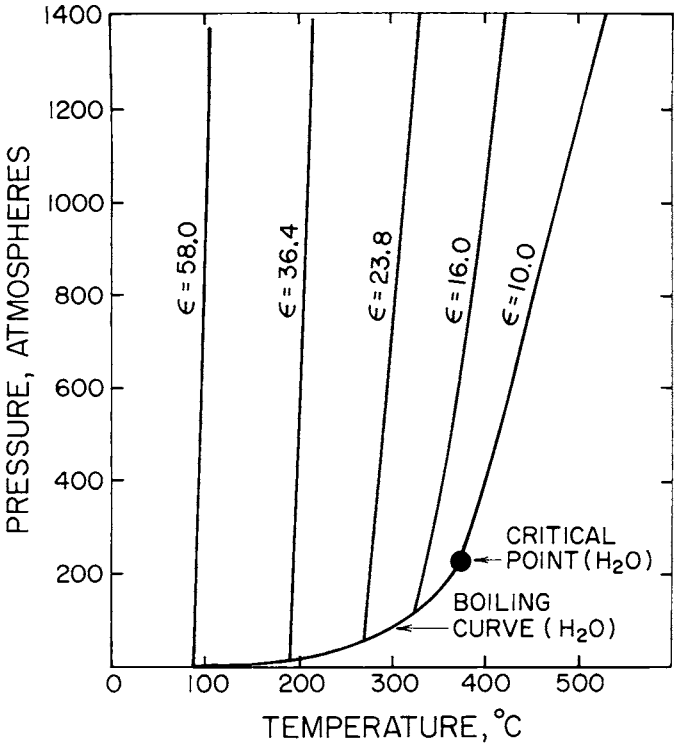

Fig. 4. Isodielectric curves for water in the liquid and supercritical phase regions. The curves were drawn from dielectric constant values taken from Quist and Marshall (1965) and density data for water obtained from Holser and Kennedy (1958).

Isodielectric curves for water are plotted in figure 4 to illustrate the order of magnitude of pressure effects on dissociation constants. For example, suppose that the molal dissociation constant for

$$H_2S_{(aq)} \rightleftarrows 2H^+ + S^{--} \tag{53}$$

at 1000 atm and 400°C is required for a given geochemical calculation. In figure 4 it can be seen that the dielectric constant of water under these conditions is the same as it is at 120 atm and 325°C on the boiling curve. Pressure effects contribute only slightly to dissociation constants calculated for a 1 atm standard state from high temperature experimental data obtained along the vapor + liquid pressure-temperature curve for water to ~325°C. For this reason, and also because appropriate ionic volumes are rarely available, the pressure correction (119 atm in this case) is commonly neglected, and the experimental log K(T) values obtained from such experiments are assigned to the 1 atm standard state. Because the molal value of log K(T) for the dissociation of a neutral complex in water at high temperatures is essentially constant along an isodielectric curve, the molal dissociation constant computed for 325°C

and 1 atm (or more accurately, 120 atm) is approximately equivalent to that at 400°C and 1000 atms.

The relation described above between log K(T,P) and the dielectric constant of the solvent is more useful for the purpose of estimating molal log K(T,P) values at high temperatures and pressures than density relations. This is true because log K(T,P) for a given reaction cannot be characterized as a single monotonic function of density at all pressure and temperature combinations contributing to constant density. On the other hand, isentropes for water are essentially coincident with the isodielectric curves shown in figure 4, which means that log K(T,P) can also be approximated as a monotonic function of the entropy of the solvent (Helgeson, 1964).

If a molar scale of concentration is used and the dissociational reaction is written to include the correct degree of solvation of the participating species in solution, the corresponding supercritical dissociation constant is independent of pressure (Quist and Marshall, 1968a). Consequently, these dissociation constants can be computed for any pressure-temperature condition solely from predictive equations involving temperature, such as those presented in the preceding pages. However, in practice this approach is usually precluded by the dearth of information concerning the actual extent of solvation (hydration numbers) of the various species in hydrothermal solutions at high temperatures.

COMPUTER CALCULATIONS AND RESULTS

The equations and methods of calculation summarized in the preceding pages have been programmed for machine computation. The results of calculations carried out with the aid of these computer programs are discussed below and presented in tables 1 to 14 and figures 5 to 21. The data employed in the calculations are also presented in the tables, along with references to the sources from which they were taken. In certain cases (noted in the footnotes in the tables) thermodynamic values reported in the literature have been changed (within the margins of uncertainty reported in the source references) to agree with other experimental and geologic observations, and estimates of thermodynamic properties are given for a number of species for which data are incomplete. The values listed in the tables are the result of a critical compilation, and they are intended to constitute an internally consistent array of thermodynamic data.

Dissociation Constants

Thermodynamic data at 25°C and 1 atm for various species and dissociational reactions of interest in hydrothermal studies are summarized in tables 3 and 4 along with calculated average heat capacities and log K(T) values for higher temperatures. The dissociation constants, which were computed from equations (11) to (17) using thermodynamic data given in tables 3 and 4, are also plotted in figure 5 to illustrate the changes in the stabilities of hydrothermal species with increasing temperature.

TABLE 3

Thermodynamic data for species in aqueous solution at 25°C and 1 atm

Species	ΔH°_f[a] (cal mole^{-1})	S° (cal mole^{-1} deg^{-1})	Average heat capacity[a] (cal mole^{-1} deg^{-1})					
			60°C	100°C	150°C	200°C	250°C	300°C
H_4SiO_4	—348,060[b]	45.84[b]	49[p]	49[p]	46[p]	46[p]	46[p]	45[p]
H_2S	—9,030[c]	30.9[d]	46[m]	39[m]	35[m]	32[m]	33[n]	35.5[n]
HS^-	—4,230[e]	15.0[e]	—52	—58	—62	—66	—70	—76
S^{--}	9,070[f]	—4.0[g,r]	—48	—58	—61	—65	—69	—75
SO_4^{--}	—217,320[e]	4.8[e]	—99	—108	—105	—114	—120	—126
CO_3^{--}	—161,840[e]	—13.6[e]	—132	—146	—138	—151	—162	—171
OH^-	—54,970[e]	—2.57[e]	—47	—58	—61	—65	—69	—76
Cl^-	—39,950[e]	13.51[s]	—51	—58	—62	—66	—70	—76
F^-	—79,500[e]	—3.3[e]	—47	—58	—61	—65	—69	—75
$H_2O_{(liq)}$	—68,315[e]	16.71[e]	18	18	18	18	18	18
H^+	0.0	0.0	23	31	33	35	37	39
Ag^+	25,310[g]	17.69[g]	30	39	39	43	45	47
Cu^+	16,930[h]	9.4[i]	33	44	43	47	50	53
Cu^{++}	15,390[g]	—23.6[g]	49	65	66	71	75	79
Pb^{++}	—400[e]	2.5[e]	37	49	49	54	58	61
Zn^{++}	—36,780[e]	—26.0[j,t]	50	66	67	73	77	81
Hg^{++}	41,590[g]	—5.4[j]	41	54	55	60	63	67
Fe^{++}	—21,000[g]	—27.1[g]	50	66	68	73	78	82

Species	ΔH°_f[q] (cal mole^{-1})	S° (cal mole^{-1} deg^{-1})	Average heat capacity[a] (cal mole^{-1} deg^{-1})					
			60°C	100°C	150°C	200°C	250°C	300°C
Fe^{+++}	—11,400[g]	—70.1[g]	70	93	96	105	109	115
Ca^{++}	—129,770[g]	—13.2[g]	45	59	60	66	68	72
Mg^{++}	—110,410[g]	—28.2[g]	51	67	69	75	79	83
Ba^{++}	—128,670[g]	3.0[g]	38	50	50	55	58	61
K^+	—60,040[g]	24.5[g]	27	35	35	39	41	43
Na^+	—57,279[g]	14.4[g]	35	41	41	45	47	49
Al^{+++}	—127,000[e]	—76.9[e]	72	95	99	108	114	120
Au^+		22.0[k]	29	37	37	41	43	45
Au^{+++}		—23.0[l]	50	67	69	74	78	82

[a] Computed from equations (2) to (5) and the entropies shown above (Criss and Cobble, 1964a and b). [b] Computed from a constant $\Delta C^\circ_{P,r}$ least squares fit of quartz solubilities measured by Morey, Fournier, and Rowe (1962) and Kennedy (1950) using the thermodynamic data for quartz given in table 7. [c] Computed from $\Delta H^\circ_{f,H_2S_{(g)}} = -4930$ cal mole^{-1} (Wagman and others, 1968) and a value of ΔH°_r for $H_2S_{(g)} \rightleftarrows H_2S_{(aq)}$ of —4100 cal mole^{-1} (Pohl, 1961; table 10). [d] computed from $S^\circ_{H_2S_{(g)}} = 49.16$ cal mole^{-1} deg^{-1} (Wagman and others, 1968) and a value of ΔS°_r for $H_2S_{(g)} \rightleftarrows H_2S_{(aq)}$ of —18.3 cal mole^{-1} deg^{-1} (Pohl, 1961; Wright and Maass, 1932; table 10). [e] Wagman and others (1965, 1966, 1968). [f] Calculated from log $K_{HS^-} = -13.9$ (Maronny, 1959; Muhammed and Sundaram, 1961) and the entropy values shown above for HS^- and S^{--}. This value of $\Delta H^\circ_{f,S^{--}}$, which is consistent with the other data given above for species involving S^{--}, differs from that (7900 cal mole^{-1}) reported by Wagman and others (1968). [g] Latimer (1952). [h] Calculated from log $K(T_r)$ for the disproportionation of the cuprous ion (Fenwick, 1926; table 10) using the values of $S^\circ_{Cu^+}$, $S^\circ_{Cu^{++}}$, and $\Delta H^\circ_{f,Cu^{++}}$ shown above together with the data for $Cu_{(c)}$ given in table 6. [i] Wagman (1951). [j] Wulff (1957). [k] Computed from a prediction of the dissociational entropy for AuCl from equations (25) and (27), $S^\circ_{Cl^-} = 13.51$ (Ahluwalia and Cobble, 1964), and a value of S°_{AuCl} computed from Cobble's (1953) equation for neutral species. [l] Calculated from the predicted dissociational entropy for $AuCl_4^-$ in table 1 using $S^\circ_{AuCl_4^-} = 61$ cal mole^{-1} deg^{-1} (Latimer, 1952). [m] Helgeson (1967a). [n] Computed (Helgeson, 1967a) from least squares fits of equation (17) to equilibrium constants for $H_2S_{(g)} \rightleftarrows H_2S_{(aq)}$ at elevated temperatures (Kozinsteva, 1964). The high temperature values of $\Delta H^\circ_{H_2S_{(g)}}$ used in the calculations were computed from a heat capacity power function (eq 10, table 8) and the value of $\Delta H^\circ_{f,H_2S_{(g)}}$ at 25°C given in footnote c above. [p] Calculated from quartz solubilities (Morey, Fournier, and Rowe, 1962; Kennedy, 1950) and the thermodynamic data given in table 7 for quartz. [q] Enthalpy of formation from the elements. [r] Compared to —3.5 cal mole^{-1} deg^{-1} (Wagman and others, 1968). [s] Ahluwalia and Cobble (1964). [t] Compared to —26.8 cal mole^{-1} deg^{-1} (Wagman and others, 1968).

TABLE 4

Thermodynamic data for dissociational equilibria in aqueous solution[bbb]

Reaction[a]	$\Delta H^\circ_r (T_r)$ (cal mole^{-1})	$\Delta S^\circ_r (T_r)$ (cal mole^{-1} deg^{-1})	log K(T)[jj] 25°C	50°C	60°C	100°C	150°C	200°C	250°C	300°C
$H_2O_{(liq)} \rightleftarrows H^+ + OH^-$	13,335[b]	— 19.31[c]	—14.00[d,ff]	—13.27[d,ff]	—13.03[d,ff]	—12.26[d,ff]	—11.64[d,ff]	—11.27[d,ff]	—11.13[d,ff]	—11.39[d,ff]
$H_2S \rightleftarrows H^+ + HS^-$	4,800[e]	— 15.9[f]	— 6.99[g]	— 6.77[h,qq]	— 6.72[h,qq]	— 6.63[h,qq]	— 6.72[h]	— 6.96[h]	— 7.35[h]	— 8.06[h]
$HS^- \rightleftarrows H^+ + S^{--}$	13,300[e]	— 19.0[f]	—13.90[i]	—13.13[h,qq]	—12.84[h,qq]	—11.78[h,qq]	—10.62[h]	— 9.57[h]	— 8.61[h]	— 7.72[h]
$HSO_3^- \rightleftarrows H^+ + SO_3^{--}$	— 3,850[d]	— 22.0[j]	— 1.99[k,l]	— 2.27[l]	— 2.40[d,ff]	— 2.99[l]	— 3.74[l]	— 4.49[l]	— 5.41[d,ff]	— 7.06[d,ff]
$H_2SO_3 \rightleftarrows H^+ + HSO_3^-$									0.6[m]	0.5[m]
$H_2CO_{3(app)}$[hh] $\rightleftarrows H^+ + HCO_3^-$	1,840[n]	— 22.9[c]	— 6.35[p]	— 6.31[d,ff]	— 6.32[d,ff]	— 6.45[d,ff]	— 6.73[d,ff]	— 7.08[d,ff]	— 7.63[d,ff]	— 8.86[d,ff]
$HCO_3^- \rightleftarrows H^+ + CO_3^{--}$	3,600[n]	— 35.16[c]	—10.32[q]	—10.17[d,ff]	—10.15[d,ff]	—10.16[d,ff]	—10.29[d,ff]	—10.68[d,ff]	—11.43[d,ff]	—13.38[d,ff]
$H\ As(OH)_3 \rightleftarrows H^+ + H_2As\ (OH)_3^-$	3,430[rr]	— 82.9[rr]	—20.6[ww]	—20.5[t]	—20.5[t]	—20.8[t]	—21.8[t]	—23.6[t]		
$H_2As(OH)_3^- \rightleftarrows H^+ + HAs(OH)_3^{--}$	5,120[rr]	— 66.9[rr]	—18.4[ww]	—18.2[t]	—18.1[t]	—18.2[t]	—18.8[t]	—20.1[t]		
$HAs(OH)_3^{--} \rightleftarrows H^+ + As(OH)_3^{---}$	4,350[rr]	— 38.9[rr]	—11.7[ww]	—11.5[t]	—11.4[t]	—11.4[t]	—11.7[t]	—12.3[t]		
$HAs(OH)_4 \rightleftarrows H^+ + As(OH)_4^-$	6,560[rr]	— 20.2[rr]	— 9.2[ww]	— 8.9[t]	— 8.8[t]	— 8.4[t]	— 8.3[t]	— 8.4[t]		
$As(OH)_4^- \rightleftarrows As(OH)_3 + OH^-$	6,800[e,rr]	0.7[rr]	— 4.8[ww]	— 4.4[t]	— 4.3[t]	— 3.8[t]	— 3.3[t]	— 2.9[t]		
$Al(OH)_4^- \rightleftarrows Al^{+++} + 4OH^-$	10,300[x]	—115.2[ss]	—32.73[tt]	—32.3[t]	—32.2[t]	—32.2[t]	—33.0[t,vv]	—34.6[t,vv]	—36.7[t,vv]	—39.5[t,vv]
$Al(OH)^{++} \rightleftarrows Al^{+++} + OH^-$	— 1,990[x]	— 49.0[uu]	— 9.25[yy]	— 9.4[t]	— 9.5[t]	—10.0[t]	—10.8[t,vv]	—11.9[t,vv]	—13.1[t,vv]	—14.7[t,vv]
$KSO_4^- \rightleftarrows K^+ + SO_4^{--}$	— 2,635[ff,xx]	— 12.7[ff,xx]	— 0.84[ff,xx]	— 1.00[ff,xx]	— 1.06[ff,xx]	— 1.30[ff,xx]	— 1.60[ff,xx]	— 1.94[ff,xx]		
$KHSO_4 \rightleftarrows K^+ + HSO_4^-$									0.8[r]	— 0.3[r]
$CaSO_4 \rightleftarrows Ca^{++} + SO_4^{--}$	— 1,760[d,pp]	— 16.5[d,pp]	— 2.31[s,pp]	— 2.4[d,t,pp]	— 2.5[d,t,pp]	— 2.7[d,t,pp]	— 3.1[d,t,pp]	— 3.6[d,t,pp]		
$MgSO_4 \rightleftarrows Mg^{++} + SO_4^{--}$	— 4,920[d,pp]	— 26.8[d,pp]	— 2.25[d,pp]	— 2.6[d,t,pp]	— 2.7[d,t,pp]	— 3.2[d,t,pp]	— 3.9[d,t,pp]	— 4.8[d,t,pp]		
$MnSO_4 \rightleftarrows Mn^{++} + SO_4^{--}$	— 3,700[d]	— 22.7[d]	— 2.25[v]	— 2.5[d,t]	— 2.6[d,t]	— 3.0[d,t]	— 3.6[d,t]	— 4.3[d,t]		

$ZnSO_4 \rightleftarrows Zn^{++} + SO_4^{--}$	— 4,090[d]	— 24.5[d]	— 2.38[u]	— 2.6[d,t]	— 2.7[d,t]	— 3.2[d,t]	— 3.8[d,t]	— 4.6[d,t]			
$AgSO_4^- \rightleftarrows Ag^+ + SO_4^{--}$	— 1,500[w]	— 11.0[w]	— 1.30[w]	— 1.4[t]	— 1.4[t]	— 1.6[t]	— 1.9[t]	— 2.2[t]			
$CaCO_3 \rightleftarrows Ca^{++} + CO_3^{--}$	— 3,130[x]	— 25.1[y]	— 3.20[z]	— 3.4[t,kk]	— 3.5[t,kk]	— 3.9[t,kk]	— 4.5[t,kk]	— 5.2[t,kk]			
$NaCl \rightleftarrows Na^+ + Cl^-$							0.97[aa,bb]	0.42[aa,bb]	— 0.15[aa,bb]	— 0.82[ll,bb]	
$KCl \rightleftarrows K^+ + Cl^-$								0.9[aa,cc]	0.3[aa,cc]	— 0.6[ll,cc]	
$HCl \rightleftarrows H^+ + Cl^-$	—18,630[d]	— 34.4[d]	6.1[dd]	5.0[dd]	4.56[d,ff]	2.90[d,ff]	1.23[d,ff]	0.06[ff]	— 0.67[d,ff]	— 1.24[d,ee]	
$Mg(OH)^+ \rightleftarrows Mg^{++} + OH^-$	— 2,140[x]	— 19.0[uu]	— 2.60[zz]	— 2.7[t]	— 2.8[t]	— 3.1[t]	— 3.6[t]	— 4.1[t,vv]			
$Fe(OH)^+ \rightleftarrows Fe^{++} + OH^-$	2,700[x]	— 17.0[uu]	— 5.7[aaa]	— 5.6[t]	— 5.5[t]	— 5.4[t]	— 5.5[t]	— 5.7[t,vv]			

[a] All species shown in this column are aqueous, and H_2O refers to liquid water. [b] Hale, Izat, and Christensen (1963) and Vanderzee and Swanson (1963). [c] Calculated from log $K(T_r)$ and $\Delta H°_r(T_r)$. [d] Helgeson (1967a). [e] Computed from data given in table 3. [f] Cobble (1964). [g] Ellis and Golding (1959) and Muhammad and Sundaram (1961). [h] Computed from data given in table 3 using equation (6). [i] Maronny (1959) and Muhammad and Sundaram (1961). [j] Criss and Cobble (1964b). [k] Young and Irish (1962). [l] Lietzke and Stoughton (1961). [m] Extrapolated as a dielectric constant function from supercritical log K(T,P) values published by Quist and Marshall (1965). [n] Pitzer (1937). [p] Harned and Davis (1943). [q] Harned and Scholes (1941). [r] Extrapolated as a dielectric constant function from supercritical log K(T,P) values published by Quist and Marshall (1966). [s] Bell and George (1953). [t] Estimates calculated from equation (16). [u] Nair and Nancollas (1958). [v] Nair and Nancollas (1959). [w] Hopkins and Wulff (1965). [x] Calculated from log $K(T_r)$ and $\Delta S°_r(T_r)$. [y] Estimated from an entropy correlation plot by Lafon (ms). [z] Garrels and Thompson (1962). [aa] Extrapolated. [bb] Figure 2 and table 2. [cc] Figure 2. [dd] Robinson (1936). [ee] Pearson, Copeland, and Benson (1963b) and Wright, Lindsay, and Druga (1961). [ff] Calculated from equation (17). [gg] Quist and others (1963). [hh] The subscript (app) indicates that the species referred to is the undifferentiated sum of $H_2CO_{3(aq)}$ and $CO_{2(aq)}$. [ii] Interpolated. [jj] All log K values given in the table are consistent with molal units of concentration. The values given for the dissociation of water are for the activity product constant (K_w). [kk] These values have large uncertainties owing to assumptions made regarding $\Delta S°_r(T_r)$—see footnote y above. [pp] These values were accepted instead of those reported by Marshall (1967) and Yeatts and Marshall (1969) because sulfate complexing of Na^+ was not taken into account in the interpretation of the solubility data from which their log K values were derived. [qq] These values are consistent with the experimental data reported by Ellis and Milestone (1967) from 22°-90°C. [rr] Computed from the thermodynamic data for the arsenic species given by Wagman and others (1968) [ss] Calculated from data given in table 3 and a value of 28.0 cal $mole^{-1}$ deg^{-1} for $S°_{Al(OH)_4^-}$ (Wagman and others, 1968) [tt] Computed from the free energy of formation of crystalline gibbsite (table 12), the hydrolysis equilibrium constant for crystalline gibbsite $(Al(OH)_{3(crystalline\ gibbsite)} + H_2O_{(liq)} \rightleftarrows Al(OH)_4^- + H^+$; log $K(T_r) = -15.3$, Kittrick, 1966), and the $\Delta G°_f(T_r)$ values for Al^{+++} and OH^- given by Wagman and others (1968). [uu] Estimated entropy of dissociation calculated from an expression analogous to equation (25) and an entropy correlation plot for hydroxyl complexes similar to that shown in figure 1 for chloride species but including provision for charge. [vv] Calculated by applying correction factors to log K values computed from equation (16). The correction factors were taken to be equivalent to those for ammonium hydroxide (0.86 at 300°C, Helgeson, 1967a). [ww] Computed from $\Delta H°_r(T_r)$ and $\Delta S°_r(T_r)$. [xx] Computed by the method of least squares from log K(T) values reported by Truesdell and Hostetler (1968) and Quist and others (1963). [yy] Computed from the equilibrium constant for $Al^{+++} + H_2O_{(liq)} \rightleftarrows Al(OH)^{++} + H^+$ ($10^{-4.75}$; Hem and Roberson, 1967). [zz] Hostetler (1963). [aaa] Leussing and Kolthoff (1953). [bbb] Dissociation constants for $NaCO_3^-$, $MgCO_3$, $MgHCO_3^+$ $CaHCO_3^+$, and $NaSO_4^-$, which are not included in this table, have been computed recently by Lafon (ms) for temperatures from 0° to 100°C.

TABLE 5

Predicted dissociation constants for metal chloride complexes in aqueous solution at elevated temperatures

Dissociational Reaction	$\Delta H^\circ_r(T_r)$[a] (cal mole^{-1})	$\Delta S^\circ_r(T_r)$[b] (cal mole^{-1} deg^{-1})	log β(T)[c] 25°C	50°C	100°C	150°C	200°C	250°C	300°C
$AgCl \rightleftarrows Ag^+ + Cl^-$	2,540	— 6.6	— 3.31[d]	— 3.17	— 2.99	— 2.92	(— 2.9)	(— 3.0)[t]	(— 3.4)[t]
$AgCl_2^- \rightleftarrows Ag^+ + 2Cl^-$	4,230	— 9.8	— 5.25[d]	— 5.02	— 4.71	— 4.57	(— 4.6)	(— 4.7)[t]	(— 5.2)[t]
$AgCl_3^{--} \rightleftarrows Ag^+ + 3Cl^-$	3,280	—13.2	— 5.25[e]	— 5.08	— 4.88	— 4.85	(— 5.0)	(— 5.3)[t]	(— 6.0)[t]
$AgCl_4^{---} \rightleftarrows Ag^+ + 4Cl^-$	2,680	—16.4	— 5.51[e]	— 5.38	— 5.26	— 5.31	(— 5.6)	(— 6.0)[t]	(— 6.9)[t]
$CuCl_2^- \rightleftarrows Cu^+ + 2Cl^-$	420	—21.2	— 4.94[f]	— 4.94	— 5.06	— 5.35	(— 5.8)	(— 6.5)[t]	(— 7.4)[t]
$CuCl_3^{--} \rightleftarrows Cu^+ + 3Cl^-$	— 260	—24.4	— 5.14[g]	— 5.18	— 5.39	— 5.77	(— 6.4)	(— 7.2)[t]	(— 8.3)[t]
$CuCl^+ \rightleftarrows Cu^{++} + Cl^-$	— 8,650	—29.1	— 0.01[h]	— 0.53	— 1.54	— 2.57	(— 3.7)	(— 4.8)[t]	(— 6.0)[t]
$CuCl_2 \rightleftarrows Cu^{++} + 2Cl^-$	—10,560	—32.2	0.69[i]	0.06	— 1.15	— 2.36	(— 3.7)	(— 4.9)[t]	(— 6.5)[t]
$CuCl_3^- \rightleftarrows Cu^{++} + 3Cl^-$	—13,690	—35.4	2.29[i]	1.48	— 0.04	— 1.52	(— 3.1)	(— 4.6)[t]	(— 6.5)[t]
$CuCl_4^{--} \rightleftarrows Cu^{++} + 4Cl^-$	—17,780	—38.6	4.59[i]	3.54	1.63	— 0.18	(— 2.0)	(— 3.9)[t]	(— 6.1)[t]
$PbCl^+ \rightleftarrows Pb^{++} + Cl^-$	— 380	— 8.6	— 1.60[j]	— 1.63	— 1.73	— 1.88	(— 2.1)	(— 2.4)[t]	(— 3.0)[t]
$PbCl_2 \rightleftarrows Pb^{++} + 2Cl^-$	— 1,080	—11.8	— 1.78[j]	— 1.85	— 2.04	— 2.29	(— 2.6)	(— 3.1)[t]	(— 3.9)[t]
$PbCl_3^- \rightleftarrows Pb^{++} + 3Cl^-$	— 2,170	—15.0	— 1.68[j]	— 1.81	— 2.13	— 2.50	(— 3.0)	(— 3.6)[t]	(— 4.6)[t]
$PbCl_4^{--} \rightleftarrows Pb^{++} + 4Cl^-$	— 3,530	—18.2	— 1.38[j]	— 1.59	— 2.05	— 2.57	(— 3.2)	(— 4.0)[t]	(— 5.3)[t]
$ZnCl^+ \rightleftarrows Zn^{++} + Cl^-$	— 7,790	—28.1	— 0.43[k]	— 0.90	— 1.82	— 2.78	(— 3.9)	(— 4.8)[t]	(— 6.0)[t]
$ZnCl_2 \rightleftarrows Zn^{++} + 2Cl^-$	— 8,500[l]	—31.3	— 0.61[k]	— 1.12	— 2.13	— 3.19	(— 4.4)	(— 5.5)[t]	(— 6.9)[t]
$ZnCl_3^- \rightleftarrows Zn^{++} + 3Cl^-$	— 9,560	—34.5	— 0.53[k]	— 1.14	— 2.23	— 3.34	(— 4.8)	(— 6.0)[t]	(— 7.7)[t]

$ZnCl_4^{--} \rightleftarrows Zn^{++} + 4Cl^-$	—10,960	—37.7	— 0.20[k]	— 0.89	— 2.14	— 3.35	(— 5.0)	(— 6.4)[t]	(— 8.3)[t]
$HgCl^+ \rightleftarrows Hg^{++} + Cl^-$	4,800[m]	—12.5	— 6.25[n]	— 5.99	— 5.65	— 5.50	(— 5.5)	(— 5.8)[t]	(— 6.4)[t]
$HgCl_2 \rightleftarrows Hg^{++} + 2Cl^-$	13,400[p]	—15.7	—13.25[n]	—12.51	—11.41	—10.71	(—10.4)	(—10.3)[t]	(—10.8)[t]
$HgCl_3^- \rightleftarrows Hg^{++} + 3Cl^-$	15,300[p]	—18.9	—15.35[n]	—14.50	—13.25	—12.46	(—12.1)	(—12.1)[t]	(—12.7)[t]
$FeCl^{++} \rightleftarrows Fe^{+++} + Cl^-$	— 7,910	—33.3	— 1.48[q]	— 1.96	— 2.94	— 3.98	(— 5.1)[t]	(— 6.2)[t]	(— 7.5)[t]
$FeCl_2^+ \rightleftarrows Fe^{+++} + 2Cl^-$	— 7,970	—36.5	— 2.13[q]	— 2.62	— 3.63	— 4.72	(— 5.9)	(— 7.1)[t]	(— 7.7)[t]
$FeCl_3 \rightleftarrows Fe^{+++} + 3Cl^-$	—10,290	—39.7	— 1.13[q]	— 1.76	— 3.00	— 4.30	(— 5.7)	(— 7.1)[t]	(— 8.0)[t]
$FeCl_4^- \rightleftarrows Fe^{+++} + 4Cl^-$	—13,860	—42.9	0.79[r]	— 0.05	— 1.63	— 3.23	(— 4.9)	(— 6.6)[t]	(— 7.8)[t]
$AuCl_2^- \rightleftarrows Au^+ + 2Cl^-$	10,490	— 6.0	— 9[s,v]	— 8.4	— 7.5	— 6.9	(— 6.4)	(— 6.2)[t]	(— 6.2)[t]
$AuCl_4^- \rightleftarrows Au^{+++} + 4Cl^-$	26,460	—30.2	—26[u,v]	—24.5	—22.4	—21.0	(—20.2)	(—20.2)[t]	(—21.1)[t]

[a] Except where otherwise indicated, values in this column were computed from log $K(T_r)$ and $\Delta S°_r(T_r)$. [b] All $\Delta S°_r(T_r)$ values were calculated from equations (25) and (27) using ionic radii (table 1) and the values of $S°_{Cl^-}$ and $S°_{H_2O}$ at 25°C given in footnote b, table 1. [c] The values of the overall dissociation constants were computed from log K(T) values (eq 48) predicted from equation (16) using the $\Delta S°_r(T_r)$ and $\Delta H°_r(T_r)$ values shown above. The dissociation constants are consistent with molal units of concentration—those that are more uncertain are given in parentheses. [d] Jonte and Martin (1952). [e] Leden (1952); Berne and Leden (1953). [f] Chaltykian (1948). [g] Hurlen (1961). [h] Näsänen (1953). [i] Bjerrum (1946). [j] Nelson and Kraus (1954); Marcus (1956). [k] Marcus and Mayden (1963). [l] This value is consistent with high temperature log K(T) values (Kraus and Raridon, 1960)—see footnote g, table 1. [m] Malcolm, Parton, and Watson (1961). [n] Calculated from $\Delta H°_r(T_r)$ and $\Delta S°_r(T_r)$. [p] Williams (1954) [q] Rabinowitch and Stockmayer (1942). [r] Marcus (1960). [s] Computed from the free energy of formation of Au^+ (Latimer, 1952) and the oxidation potential for the reaction $AuCl_2^- + e^- \rightleftarrows Au_{(c)} + 2Cl^-$ (Bjerrum and Kirschner, 1918; Bjerrum, 1948). [t] Extrapolated. [u] Computed from the free energy of formation of Au^{+++} (Latimer, 1952) and the oxidation potential for $AuCl_4^- + 3e^- \rightleftarrows Au_{(c)} + 4Cl^-$ (Bjerrum and Kirschner, 1918; Bjerrum, 1948). [v] These values are actually for 18°C, but they are uncertain to the extent that a 7 degree correction to 25°C is unwarranted.

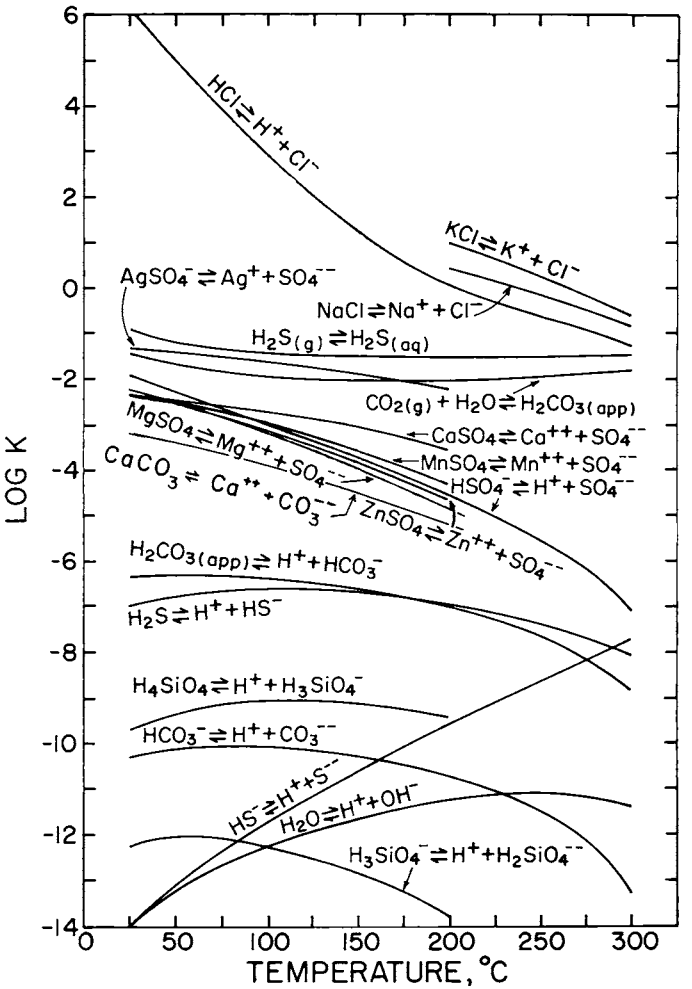

Fig. 5. Dissociation constants for complexes in hydrothermal solutions at elevated temperatures (table 4). The curves shown for the dissociation of H_4SiO_4 and $H_3SiO_4^-$ are those computed by Cobble (1964); the log K values defined by these curves are more consistent with low temperature thermodynamic data than those obtained at high temperatures by Ryzhenko (1967).

Predicted high temperature dissociation constants for chloride complexes of the ore-forming metals are shown in table 5. Log K(T) curves for these reactions are plotted in figures 6 and 7. Because the uncertainty resulting from calculation of log K(T) values with equation (16) increases substantially above 200°C (Helgeson, 1967a), and because entropy estimates (eqs 25 and 27) were used in the calculations, the numerical values for log β(T) given in table 5 as well as the log K(T) curves in figures 6 and 7 should be regarded as approximations.

It can be deduced from figures 5 to 7 that high temperature electrolyte solutions are highly associated. The high degree of formation attained by metal-ion chloride complexes is particularly significant with respect to the transport and deposition of the ore-forming metals in hydrothermal systems. As indicated above, calculations of sulfide solubilities in sodium chloride solutions at elevated temperatures suggest that more than adequate quantities of these metals can be carried in hydrothermal solutions to account for major ore deposits (Helgeson, 1964, 1967c; Helgeson, Garrels, and MacKenzie, 1969; Helgeson and Garrels, 1968). The results of a few such calculations involving thermodynamic values given in the tables are presented in later pages of this communication.

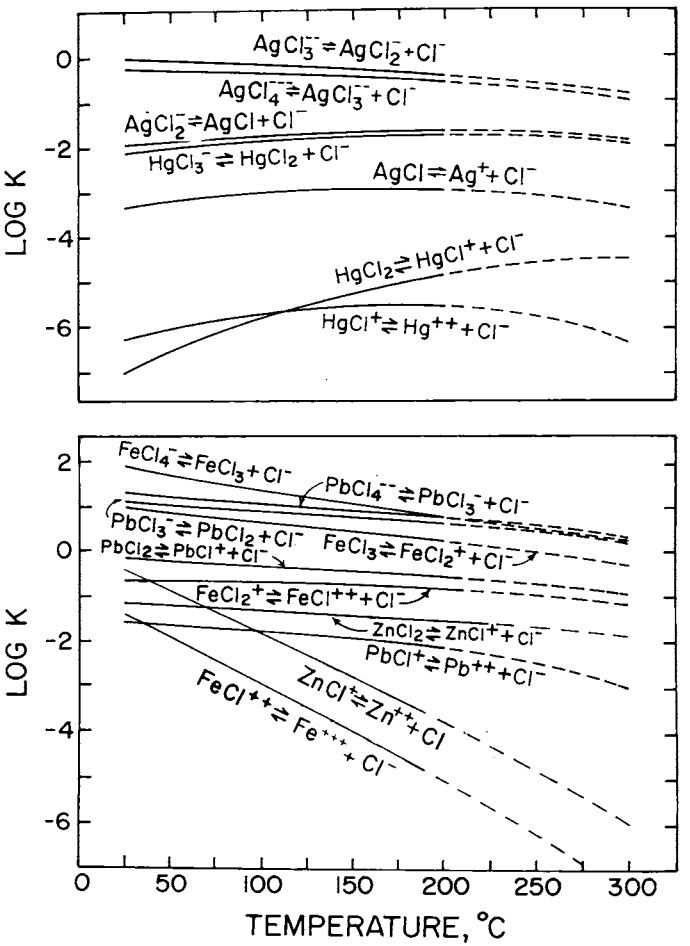

Fig. 6. Predicted dissociation constants for metal chloride complexes at elevated temperatures (table 5). The curves below 200°C were computed from equation (16) using entropy estimates from equations (25) and (27)—see text. The dashed extensions of the curves are extrapolations.

TABLE 6

Enthalpies[a] and entropies[b] of elements of interest in hydrothermal studies[c]

Element		Temperature, °C											
		25	50	60	100	150	200	250	300	350	400	450	500
$Au_{(c)}$	$H°(T)—H°(T_r)$	0.0	151	212	456	763	1074	1388	1705	2025	2348	2675	3004
	$S°$	11.31[d]	11.80	11.98	12.67	13.45	14.14	14.77	15.35	15.88	16.38	16.85	17.29
$Ag_{(c)}$	$H°(T)—H°(T_r)$	0.0	152	213	457	764	1073	1386	1702	2033	2347	2677	3011
	$S°$	10.20[d]	10.69	10.88	11.57	12.34	13.03	13.66	14.23	14.77	15.27	15.74	16.19
$Hg_{(liq)}$	$H°(T)—H°(T_r)$	0.0	166	232	496	824	1151	1476	1802	2126	2450	2774	3098
	$S°$	18.2[d]	18.7	18.9	19.7	20.5	21.2	21.9	22.5	23.0	23.5	24.0	24.4
$Cu_{(c)}$	$H°(T)—H°(T_r)$	0.0	147	206	443	744	1048	1356	1667	1983	2302	2625	2951
	$S°$	7.97[d]	8.44	8.62	9.30	10.05	10.73	11.35	11.92	12.45	12.94	13.40	13.84
$O_{2(g)}$	$H°(T)—H°(T_r)$	0.0	176	247	535	900	1271	1646	2024	2407	2792	3181	3573
	$S°$	48.996[d,e]	49.56	49.78	50.60	51.51	52.34	53.09	53.79	54.43	55.02	55.58	56.10
$H_{2(g)}$	$H°(T)—H°(T_r)$	0.0	172	241	517	862	1208	1556	1906	2257	2609	2964	3320
	$S°$	31.21[d,e]	31.76	31.97	32.76	33.62	34.40	35.10	35.73	36.32	36.87	37.37	37.85

[a] In cal $mole^{-1}$ where T_r refers to 298.15°K. [b] In cal $mole^{-1}$ deg^{-1}. [c] The values shown in this table are for a standard state of 1 atm and the indicated temperature. The subscripts (c), (liq), and (g) refer to crystalline, liquid, and gas respectively. All the enthalpies and entropies for temperatures of 50°C and above were computed from a statement of equation (11) written in terms of $H°_i$ and equation (12), respectively, using the coefficients shown in table 8. [d] Robie (1966); Robie and Waldbaum (1968). [e] Wagman and others (1965, 1968).

Standard Enthalpies, Entropies, and Heat Capacities

High temperature thermodynamic data for a variety of solids and gases of interest in hydrothermal studies are summarized in tables 6 and 7. The values shown in the tables were computed from equations (11) and (12) using the heat capacity power function coefficients for equation (10) shown in table 8. Average heat capacities of ions and several neutral species in aqueous solution are given in table 3 for temperatures from 25° to 300°C.

Equilibrium Constants for Oxidation-Reduction and Dissolution Reactions

Thermodynamic data for a variety of hydrothermal oxidation-reduction and solubility reactions are presented in tables 9 to 12. The log K(T) values shown in these tables were computed from equations (11) to (17) and data presented in tables 3, 6, 8, and 9 to 12. A number of the activity product constants are plotted against temperature in figure 8. Although reactions involving a large number of minerals are presented in table 12, the fact that a reaction is included in the table is not meant to imply that the mineral involved is necessarily stable in the presence of H_2O at the temperatures indicated. The log K values given in table 12 are "idealized"; they can be used to describe stable or metastable

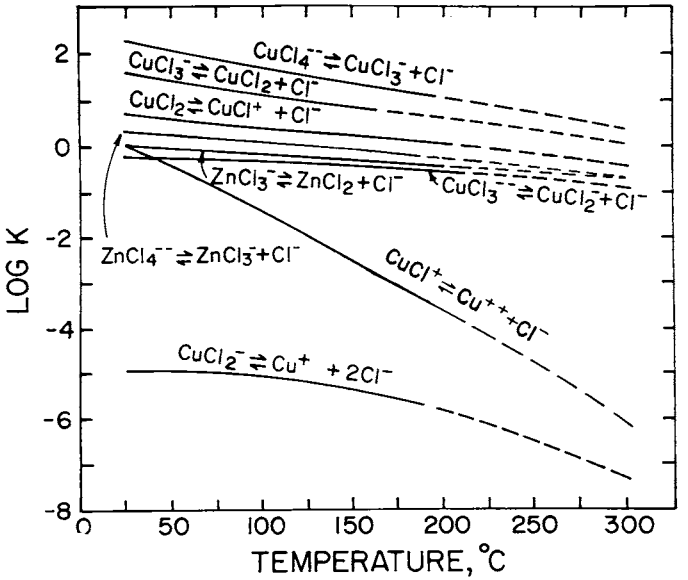

Fig. 7. Predicted dissociation constants for metal chloride complexes at elevated temperatures (table 5). The curves below 200°C were computed from equation (16) using entropy estimates from equations (25) and (27)—see text. The dashed extensions of the curves are extrapolations.

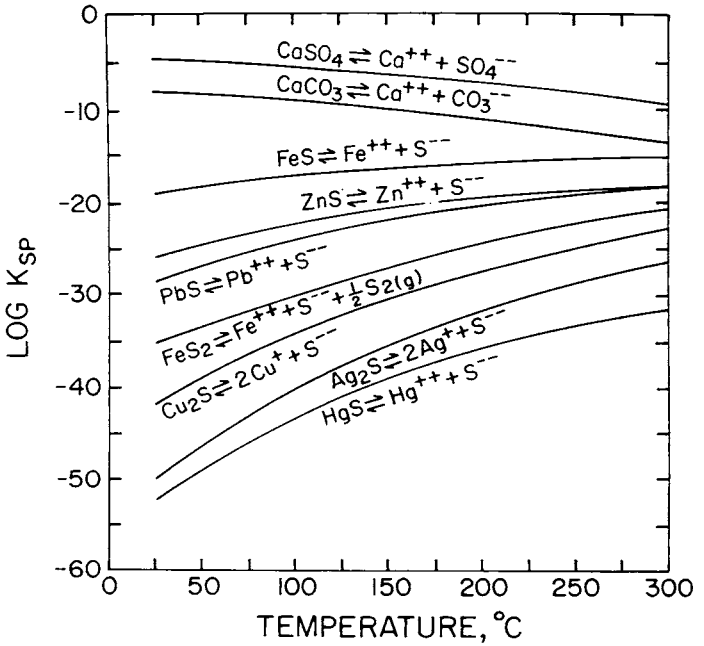

Fig. 8. Activity product constants for anhydrite, calcite, and various sulfides at elevated temperatures (table 11). HgS refers to metacinnabar.

TABLE 7

Standard entropies[a] and enthalpies[b] for various minerals and gases of interest in hydrothermal studies[c]

Species		Temperature, °C				
		25°	50°	60°	100°	150°
α Ag_2S	$\Delta H°$	—7,731[d]	—7,273	—7,085	—6,307	—5,275
(acanthite)	$S°$	34.14[d]	35.62	36.19	38.39	40.97
α Cu_2S	$\Delta H°$	—19,148[d]	—18,660	—18,465	—17,685	—16,710
(chalcocite)	$S°$	28.86[d]	30.43	31.02	33.23	35.69
CuS	$\Delta H°$	—11,610[d]	—11,324	—11,210	—10,748	—10,166
(covellite)	$S°$	15.93[d]	16.85	17.20	18.51	19.97
PbS	$\Delta H°$	—23,350[d]	—23,053	—22,934	—22,452	—21,841
(galena)	$S°$	21.84[d]	22.80	23.16	24.53	26.06
ZnS	$\Delta H°$	—49,750[d]	—49,475	—49,365	—48,914	—48,337
(sphalerite)	$S°$	13.77[d]	14.67	14.99	16.27	17.72
HgS	$\Delta H°$	—11,058[d]	—10,869	—10,748	—10,261	—9,643
(metacinnabar)	$S°$	23.00[d]	23.97	24.34	25.72	27.27
FeS	$\Delta H°$	—24,130[d]	—23,795	—23,657	—23,076	—22,291
(pyrrhotite)	$S°$	14.42[d]	15.50	15.92	17.56	19.54
FeS_2	$\Delta H°$	—41,000[d]	—40,620	—40,470	—39,830	—39,010
(pyrite)	$S°$	12.65[d]	13.87	14.34	16.14	18.21
α Fe_2O_3	$\Delta H°$	—197,300[d]	—196,660	—196,397	—195,309	—194,877
(hematite)	$S°$	20.89[d]	22.95	23.75	26.83	30.43
α Fe_3O_4	$\Delta H°$	—267,400[d]	—266,480	—266,100	—264,550	—262,490
(magnetite)	$S°$	36.03[d]	39.00	40.14	44.55	49.71
$CaCO_3$	$\Delta H°$	—288,420[p]	—287,916	—287,706	—286,832	—285,676
(calcite)	$S°$	22.15[d]	23.77	24.41	26.89	29.79
$CaSO_4$	$\Delta H°$	—343,321[d]	—342,718	—342,473	—341,468	—340,160
(anhydrite)	$S°$	25.5[d]	27.44	28.19	31.03	34.32
α SiO_2	$\Delta H°$	—217,650[d]	—217,380	—217,260	—216,780	—216,140
(quartz)	$S°$	9.88[d]	10.76	11.11	12.46	14.07
$KAlSi_3O_8$	$\Delta H°$	—946,000[d,f,q]	—944,720	—944,224	—942,037	—939,129
(microcline)	$S°$	52.47[d]	56.50	58.10	64.29	71.60
$NaAlSi_3O_8$	$\Delta H°$	—937,300[d,f,q]	—936,040	—935,510	—933,330	—930,450
(low albite)	$S°$	50.2[d]	54.26	55.85	62.03	69.29
$CaAl_2Si_2O_8$	$\Delta H°$	—1,009,300[d]	—1,008,020	—1,007,490	—1,005,260	—1,002,300
(anorthite)	$S°$	48.45[d]	52.57	54.20	60.50	67.93

Temperature, °C						
200°	250°	300°	350°	400°	450°	500°
—4,176	—3,012	—1,782	—486	876	2,304	3,798
43.44	45.76	48.02	50.19	52.29	54.35	56.33
—15,735	—14,760	—13,785	—12,810	—11,835	—10,860	—9,885
37.86	39.82	41.60	43.23	44.74	46.14	47.44
—9,577	—8,981	—8,379	—7,770	—7,154	—6,532	—5,903
21.29	22.48	23.58	24.60	25.55	26.44	27.28
—21,220	—20,589	—19,949	—19,319	—18,639	—17,969	—17,289
27.45	28.72	29.88	30.97	31.99	32.95	33.86
—47,749	—47,153	—46,549	—45,939	—45,323	—44,703	—44,078
19.03	20.23	21.33	22.35	23.30	24.19	25.03
—9,016	—8,380	—7,735	—7,081	—6,418	—5,745	—5,064
28.67	29.95	31.13	32.22	33.24	34.21	35.12
—21,440	—20,523	—19,540	—18,491	—17,376	—16,195	—14,948
21.44	23.28	25.07	26.83	28.55	30.24	31.90
—38,160	—37,295	—36,420	—35,525	—34,620	—33,720	—32,800
20.10	21.84	23.45	24.94	26.33	27.63	28.85
—192,374	—190,808	—189,183	—187,002	—185,767	—183,980	—182,141
33.79	36.93	39.90	42.71	45.39	47.95	50.41
—260,320	—258,020	—255,610	—253,070	—250,420	—247,640	—244,740
54.57	59.18	63.58	67.82	71.92	75.90	79.77
—284,464	—283,210	—281,920	—280,602	—279,267	—277,880	—276,499
32.50	35.02	37.37	39.58	41.65	43.61	45.47
—338,792	—337,365	—335,878	—334,334	—332,260	—331,068	—329,346
37.38	40.24	42.96	45.54	48.01	50.40	52.70
—215,470	—214,760	—214,020	—213,250	—212,450	—211,630	—210,790
15.58	17.01	18.36	19.64	20.87	22.05	23.17
—936,074	—932,906	—929,645	—926,306	—922,900	—919,433	—915,912
78.42	84.79	90.74	96.82	101.58	106.55	111.25
—927,430	—924,300	—921,080	—917,790	—914,435	—911,020	—907,550
76.04	82.32	88.19	93.69	98.87	103.77	108.41
—999,200	—995,980	—992,660	—989,270	—985,800	—982,280	—978,700
74.87	81.34	87.39	93.07	98.41	103.46	108.25

TABLE 7 (continued)

Species		Temperature, °C				
		25°	50°	60°	100°	150°
$Al_2Si_2O_5(OH)_4$	$\Delta H°$	—980,020[d,h,q]	—978,530	—977,920	—975,370	—972,030
(kaolinite)	$S°$	48.53[d]	53.33	55.20	62.41	70.81
$KAl_3Si_3O_{10}(OH)_2$	$\Delta H°$	—1,420,900[i,q]	—1,418,920	—1,418,090	—1,414,630	—1,410,040
(muscovite)	$S°$	69.0[j]	75.39	77.90	87.70	99.25
$NaAlSi_2O_6 \cdot H_2O$	$\Delta H°$	—786,300[d,g]	—785,050	—784,540	—782,540	—780,030
(analcime)	$S°$	56.03[d]	60.07	61.60	67.29	73.69
$CaMg(SiO_3)_2$	$\Delta H°$	—767,400[d,g]	—766,430	—766,020	—764,300	—762,000
(diopside)	$S°$	34.20[d]	37.34	38.58	43.45	49.23
$MgSiO_3$	$\Delta H°$	—370,100[d,g]	—369,610	—369,410	—368,560	—367,440
(clinoenstatite)	$S°$	16.22[d]	17.79	18.41	20.81	23.63
$Ca_2Mg_5Si_8O_{22}(OH)_2$	$\Delta H°$	—2,952,900[d,g]	—2,948,980	—2,947,410	—2,941,150	—2,933,310
(tremolite)	$S°$	131.19[d,q]	143.81	148.58	166.35	186.05
$KAlSi_2O_6$	$\Delta H°$	—721,700[d,q]	—720,720	—720,230	—718,760	—716,800
(leucite)	$S°$	44.05[d]	47.21	48.40	52.85	57.80
$NaAlSiO_4$	$\Delta H°$	—498,500[e]	—497,790	—497,490	—496,230	—494,490
(α nepheline)	$S°$	29.72[d]	32.02	32.93	36.50	40.87
$Mg_3Si_4O_{10}(OH)_2$	$\Delta H°$	—1,415,200[d,g]	—1,413,280	—1,412,510	—1,409,430	—1,405,590
(talc)	$S°$	62.34[d]	68.53	70.87	79.59	89.26
$KMg_3AlSi_3O_{10}F_2$	$\Delta H°$	—1,498,100[l]	—1,496,000	—1,495,140	—1,491,550	—1,486,850
(fluorphlogopite)	$S°$	75.90[d]	82.65	85.30	95.45	107.28
Mg_2SiO_4	$\Delta H°$	—519,000[m]	—518,270	—517,970	—516,720	—515,070
(forsterite)	$S°$	22.75[d]	25.08	26.00	29.54	33.69
Fe_2SiO_4	$\Delta H°$	—353,500[d,g]	—352,690	—352,350	—350,980	—349,180
(fayalite)	$S°$	35.45[d]	38.06	39.08	42.98	47.51
$Mg(OH)_2$	$\Delta H°$	—221,200[d]	—220,750	—220,570	—219,820	—218,860
(brucite)	$S°$	15.09[d]	16.53	17.09	19.20	21.63
$Mg_3Si_2O_5(OH)_4$	$\Delta H°$	—1,043,050[m]	—1,041,360[n]	—1,040,670[n]	—1,037,750[n]	—1,033,890[n]
(chrysotile)	$S°$	52.9[m]	58.32[n]	60.45[n]	68.71[n]	78.42[n]
$S_{2(g)}$	$\Delta H°$	30,680[k]	30,876	30,955	31,277	31,688
	$S°$	54.51[k]	55.14	55.38	56.29	57.33
$H_2S_{(g)}$	$\Delta H°$	—4,930[k]	—4,724	—4,640	—4,301	—3,866
	$S°$	49.16[k]	49.82	50.08	51.04	52.13
$H_2O_{(g)}$	$\Delta H°$	—57,796[k]	—57,954	—57,513	—57,186	—56,773
	$S°$	45.10[k]	45.75	46.00	46.93	47.97

Temperature, °C						
200°	250°	300°	350°	400°	450°	500°
—968,540	—964,950	—961,250	—957,480	—953,620	—949,690	—945,700
78.59	85.82	92.56	98.88	104.83	110.45	115.79
—1,405,200	—1,400,180	—1,395,000	—1,389,700	—1,384,260	—1,378,730	—1,373,090
110.04	120.13	129.58	138.46	146.84	154.79	162.31
—777,520	—775,010	—772,500	—769,990	—767,490	—764,980	—762,470
79.20	84.24	88.82	93.01	96.88	100.48	103.84
—759,570	—757,050	—754,450	—751,800	—749,090	—746,330	—743,540
54.65	59.71	64.45	68.90	73.08	77.03	80.77
—366,260	—365,040	—363,790	—362,510	—361,200	—359,880	—358,530
26.26	28.70	30.99	33.13	35.15	37.05	38.86
—2,925,480	—2,917,640	—2,909,810	—2,901,970	—2,894,140	—2,886,300	—2,878,470
203.56	219.30	233.60	246.71	258.80	270.03	280.50
—714,830	—712,870	—710,910	—708,950	—706,990	—705,030	—703,070
62.17	66.11	69.69	72.97	76.00	78.81	81.43
—492,580	—490,490	—488,220	—485,780	—483,160	—480,360	—477,390
45.14	49.33	53.47	57.55	61.59	65.60	69.57
—1,401,740	—1,397,900	—1,394,050	—1,390,210	—1,386,370	—1,382,520	—1,378,680
97.85	105.57	112.59	119.02	124.96	130.47	135.61
—1,481,950	—1,476,920	—1,471,760	—1,466,500	—1,461,160	—1,455,740	—1,450,250
118.20	128.30	137.70	146.50	154.80	162.50	169.90
—513,350	—511,570	—509,740	507,870	—505,970	—504,040	—502,080
37.54	41.12	44.46	47.58	50.51	53.28	55.90
—347,310	—345,390	—343,420	—341,400	—339,360	—337,270	—335,160
51.68	55.54	59.14	62.50	65.66	68.65	71.48
—217,850	—216,810	—215,720	—214,600	—213,430	—212,230	—210,990
23.88	25.98	27.46	29.84	31.63	33.36	35.02
—1,029,830[n]	—1,025,610[n]	—1,021,240[n]	—1,016,750[n]	—1,012,150[n]	—1,007,430[n]	—1,002,620[n]
87.50[n]	95.96[n]	103.93[n]	111.44[n]	118.55[n]	125.30[n]	131.74[n]
32,105	32,527	32,952	33,380	33,811	34,243	34,677
58.26	59.11	59.88	60.60	61.26	61.88	62.46
—3,420	—2,966	—2,502	—2,029	—1,548	—1,059	—5,619
53.13	54.04	54.89	55.68	56.42	57.12	57.79
—56,352	—55,926	—55,494	—55,055	—54,610	—54,160	—53,702
48.91	49.76	50.55	51.28	51.97	52.62	53.23

TABLE 7 (continued)

Species		Temperature, °C				
		25°	50°	60°	100°	150°
$CO_{2(g)}$	$\Delta H°$	—94,050[k]	—93,457	—93,233	—92,392	—91,440
	$S°$	51.06[k]	52.97	53.66	56.04	58.44

[a] In cal mole^{-1} deg^{-1}. [b] The enthalpies given in the table ($\Delta H°$) are equal to the sum of the standard enthalpy of formation from the elements of the respective compounds and gases at the reference temperature (T_r) plus the enthalpy change for the compound or gas resulting from a temperature increase from T_r to temperature T; the units are cal mole^{-1}. The values shown for the silicates (and brucite) above 25°C have been rounded to the nearest 10 cal mole^{-1}. [c] The values shown in this table are for a standard state of 1 atm at the indicated temperature. All the enthalpies and entropies for temperatures of 50° and above were computed from equations (11) and (12) respectively, using the heat capacity power function coefficients shown in table 8.

TABLE 8

Heat capacity power function coefficients (eq 10) for solids and gases[a]

Species[f]	a''	$b'' \times 10^3$	$c'' \times 10^{-5}$
αAg_2S (acanthite)	10.13	26.4	0.0
αCu_2S (chalcocite)	19.50	0.0	0.0
CuS (covellite)	10.60	2.64	0.0
PbS (galena)	10.66	3.92	0.0
ZnS (sphalerite)	11.77[l]	1.26[l]	— 1.16[l]
ZnS (wurtzite)	11.82[l]	1.16[l]	— 1.04[l]
HgS (metacinnabar)	10.90	3.65	0.0
HgS (cinnibar)	11.57[e,m]		
FeS (pyrrhotite)	5.19	26.4	0.0
$CuFeS_2$ (chalcopyrite)	15.6[i]	21.6[i]	0.6[i]
FeS_2 (pyrite)	17.88	1.32	— 3.05
Cu_5FeS_4 (bornite)	44.4[i]	40.0[i]	0.6[i]
$Ag_{(c)}$ (native silver)	5.09	2.04	0.36
$Au_{(c)}$ (native gold)	5.66	1.24	0.0
$Cu_{(c)}$ (native copper)	5.41	1.50	0.0
$Hg_{(liq)}$ (native mercury)	6.44	0.0	0.19
αFe_2O_3 (hematite)	23.49	18.6	— 3.55
αFe_3O_4 (magnetite)	21.88	48.2	0.0
αSiO_2 (quartz)	11.22	8.20	— 2.70
CuO (tenorite)	9.27	4.80	0.0
Cu_2O (cuprite)	14.90	5.70	0.0
$CaCO_3$ (calcite)	24.98	5.24	— 6.20
$CaMg(CO_3)_2$ (dolomite)	37.65[e,k]		
$ZnCO_3$ (smithsonite)	9.30	33.0	0.0
$PbCO_3$ (cerrusite)	12.39	28.60	0.0
$FeCO_3$ (siderite)	11.63	26.80	0.0
αCaF_2 (fluorite)	14.30	7.28	0.47
$CaSO_4$ (anhydrite)	16.78	23.60	0.0
$BaSO_4$ (barite)	33.80	0.0	—8.43
$PbSO_4$ (anglesite)	10.96	31.0	4.20
$KAlSi_3O_8$ (microline, orthoclase, adularia, and sanidine)	63.83	12.90	—17.05
$NaAlSi_3O_8$ (low albite)	61.70	13.90	—15.01
$CaAl_2Si_2O_8$ (anorthite)	64.42	13.70	—16.89
$Al_2Si_2(OH)_4$ (kaolinite)	67.93[j,b]	19.22[j,b]	—13.78[j,b]
$KAl_3Si_3O_{10}(OH)_2$ (muscovite)	97.56[d]	26.38[d]	—25.44[d]
$K_{0.6}Mg_{0.25}Al_{2.30}Si_{3.5}O_{10}(OH)_2$ (illite)	87.9[j,n]	35.0[j,n]	—19.5[j,n]
$KFe_3AlSi_3O_{10}(OH)_2$ (annite)	100.4[j,n]	36.4[j,n]	—14.3[j,n]
$Mg_5Al_2Si_3O_{10}(OH)_8$ (chlorite)	96.8[j]	36.1[j]	—23.9[j]

Temperature, °C						
200°	250°	300°	350°	400°	450°	500°
—90,563	—89,739	—88,952	—88,192	—87,451	—86,726	—86,011
60.40	62.05	63.49	64.76	65.91	66.94	67.90

[d] Robie and Waldbaum (1968). [e] Computed from the enthalpy of formation from the oxides (Robie, 1966) using enthalpies of formation of the oxides from the elements reported by Robie and Waldbaum (1968). [f] Waldbaum (1966). [g] Rounded to the nearest even 50 cal mole^{-1}. [h] Barany and Kelley (1961). [i] Barany (1964). [j] Weller and King (1963). [k] Wagman and others (1965, 1968). [l] Kelley and others (1959). [m] King and others (1967). [n] Computed using the heat capacity power function for antigorite (table 8). [p] Computed from the entropy given above for calcite and an activity product constant of $10^{-8.37}$ (Berner, 1967) at 25°C and 1 atm. [q] Adjusted (within the uncertainty range reported in the source reference) to achieve internal consistency among equilibrium constants describing mineral assemblages at 25°C.

TABLE 8 (continued)

Heat capacity power function coefficients (eq 10) for solids and gases[a]

Species[f]	a''	$b'' \times 10^3$	$c'' \times 10^{-5}$
$Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$ (montmorillonite)	84.9[j]	34.3[j]	—19.7[j]
$K_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$ (montmorillonite)	85.3[j,n]	34.9[j,n]	—19.7[j,n]
$Ca_{0.167}Al_{2.33}Si_{3.67}O_{10}(OH)_2$ (montmorillonite)	84.2[j]	33.6[j]	—20.0[j]
$Mg_{0.167}Al_{2.33}Si_{3.67}O_{10}(OH)_2$ (montmorillonite)	84.0[j]	33.7[j]	—19.9[j]
$NaAlSi_2O_6 \cdot H_2O$ (analcime)	50.17[c]		
$CaMg(SiO_3)_2$ (diopside)	52.87	7.84	—15.74
$MgSiO_3$ (clinoenstatite)	24.55	4.74	— 6.28
$Ca_2Mg_5Si_8O_{22}(OH)_2$ (tremolite)	156.7[c,e]		
$KAlSi_2O_6$ (leucite)	39.23[c]		
$NaAlSiO_4$ (α nepheline)	6.63	70.60	0.0
$Mg_3Si_4O_{10}(OH)_2$ (talc)	76.89[c,e]		
$KMg_3AlSi_3O_{10}F_2$ (fluorphlogopite)	100.86	17.16	—21.46
Mg_2SiO_4 (forsterite)	35.81	6.54	— 8.52
Fe_2SiO_4 (fayalite)	36.51	9.36	— 6.70
$Mg(OH)_2$ (brucite)	13.04	15.80	0.0
$Al(OH)_3$ (gibbsite)	8.65	45.6	0.0
$Mg_3Si_2O_5(OH)_4$ (antigorite)	75.82[h]	31.6[h]	—17.58[h]
$S_{2(g)}$	8.72	0.16	— 0.90
$H_2S_{(g)}$	7.81	2.96	— 0.46
$H_2O_{(g)}$	7.30	2.46	0.0
$O_{2(g)}$	7.16	1.0	— 0.40
$H_{2(g)}$	6.52	0.78	0.12
$CO_{2(g)}$	10.57	2.10	— 2.06

[a] Kelley (1960). [b] The estimated power-function coefficients for kaolinite give 58.16 cal mole^{-1} deg^{-1} for the heat capacity of kaolinite at 25°C, compared to 58.62 cal mole^{-1} deg^{-1} reported by King and Weller (1961). [c] Heat capacity at 25°C (cal mole^{-1} deg^{-1}). When this quantity is used as the a'' coefficient in equations (11) and (12) with b'' and c'' set to zero, the heat capacity is treated as a constant. [d] Pankratz (1964). [e] Robie and Stout (1963). [f] The subscripts (c), (liq), and (g) refer to crystalline, liquid, and gas, respectively. [h] King and others, 1967. [i] Estimated by summing (in appropriate proportions) the coefficients in the heat capacity power functions for the elements (Kelley, 1960) in the mineral (see text). [j] Estimated by summing (in mole proportions) the coefficients in the heat capacity power functions of the oxide components (Kelley, 1960) in the mineral using ice ($C°_P = a'' = 9.0$ cal mole^{-1} deg^{-1}) to represent H_2O (see text). [k] Stout and Robie (1963). [l] Pankratz and King (1965). [m] King and Weller (1962). Computed using $C_{P,K_2O} = 18.1 + 8.8 \times 10^{-3}$ T obtained by fitting the enthalpies for K_2O between 400° and 1000°K reported by Robie and Waldbaum (1968).

mineral assemblages, define mineral stabilities, and predict (by controlled extrapolation) higher temperature stability regions.

Activity Coefficients and Degrees of Formation of Complexes

Stoichiometric individual ion activity coefficients for Al^{+++}, S^{--}, SO_4^{--}, CO_3^{--}, and various ore-forming metals in concentrated NaCl solutions to 300°C are shown in tables 13 and 14 and plotted in figures 9 to 14. These values, together with the activity coefficients for Na^+, K^+, and Ca^{++} in tables 13 and 14, were computed from equilibrium constants given in tables 4 and 5, mass balance expressions of the kind shown in equation (49), true individual ion activity coefficients computed from equation (43) using 25°C å values[7], and the data in table 2. Values of γ_{CO_2} in NaCl solutions (table 2) were used in the calculations to represent the activity coefficients of the neutral species. Also, a_{Cl^-}, $\bar{I}$, and $\dot{B}$ in the calculations were taken to be those in pure NaCl solutions (table 2) because other constituents in hydrothermal solutions are commonly present in small concentrations compared to NaCl. The stoichiometric individual ion activity coefficients shown in table 14 are conservative values; that is, they do not include provision for divalent and trivalent complexes of the metal ions (see discussion above and footnote a, table 14). The complexes with the higher charges were omitted to preclude any substantial errors that might be introduced by the assumption of constant å values.

The degrees of formation achieved by metal chloride complexes in concentrated sodium chloride solutions at high temperatures are depicted in figure 15. The distribution of species shown in figure 15 is based on evaluation of

$$\alpha_{\check{c}} = \frac{a_{Cl^-}^{y}\,\dot{\gamma}_i}{\beta_{\check{c}}\gamma_{\check{c}}} \tag{54}$$

where $\alpha_{\check{c}}$ is the degree of formation of the $\check{c}$th mononuclear complex containing y moles of chloride and 1 mole of the ith cation. The curves for the respective metal ions in figure 15 include provision for all of the reactions and species involving those ions shown in table 5; the $\beta_{\check{c}}$, $\gamma_{\check{c}}$, and $\dot{\gamma}_i$ values used in the calculations were computed in the manner described above. Because 25°C å values were used to compute the activity coefficients required to evaluate equation (54), appreciable error may have been incorported into the calculations of $\alpha_{\check{c}}$ for the divalent complexes at the higher temperatures. Figure 15 thus illustrates only the distribution of species in solution that occurs if the å values for the ions remain essentially constant from 25°C to 300°C. If they in fact increase significantly, the diagrams in figure 15 will change substantially, but the $\dot{\gamma}_i$ values presented in tables 13 and 14 and figures 9 to 14 will be affected only slightly owing to the fact that the divalent (and higher

[7] The values of å were assigned on the basis of Kielland's (1937) å values assuming equalities for similar complexes.

TABLE 9

Equilibrium constants for hydrothermal oxidation-reduction reactions involving aqueous species at high temperatures

Reaction[a]	$\Delta H^\circ_r(T_r)$[b] (cal mole^{-1})	$\Delta S^\circ_r(T_r)$[b] (cal mole^{-1} deg^{-1})	log K(T)[c] 25°C	50°C	60°C	100°C	150°C	200°C	250°C	300°C
$2H_2S + O_{2(g)} \rightleftarrows S_{2(g)} + 2H_2O^d$	— 87,890	— 22.9	59.44	54.4[e]	52.57	46.27	39.99	35.05	30.6[e]	27.21
$H_2S + 2O_{2(g)} \rightleftarrows H^+ + HSO_4^-$	—204,440	—102.2	127.54	115.5[e]	111.71	97.30	83.05	71.62	62.5[e]	55.61
$H_2S + 2O_{2(g)} \rightleftarrows 2H^+ + SO_4^{--}$	—208,290	—124.2	125.55	113.2[e]	109.31	94.31	79.31	67.13	57.1[e]	48.55
$HS^- + 2O_{2(g)} \rightleftarrows H^+ + SO_4^{--}$	—213,090	—108.4	132.53	120.0[e]	116.02	100.93	86.03	74.09	64.4[e]	56.61
$2H^+ + S^{--} + \frac{1}{2}O_{2(g)} \rightleftarrows \frac{1}{2}S_{2(g)} + H_2O^d$	— 62,040	23.5	50.62	47.1[e]	45.85	41.54	37.33	34.05	31.3[e]	29.39
$2HS^- + O_{2(g)} + 2H^+ \rightleftarrows S_{2(g)} + 2H_2O^d$	— 97,490	8.9	73.42	68.0[e]	66.01	59.53	53.43	48.97	45.3[e]	43.33
$S^{--} + 2O_{2(g)} \rightleftarrows SO_4^{--}$	—226,390	— 89.4	146.43	133.9[e]	128.86	112.70	96.68	83.74	72.7[e]	64.26
$Fe^{+++} + \frac{1}{2}H_2O \rightleftarrows Fe^{++} + \frac{1}{4}O_{2(g)} + H^+$	24,557	46.89	— 7.75	— 6.35[e]	— 5.87	— 4.16	— 2.48	— 1.15	— 0.1[e]	0.84
$Cu^{++} + \frac{1}{2}H_2O^d \rightleftarrows Cu^+ + \frac{1}{4}O_{2(g)} + H^+$	35,697	36.89	— 18.10	— 16.1[e]	— 15.35	— 12.83	—10.34	— 8.35	— 6.64[e]	— 5.33
$S^{--} + 4H_2O^d \rightleftarrows SO_4^{--} + 4H_{2(g)}$	46,870	66.80	— 19.76	— 17.15[e]	— 16.26	— 13.30	—10.69	— 8.92	— 7.6[e]	— 6.87
$8Fe^{+++} + 4H_2O^d + S^{--} \rightleftarrows 8Fe^{++} + SO_4^{--} + 8H^+$	— 29,930	285.72	84.43	83.1[e]	81.90	79.42	76.84	74.62	71.9[e]	70.98
$8Cu^{++} + 4H_2O^d + S^{--} \rightleftarrows 8Cu^+ + SO_4^{--} + 8H^+$	59,190	205.72	1.63	5.1[e]	6.06	10.06	13.96	16.70	19.6[e]	21.62
$Cu^+ + Fe^{+++} \rightleftarrows Cu^{++} + Fe^{++}$	— 11,140	10.00	10.35	9.7[e]	9.48	8.67	7.86	7.20	6.6[e]	6.17

[a] All reactants and products are aqueous unless otherwise indicated by the subscript (g) for gas. [b] Computed from thermodynamic data given in tables 3, 6, and 7. [c] The log K(T) values shown for 25°C were computed from the $\Delta H^\circ_r(T_r)$ and $\Delta S^\circ_r(T_r)$ values shown in the table; those for 60°C and above were calculated using $\Delta H^\circ_{f,i}(T_r)$, $S^\circ_i(T_r)$ and average heat capacity values for the ions, $H_2S_{(aq)}$, and $H_2O_{(liq)}$ (table 3) to first compute $\Delta H^\circ_i(T)$ and $S^\circ_i(T)$ for these species at elevated temperatures (eqs 13 and 14). These values were then used together with those for gases in tables 6 and 7 to evaluate equation (15). All the log K(T) values are consistent with molal units of concentration. [d] Liquid water. [e] Interpolated.

TABLE 10

Equilibrium constants for the disproportionation of aqueous ions, oxidation-reduction of hydrothermal minerals, and dissolution of gases in aqueous solution at elevated temperatures

Reaction[a]	$\Delta H^\circ_r(T_r)$[b] (cal mole^{-1})	$\Delta S^\circ_r(T_r)$[b] (cal mole^{-1} deg^{-1})	log K(T)[c]							
			25°C	50°C	60°C	100°C	150°C	200°C	250°C	300°C
$2Cu^+ \rightleftarrows Cu^\circ_{(c)} + Cu^{++}$	— 18,470	— 34.45	6.01	4.92[d]	4.57	3.20	1.84	0.66	— 0.37	— 1.27
$3Au^+ \rightleftarrows 2Au^\circ_{(c)} + Au^{+++}$	— 33,200[f]	— 66.4	9.82[g]	7.91[h]	7.22[h]	4.76[h]	2.24[h]	0.16[h]	— 1.60[h]	— 3.11[h]
$Cu_5FeS_4 + 4FeS_2 \rightleftarrows 5CuFeS_2 + S_{2(g)}$	56,750[k]	68.91[l]	— 26.5	— 23.2[d]	— 22.2	— 18.2	— 14.2	— 11.1	— 8.5	— 6.4[l]
$4FeS_2 + 4H_2O \rightleftarrows 4Fe^{++} + 7S^{--} + SO_4^{--} + 8H^+$	199,430	—249.04	—200.57	—189.7[d]	—185.46	—171.89	—158.96	—149.17	—141.49	—136.04
$3Fe_2O_{3(c)} \rightleftarrows 2Fe_3O_{4(c)} + \frac{1}{2}O_{2(g)}$	57,100	33.89	— 34.43	— 31.13[d]	— 30.04	— 26.02	— 22.07	— 18.95	— 16.44	— 14.35
$FeS_{2(c)} \rightleftarrows FeS_{(c)} + \frac{1}{2}S_{2(g)}$	32,210	29.02	— 17.26	— 15.42[d]	— 14.78	— 12.50	— 10.25	— 8.48	— 7.03	— 5.81
$FeS_{(c)} + FeS_{2(c)} + 3/2O_{2(g)} \rightleftarrows Fe_2O_{3(c)} + 3/2S_{2(g)}$	307,350	7.49	63.69	58.67[d]	56.96	50.89	44.92	40.20	36.38	33.22
$FeS_{2(c)} + 3/2O_{2(g)} \rightleftarrows Fe_2O_{3(c)} + 2S_{2(g)}$	— 53,940	31.12	46.33	43.18[d]	42.18	38.39	34.66	31.72	29.35	28.19
$3FeS_{2(c)} + 2O_{2(g)} \rightleftarrows Fe_3O_{4(c)} + 3S_{2(g)}$	— 52,360	63.98	52.27	49.15[d]	48.24	44.57	40.95	38.11	35.81	33.93
$Cu_2S_{(c)} + \frac{1}{2}S_{2(g)} \rightleftarrows 2CuS_{(c)}$	— 19,412	24.20	8.92	7.71[d]	7.32	6.06	4.72	3.66	2.77	2.09
$Cu^\circ_{(c)} + 2H^+ + \frac{1}{2}O_{2(g)} \rightleftarrows Cu^{++} + H_2O_{(liq)}$	— 52,925	— 39.34	30.19	27.1[d]	26.13	22.45	18.84	16.04	13.78	11.94
$2Cu^\circ_{(c)} + \frac{1}{2}S_{2(g)} \rightleftarrows Cu_2S_{(c)}$	— 34,488	— 14.29	22.15	20.20[d]	19.50	17.09	14.78	12.88	11.38	10.16
$Cu^\circ_{(c)} + H^+ + \frac{1}{4}O_{2(g)} \rightleftarrows Cu^+ + \frac{1}{2}H_2O_{(liq)}$	— 17,227	— 2.44	12.09	11.1[d]	10.78	9.63	8.50	7.69	7.07	6.61
$Cu^\circ_{(c)} + \frac{1}{2}S_{2(g)} \rightleftarrows CuS_{(c)}$	— 26,945	— 19.27	15.54	14.01[d]	13.46	11.58	11.35	9.94	7.09	6.13
$Ag^\circ_{(c)} + H^+ + \frac{1}{4}O_{2(g)} \rightleftarrows Ag^+ + \frac{1}{2}H_2O_{(liq)}$	— 8,847	3.60	7.27	6.74[d]	6.60	6.01	5.44	5.06	4.74	4.50
$2Ag^\circ_{(c)} + \frac{1}{2}S_{2(g)} \rightleftarrows Ag_2S_{(c)}$	— 23,077	— 13.51	13.96	12.65[d]	12.19	10.57	9.00	7.77	6.79	5.99
$Hg^\circ_{(liq)} + 2H^+ + \frac{1}{2}O_{2(g)} \rightleftarrows Hg^+ + H_2O_{(liq)}$	— 26,725	— 31.69	12.66	11.13[d]	10.61	8.72	6.84	5.37	4.15	3.14

$Hg^{o}_{(liq)} + \frac{1}{2}S_{2(g)} \rightleftarrows HgS_{(c)}$[i]	— 26,500	— 22.75	14.43	12.86[d]	12.40	10.55	8.73	7.30	6.14	5.19
$Au^{o}_{(c)} + 3/4O_{2(g)} + 3H^{+} \rightleftarrows Au^{+++} + 3H_2O_{(liq)}$	4,850[f]	— 46.0	— 13.61[g]	— 13.34[h]	— 13.24[h]	— 12.91[h]	— 12.59[h]	— 12.35[h]	— 12.17[h]	— 12.02[h]
$Au^{o}_{(c)} + \frac{1}{4}O_{2(g)} + H^{+} \rightleftarrows Au^{+} + \frac{1}{2}H_2O_{(liq)}$	12,680[f]	6.8	— 7.81[g]	— 7.08[h]	— 6.82[h]	— 5.89[h]	— 4.94[h]	— 4.17[h]	— 3.52[h]	— 2.97[h]
$CO_{2(g)} + H_2O_{(liq)} \rightleftarrows H_2CO_{3(app)}$[e]	— 4,650	— 22.3	— 1.46	— 1.70[d]	— 1.78	— 1.97	— 2.07	— 2.06	— 1.98	— 1.83
$H_2S_{(g)} \rightleftarrows H_2S_{(aq)}$	— 4,100	— 18.3	— 0.99	— 1.20[d]	— 1.26	— 1.43	— 1.52	— 1.54	— 1.52	— 1.46

[a] All reactants and products are aqueous unless otherwise indicated by the subscripts (c) for crystalline or (g) for gas; the subscript (liq) refers to liquid. The crystalline compounds correspond to the mineral designations given in tables 7 and 8. [b] Except where noted otherwise, these values were computed from thermodynamic data given in tables 3, 6, and 7. [c] Except where noted otherwise, the log K(T) values for 25°C were computed from the values of $\Delta H^{o}_{r}(T_r)$ and $\Delta S^{o}_{r}(T_r)$ shown in the table; those for 60°C and above were calculated using $\Delta H^{o}_{f,i}(T_r)$, $S^{o}_{i}(T_r)$, and average heat capacities for the ions, $H_2O_{(liq)}$, and $H_2S_{(aq)}$ (table 3) to first compute $\Delta H^{o}_{i}(T)$ and $S^{o}_{i}(T)$ for these species at elevated temperatures (eqs 13 and 14). These values were then used together with those computed from equations (11) and (12) using data given in tables 6, 7, and 8 for minerals and gases to evaluate equation (15). The enthalpies of formation and entropies of chalcopyrite used in the calculations are given in footnotes j and k below. All the log K(T) values are consistent with molal units of concentration. [d] Interpolated. [e] The subscript (app) indicates that the species referred to is the undifferentiated sum of $H_2CO_{3(aq)}$ and $CO_{2(aq)}$. [f] Computed from $\Delta S^{o}_{r}(T_r)$ and log $K(T_r)$. [g] Computed from free energies of formation from the elements (Latimer, 1952). [h] Predicted assuming a constant $\Delta C^{o}_{P,r}(T)$ equal to a mean value computed from average heat capacities for the respective ions (table 3) and the true heat capacities of the other species calculated from equation (10) using the coefficients in table 8. [i] Metacinnibar. [j] Computed from entropies given in table 7 and estimates of the entropy of chalcopyrite (31.2 cal $mole^{-1}$ deg^{-1}) and bornite (91 cal $mole^{-1}$ deg^{-1}) at 25°C obtained by summing (in appropriate proportions) the values tabulated by Latimer (1952) for the entropy contributions of iron, copper, and sulfide in solids—see text. [k] Computed from enthalpies of formation given in table 7 and those for chalcopyrite (—44,550 cal $mole^{-1}$) and bornite (—84,820 cal $mole^{-1}$) calculated from estimated free energies of formation for these minerals (—45,000 cal $mole^{-1}$ and —89,000 cal $mole^{-1}$, respectively) at 25°C (Bartholomé, 1958) together with corresponding entropies of formation of the minerals from the elements calculated from the entropy estimates given in footnote j above and data for the elements taken from Robie and Waldbaum (1968). Bartholomé's values for the free energies of chalcopyrite and bornite appear to be more consistent with high temperature equilibrium data for the sulfides (Barton and Skinner, 1967) than do Young's (1967). [l] This value compares favorably with that (—6.9) reported by Barton and Skinner (1967), but the slope of log K(T) is more positive. Barton and Skinner assumed the heat capacity of reaction to be zero; the present calculations indicate that the heat capacity is neither zero nor constant.

TABLE 11

Activity products for hydrothermal minerals and equilibrium constants for various silicate reactions involving an aqueous phase at high temperatures

Reaction[a]	$\Delta H^\circ_{r(T_r)}$[b] (cal mole^{-1})	$\Delta S^\circ_{r(T_r)}$[b] (cal mole^{-1} deg^{-1})	log K(T)[c]							
			25°C	50°C	60°C	100°C	150°C	200°C	250°C	300°C
$Cu_5FeS_{4(bornite)} \rightleftarrows 4Cu^+ + Cu^{++} + Fe^{++} + 4S^{--}$	183,210[d]	—120.10[d]	—160.5	—150.0[e]	—146.4	—133.4	—120.8	—110.6	—102.3	— 95.6
$CuFeS_{2(chalcopyrite)} \rightleftarrows Cu^{++} + Fe^{++} + 2S^{--}$	57,080[d]	— 89.90[d]	— 61.5	— 58.4[e]	— 57.1	— 53.1	— 49.2	— 46.2	— 43.7	— 41.9
$PbS \rightleftarrows Pb^{++} + S^{--}$	32,030	— 23.34	— 28.57	— 26.67[e]	— 26.14	— 23.96	— 21.93	— 20.36	— 19.14	— 18.31
$ZnS_{(sphalerite)} \rightleftarrows Zn^{++} + S^{--}$	22,040	— 43.77	— 25.72	— 24.44[e]	— 24.03	— 22.48	— 21.01	— 19.81	— 18.86	— 18.17
$ZnS_{(wurtzite)} \rightleftarrows Zn^{++} + S^{--}$	18,385[i]	— 46.56[i]	— 23.65	— 22.58[e]	— 22.24	— 20.96	— 19.73	— 18.73	— 17.95	— 17.39
$Ag_2S \rightleftarrows 2Ag^+ + S^{--}$	67,427	— 2.76	— 50.02	— 46.17[e]	— 44.83	— 40.08	— 35.45	— 31.71	— 28.74	— 26.36
$Cu_2S \rightleftarrows 2Cu^+ + S^{--}$	62,080	— 14.06	— 48.57	— 45.05[e]	— 43.79	— 39.37	— 35.05	— 31.54	— 28.65	— 26.32
$CuS \rightleftarrows Cu^{++} + S^{--}$	36,070	— 43.53	— 35.96	— 33.91[e]	— 33.18	— 30.66	— 28.21	— 26.28	— 24.73	— 23.56
$HgS_{(metacinnibar)} \rightleftarrows Hg^{++} + S^{--}$	61,830	— 32.40	— 52.37	— 48.84[e]	— 47.64	— 43.36	— 39.23	— 35.98	— 33.42	— 31.45
$HgS_{(cinnibar)} \rightleftarrows Hg^{++} + S^{--}$	64,560[i]	— 29.12[i]	— 53.68	— 50.02[e]	— 48.73	— 44.25	— 39.91	— 36.51	— 33.83	— 31.72
$FeS \rightleftarrows Fe^{++} + S^{--}$	12,200	— 42.52	— 18.89	— 18.17[e]	— 17.96	— 17.12	— 16.33	— 15.71	— 15.22	— 14.94
$FeS_2 \rightleftarrows Fe^{++} + S^{--} + \frac{1}{2}S_{2(g)}$	29.070	— 43.75	— 36.15	— 33.50[e]	— 32.74	— 30.17	— 26.60	— 24.19	— 22.25	— 20.75
$CaSO_4 \rightleftarrows Ca^{++} + SO_4^{--}$	— 3,755	— 34.10	— 4.70[n]	— 4.99[e,n]	— 5.09[e,n]	— 5.63[n]	— 6.35[n]	— 7.18[n]	— 8.12[n]	— 9.05[n]
$BaSO_{4(barite)} \rightleftarrows Ba^{++} + SO_4^{--}$	6,140[i]	— 23.80[i]	— 9.70	— 9.42[e]	— 9.34	— 9.22	— 9.34	— 9.76	— 10.34	— 11.05
$PbSO_{4(anglesite)} \rightleftarrows Pb^{++} + SO_4^{--}$	220[i]	— 28.2[i]	— 7.75	— 7.70[e]	— 7.70	— 7.86	— 8.26	— 8.88	— 9.60	— 10.44
$CaCO_3 \rightleftarrows Ca^{++} + CO_3^{--}$	— 3,190	— 49.0	— 8.37	— 8.62[e]	— 8.74	— 9.39	— 10.25	— 11.37	— 12.72	— 14.10

$CaMg(CO_3)_{2(dolomite)} \rightleftarrows Ca^{++} + Mg^{++} + 2CO_3^{--}$	— 8,290[h,i]	—105.69[j]	— 17.02[k]	— 17.63[r]	— 17.92	— 19.28	— 21.02	— 23.26	— 25.83	— 28.46
$ZnCO_{3(smithsonite)} \rightleftarrows Zn^{++} + CO_3^{--}$	— 4,420[i]	— 59.30[i]	— 9.72	— 10.05[r]	— 10.19	— 10.88	— 11.77	— 12.90	— 14.18	— 15.52
$PbCO_{3(cerrusite)} \rightleftarrows Pb^{++} + CO_3^{--}$	5,710[i]	— 42.40[i]	— 13.45	— 13.19[r]	— 13.16	— 13.21	— 13.54	— 14.30	— 15.31	— 16.50
$FeCO_{3(siderite)} \rightleftarrows Fe^{++} + CO_3^{--}$	— 5,030[i]	— 65.8[i]	— 10.69	— 11.04[r]	— 11.21	— 11.95	— 12.86	— 14.05	— 15.32	— 16.67
$CaF_{2(fluorite)} \rightleftarrows Ca^{++} + 2F^-$	1,530[i]	— 36.26[i]	— 9.04	— 9.01[r]	— 9.01	— 9.20	— 9.66	— 10.26	— 11.08	— 12.13
$KAlSi_3O_8 + Na^+ \rightleftarrows NaAlSi_3O_8 + K^+$	5.939	7.83	— 2.64	— 2.29[r]	— 2.19	— 1.80	— 1.43	— 1.15	— 0.95	— 0.79
$3KAlSi_3O_8 + 2H^+ \rightleftarrows KAl_3Si_3O_{10}(OH)_2 + 2K^+ + 6SiO_{2(qtz)}$	— 8,880	19.87	10.85	10.31[r]	10.17	9.55	8.91	8.49	8.12	7.82
$2KAl_3Si_3O_{10}(OH)_2 + 2H^+ + 3H_2O^e \rightleftarrows 3Al_2Si_2O_5(OH)_4 + 2K^+$	— 13.395	6.46	11.22	10.45[r]	10.16	9.12	7.96	7.04	6.20	5.44
$4CaMg(SiO_3)_2 + Mg^{++} + 2H^+ \rightleftarrows Ca_2Mg_5Si_8O_{22}(OH)_2 + 2Ca^{++}$	— 32.430	— 3.81	22.93	21.00[r]	20.42	18.08	15.62	13.63	11.76	10.13
$NaAlSiO_4 + K^+ + H_4SiO_4 \rightleftarrows KAlSi_2O_6 + Na^+ + 2H_2O$	— 9.009	— 8.19	4.81	4.32[r]	4.13	3.50	2.92	2.45	2.05	1.75
$2Al(OH)_3^{(m)} + 2H_4SiO_4 \rightleftarrows Al_2Si_2O_5(OH)_4 + 5H_2O^e$	— 9.275	6.90	8.29	7.8[r]	7.59	6.97	6.44	6.02	5.70	5.54
$Mg_5Al_2Si_3O_{10}(OH)_8 + 10H^+ \rightleftarrows Al_2Si_2O_5(OH)_4 + 5Mg^{++} + H_4SiO_4 + 5H_2O^e$	—111,865	— 75.08	65.57	59.6[r]	57.15	49.81	42.86	37.95	34.18	31.26

TABLE 11 (continued)

Reaction[a]	$\Delta H^\circ_r(T_r)$[b] (cal mole^{-1})	$\Delta S^\circ_r(T_r)$[b] (cal mole^{-1} deg^{-1})	log K(T)[c] 25°C	50°C	60°C	100°C	150°C	200°C	250°C	300°C
$4CaAl_2Si_2O_8 + 5Mg^{++} + 18H^+ \rightleftarrows Ca_2Mg_5Si_8O_{22}(OH)_2 + 2Ca^{++} + 8Al^{+++} + 8H_2O$[e]	—185,710	—429.53	42.25	39.1[f]	28.06	15.28	2.74	— 6.65	— 14.48	— 20.79
$Mg_5Al_2Si_3O_{10}(OH)_8 + 2Ca^{++} + 5H_4SiO_4 + 2H^+ \rightleftarrows Ca_2Mg_5Si_8O_{22}(OH)_2 + 2Al^{+++} + 14H_2O$[e]	— 53,630	—103.47	16.69	13.6[f]	12.68	9.96	6.32	4.22	2.84	1.97
$Mg_3Si_4O_{10}(OH)_2 + 5H_2O$[e] $\rightleftarrows Mg_3Si_2O_5(OH)_4$[h] $+ 2H_4SiO_4$	17,605	— 1.31	— 13.19	— 12.20[f]	— 11.83[g]	— 10.60[g]	— 9.43[g]	— 8.47[g]	— 7.68[g]	— 7.08[g]

[a] Where no indication is given, all reactants and products except liquid water, H_4SiO_4, and ionic species correspond to the mineral designations given in table 7. H_4SiO_4 and all ionic species are in the aqueous standard state. [b] Except where noted otherwise, the values in these columns were computed from thermodynamic data given in tables 3, 7, and 10 (footnotes j and k). [c] Except where noted otherwise, the log K(T) values for 25°C were computed from the values of $\Delta H^\circ_r(T_r)$ and $\Delta S^\circ_r(T_r)$ shown in the table; those for 60°C and above were calculated using $\Delta H^\circ_{f,i}(T_r)$, $S^\circ_i(T_r)$, and average heat capacity values for the ions, $H_2O_{(liq)}$, and H_4SiO_4 (table 3) to first compute $\Delta H^\circ_i(T)$ and $S^\circ_i(T)$ for these species at elevated temperatures (eqs 13 and 14). These values were then used together with those computed from eq (11) and (12) using data given in tables 7, 8, and 10 (footnotes j and k) for the solids and $S_{2(g)}$ to evaluate equation (15). With the exception of dolomite (see footnote l below), values of $\Delta H^\circ_f(T_r)$ and $S^\circ(T_r)$ for minerals not included in tables 7 and 10 were taken from Robie and Waldbaum (1968). All the log K(T) values are consistent with molal units of concentration. [d] See footnotes j and k, table 10. [e] Liquid water. [f] Interpolated. [g] Computed using the heat capacity power function for antigorite (table 8) to represent chrysotile. [h] Chrysotile. [i] Computed from data given in table 3 for the ionic species and, except where noted otherwise, the enthalpies of formation and entropies of the minerals at 25°C tabulated by Robie and Waldbaum (1968). [j] Computed using the entropy for dolomite reported by Stout and Robie (1963). [k] Langmuir (1964); Hsu (1967); Berner (1967). [l] The $\Delta H^\circ_f(T_r)$ value for dolomite used in the calculations was computed from the activity product constant for dolomite and a calculated entropy of formation of dolomite from the elements at 25°C (see footnote j above). [m] See footnote p, table 7. [n] These values differ from those reported by Yeatts and Marshall (1969), who did not take into account explicitly the effects of calcium sulfate complexing in their calculation of the activity product for anhydrite. [m] Crystalline gibbsite.

TABLE 12

Equilibrium constants for the hydrolysis of silicates and various oxide, hydroxide, and carbonate minerals at elevated temperatures[r,s]

Reaction[a]	$\Delta H^\circ_r(T_r)$[b] (cal mole^{-1})	$\Delta S^\circ_r(T_r)$[b] (cal mole^{-1} deg^{-1})	log K(T)[c,t] 25°C	60°C	100°C	150°C	200°C	250°C	300°C
$SiO_2 + 2H_2O \rightleftharpoons H_4SiO_4$	6,220	2.54	— 4.00	— 3.52	— 3.08	— 2.67	— 2.35	— 2.11	— 1.94
$KAlSi_3O_{8(microcline)} + 4H^+ + 4H_2O \rightleftharpoons K^+ + Al^{+++} + 3H_4SiO_4$	— 11,960	— 34.19	1.29	0.42	— 0.32	— 1.14	— 1.57	— 1.96	— 2.38
$KAlSi_3O_{8(adularia)} + 4H^+ + 4H_2O \rightleftharpoons K^+ + Al^{+++} + 3H_4SiO_4$	— 12,960[d]	— 37.71[d]	1.26	0.30	— 0.50	— 1.37	— 1.88	— 2.31	— 2.77
$KAlSi_3O_{8(high\ sanidine)} + 4H^+ + 4H_2O \rightleftharpoons K^+ + Al^{+++} + 3H_4SiO_4$	— 13,580[d]	— 38.66[d]	1.51	0.50	— 0.34	— 1.25	— 1.80	— 2.26	— 2.74
$NaAlSi_3O_{8(low\ albite)} + 4H^+ + 4H_2O \rightleftharpoons Na^+ + Al^{+++} + 3H_4SiO_4$	— 17,900	— 42.02	3.94	2.61	1.48	0.31	— 0.41	— 1.01	— 1.59
$NaAlSi_3O_{8(high\ albite)} + 4H^+ + 4H_2O \rightleftharpoons Na^+ + Al^{+++} + 3H_4SiO_4$	— 20,690[d]	— 46.49[d]	5.00	3.46[q]	2.13[q]	0.75[q]	— 0.17[q]	— 0.91[q]	— 1.65[q]
$NaAlSi_2O_6 \cdot H_2O + 4H^+ + H_2O \rightleftharpoons Na^+ + Al^{+++} + 2H_4SiO_4$	— 25,780	— 43.56	9.37	7.45	5.79	4.18	3.13	2.31	1.63
$CaAl_2Si_2O_8 + 8H^+ \rightleftharpoons Ca^{++} + 2Al^{+++} + 2H_4SiO_4$	— 70,590	—123.77	24.69	19.32	14.53	9.79	6.34	3.47	1.12
$Al_2Si_2O_5(OH)_{4(kaolinite)} + 6H^+ \rightleftharpoons 2Al^{+++} + H_2O + 2H_4SiO_4$	— 38,415	— 93.94	7.63	4.75	2.27	— 0.12	— 1.72	— 2.98	— 4.02
$Al_2Si_2O_5(OH)_{4(dickite)} + 6H^+ \rightleftharpoons 2Al^{+++} + H_2O + 2H_4SiO_4$	— 39,270[d]	— 92.51[d]	8.56	5.63[m]	3.10[m]	0.69[m]	— 0.90[m]	— 2.13[m]	— 3.09[m]
$Al_2Si_2O_5(OH)_{4(halloysite)} + 6H^+ \rightleftharpoons 2Al^{+++} + H_2O + 2H_4SiO_4$	— 43,440[d]	— 94.01[d]	11.29	8.03[m]	5.21[m]	2.50[m]	0.67[m]	— 0.75	— 1.89[m]
$KAl_3Si_3O_{10}(OH)_2 + 10H^+ \rightleftharpoons K^+ + 3Al^{+++} + 3H_4SiO_4$	— 64,320	—137.68	17.05	12.21	7.97	3.80	0.93	— 1.38	— 3.31
$K_{0.6}Mg_{0.25}Al_{2.30}Si_{3.5}O_{10}(OH)_{2(illite)}[1] + 8H^+ + 2H_2O \rightleftharpoons 0.6K^+ + 0.25Mg^{++} + 2.3Al^{+++} + 3.5H_4SiO_4$	— 46,486[f]	—108.60[e]	10.34	6.85	3.82	0.81	— 1.23	— 2.87	— 4.29

TABLE 12 (continued)

Reaction[a]	$\Delta H^\circ_r(T_r)$[b] (cal mole^{-1})	$\Delta S^\circ_r(T_r)$[b] (cal mole^{-1} deg^{-1})	log K(T)[c,t] 25°C	60°C	100°C	150°C	200°C	250°C	300°C
$KFe_3AlSi_3O_{10}(OH)_{2(annite)} + 10H^+ \rightleftharpoons K^+ + 3Fe^{++} + Al^{+++} + 3H_4SiO_4$	— 60,470[g]	— 96.2[e,g]	23.3	18.7	14.7	10.8	8.0	5.8	3.9
$NaAlSiO_4 + 4H^+ \rightleftharpoons Na^+ + Al^{+++} + H_4SiO_4$	— 33,840	— 46.38	14.66	12.11	9.84	7.62	6.05	4.76	3.70
$KAlSi_3O_8 + 4H^+ + 2H_2O \rightleftharpoons K^+ + Al^{+++} + 2H_4SiO_4$	— 24,830	— 38.19	9.85	7.98	6.34	4.70	3.60	2.71	1.95
$Mg_5Al_2Si_3O_{10}(OH)_{8(chlorite)} + 16H^+ \rightleftharpoons 5Mg^{++} + 2Al^{+++} + 3H_4SiO_4 + 6H_2O$	—150,280[f]	—169.02[e]	73.20	61.90	52.08	42.74	36.23	31.20	27.24
$3Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_{2(montmorillonite)}{}^k + 22H^+ + 8H_2O \rightleftharpoons Na^+ + 7Al^{+++} + 11H_4SiO_4$	—127,900[f]	—341.74[e]	19.06	9.48	1.18	— 7.03	—12.56	—17.00	—20.89
$3K_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_{2(montmorillonite)}{}^k + 22H^+ + 8H_2O \rightleftharpoons K^+ + 7Al^{+++} + 11H_4SiO_4$	—124,420[f]	—333.44[e]	18.32	9.00	0.92	— 7.11	—12.51	—16.87	—20.70
$6Ca_{0.167}Al_{2.33}Si_{3.67}O_{10}(OH)_{2(montmorillonite)}{}^k + 44H^+ + 16H_2O \rightleftharpoons Ca^{++} + 14Al^{+++} + 22H_4SiO_4$	—264,170[f]	—715.88[e]	37.10	17.34	— 0.11	—17.00	—28.68	—38.13	—46.39
$6Mg_{0.167}Al_{2.33}Si_{3.67}O_{10}(OH)_{2(montmorillonite)}{}^k + 44H^+ + 16H_2O \rightleftharpoons Mg^{++} + 14Al^{+++} + 22H_4SiO_4$	—267,850[f]	—730.88[e]	36.60	16.49	— 0.96	—18.25	—30.09	—39.53	—47.81
$MgSiO_3 + 2H^+ + H_2O \rightleftharpoons Mg^{++} + H_4SiO_4$	— 20,055	— 15.29	11.36	9.83	8.48	7.14	6.16	5.37	4.70
$CaMg(SiO_3)_2 + 4H^+ + 2H_2O \rightleftharpoons Ca^{++} + Mg^{++} + 2H_4SiO_4$	— 32,270	— 17.34	19.86	17.41	15.23	13.01	11.41	10.03	8.85
$Ca_2Mg_5Si_8O_{22}(OH)_2 + 14H^+ + 8H_2O \rightleftharpoons 2Ca^{++} + 5Mg^{++} + 8H_4SiO_4$	— 96,650	— 65.55	56.51	49.22	42.84	36.42	32.01	28.36	25.27
$Mg_3Si_4O_{10}(OH)_2 + 6H^+ + 4H_2O \rightleftharpoons 3Mg^{++} + 4H_4SiO_4$	— 35,010	— 30.42	19.01	16.40	14.17	11.96	10.53	9.42	8.45
$Mg_3Si_2O_5(OH)_{4(chrysotile)} + 6H^+ \rightleftharpoons 3Mg^{++} + 2H_4SiO_4 + H_2O$	— 52,615	— 29.11	32.20[p]	28.23[n,p]	24.77[n,p]	21.39[n,p]	19.00[n,p]	17.10[n]	15.53[n]
$Fe_2SiO_4 + 4H^+ \rightleftharpoons 2Fe^{++} + H_4SiO_4$	— 36,560	— 43.81	17.22	14.43	11.96	9.50	7.67	6.25	5.05

$Mg_2SiO_4 + 4H^+ \rightleftharpoons 2Mg^{++} + H_4SiO_4$	— 49,880	— 33.31	29.28	25.47	22.08	18.74	16.26	14.26	12.61
$Fe_2O_3 + 6H^+ \rightleftharpoons 2Fe^{+++} + 3H_2O$	— 30,445	—110.96	— 1.93	— 4.24	— 6.28	— 8.22	— 9.69	—10.86	—11.81
$Fe_3O_4 + 8H^+ \rightleftharpoons Fe^{++} + 2Fe^{+++} + 4H_2O$	— 49,660	—136.49	6.57	2.79	— 0.57	— 3.77	— 6.21	— 8.13	— 9.69
$CuO_{(tenorite)} + 2H^+ \rightleftharpoons Cu^{++} + H_2O$	— 15,785[d]	— 17.08[d]	7.84	6.63	5.56	4.50	3.72	3.09	2.59
$Cu_2O_{(cuprite)} + 2H^+ \rightleftharpoons 2Cu^+ + H_2O$	5,945[d]	13.11[d]	— 1.49	— 1.01	— 0.48	0.05	0.62	1.16	1.70
$Mg(OH)_2 + 2H^+ \rightleftharpoons Mg^{++} + 2H_2O$	— 25,820	— 9.81	16.78	14.84	13.10	11.41	10.09	9.08	8.53
$Al(OH)_{3(crystalline\ gibbsite)} + 3H^+ \rightleftharpoons Al^{+++} + 3H_2O$[h]	— 23,845[f]	— 43.52[d,i]	7.96	6.17[j]	4.62[j]	3.16[j]	2.15[j]	1.36[j]	0.76[j]
$Al(OH)_{3(cryptocrystalline\ gibbsite)} + 3H^+ \rightleftharpoons Al^{+++} + 3H_2O$[h]	— 25,560[d]	— 43.52[d]	9.23	7.30	5.63	4.05	2.94	2.08	1.41
$CaCO_3 + 2H^+ \rightleftharpoons Ca^{++} + H_2O + CO_{2(g)}$	— 4,020	32.37	9.76	9.48	9.25	9.04	8.95	8.81	8.73

[a] Where no indication is given, all reactants other than H_2O and H^+ correspond to the mineral designations given in table 7. H_4SiO_4 and all ionic species are in the aqueous standard state, and H_2O refers to liquid water. The subscript (g) refers to gas. [b] Except where noted otherwise, the values in these columns were computed from data given in tables 3 and 7. [c] The log K(T) values for 25°C were computed from the values of $\Delta H^\circ_r(T_r)$ and $\Delta S^\circ_r(T_r)$ shown in the table; those for 60°C and above were calculated using $\Delta H^\circ_{f,i}(T_r)$, $S^\circ_i(T_r)$, and average heat capacities for the ions, $H_2O_{(liq)}$, and H_4SiO_4 (table 3) to first compute $\Delta H^\circ_i(T)$ and $S^\circ_i(T)$ for these species at elevated temperatures (eqs 13 and 14). These values were then used together with those computed from equations (11) and (12) using data given in tables 7 and 8 for the solids to evaluate equation (15). Values of $\Delta H^\circ_f(T_r)$ and $S^\circ(T_r)$ for minerals not included in table 7 were taken from Robie and Waldbaum (1968), as were data used to compute average heat capacities for high albite. All the log K(T) values are consistent with molal units of concentration. [d] Computed from data given in table 3 for ionic species, H_2O, and H_4SiO_4, and the enthalpies of formation and entropies of the minerals at 25°C tabulated by Robie and Waldbaum (1968). [e] Computed from data given in table 3 and an estimated third law entropy for the mineral at 25°C obtained by summing (in appropriate proportions) the entropies of the oxide components of the minerals using 9.4 cal $mole^{-1}$ deg^{-1} (Latimer, 1952) for H_2O—see text and footnotes f and g below. [f] Computed from data given in table 3 together with the free energies of formation of the minerals obtained from solubility studies and entropies of formation

TABLE 12 (continued)

calculated from the third law entropy estimates for the minerals given below. The calculated free energies and enthalpies of formation and estimated entropies of the minerals at 25°C are (per mole of the mineral with the composition given above):

Mineral	$\Delta H^\circ_f(T_r)$ (cal mole^{-1})	$S^\circ(T_r)$ (cal mole^{-1} deg^{-1})	$\Delta G^\circ_f(T_r)$ (cal mole^{-1})	Source of $\Delta G^\circ_f(T_r)$
Illite	—1,390,820	66.4	—1,300,980	Computed from the solubilities of illite and kaolinite in sea water reported by Mackenzie and Garrels (1965).
Mg-chlorite	—2,109,840	112	—1,954,800	Calculated from the solubilities of chlorite and kaolinite in sea water reported by Mackenzie and Garrels (1965).
Ca-montmorillonite	—1,367,980	61.2	—1,279,240	Computed from the composition of Sierra Nevada waters (Feth, Roberson, and Polzer, 1964) considered to be in equilibrium with calcium montmorillonite (Garrels and Mackenzie, 1967).
Na-montmorillonite	—1,366,840	62.8	—1,277,760	Calculated from the free energy of formation of calcium montmorillonite assuming log $(a^2_{Na^+}/a_{Ca^{++}}) = 1.1$ for the exchange of calcium for sodium (computed by R. M. Garrels (personal commun.) from data reported by Schachtschabel, 1940).
K-montmorillonite	—1,368,920	63.4	—1,279,600	Calculated from the free energy of formation of sodium montmorillonite assuming log $(a_{Na^+}/a_{K^+}) = 0.5$ for the exchange of sodium for potassium (computed by R. M. Garrels (personal commun.) from data reported by Schachtschabel, 1940).
Mg-montmorillonite	—1,364,140	61.2	—1,275,340	Calculated from the free energy of formation of calcium montmorillonite assuming log $(a_{Mg^{++}}/a_{Ca^{++}}) = 0$ for the exchange of calcium for magnesium (computed by R. M. Garrels (personal commun.) for data reported by Schachtschabel, 1940).
Crystalline gibbsite	— 308,100	16.75[1]	— 275,200	Computed from the solubility of crystalline gibbsite reported by Kittrick (1966) using data given by Wagman and others (1968)—see footnote tt, table 4.

[s] Computed from the equilibrium constant obtained by Eugster and Wones (1962) for $Fe_3O_{4(magnetite)} + KAlSi_3O_{8(sanidine)} + H_2O_{(g)} \rightleftarrows KFe_3AlSi_3O_{10}(OH)_{2(annite)} + \frac{1}{2}O_{2(g)}$ at 500°C and 2070 bars using data taken from tables 6, 7, and 8, Anderson (1967), and Robie and Waldbaum (1968). The procedure used in the calculation is described in the text. The estimated third law entropy of annite at 25°C is

100 cal mole^{-1} deg^{-1} (see footnote e above), and the calculated values of $\Delta G^\circ_f(T_r)$ and $\Delta H^\circ_f(T_r)$ for annite are —1,150,100 and —1,233,750 cal mole^{-1}, respectively. [h] It can be deduced from comparison of various equilibrium constants given above that the assemblage gibbsite + quartz is not stable with respect to kaolinite + H_2O in the temperature range 25° to 300°C. However, calculations of high temperature equilibrium constants for the hydrolysis of corundum, boehmite, and diaspore using solubilities determined by Apps (ms) or thermodynamic data compiled by Robie and Waldbaum (1968) result in values that require kaolinite to be unstable with respect to each of these minerals + quartz + H_2O at temperatures well below 300°C. In view of experimental evidence indicating that kaolinite is stable up to ~ 300°C (Hemley and Jones, 1964) it appears that the thermodynamic data for corundum, boehmite, and diaspore at 25°C are in error. On the other hand, the crystallinities of kaolinite, gibbsite, diaspore, and boehmite produced experimentally are quite variable, and thus (see footnote r below) the substantial agreement that exists between the results of solubility studies involving kaolinite and the thermodynamic data (table 7) used to compute the log K values for kaolinite given above is not necessarily a definitive criterion for resolving the conflict. [i] The illite in this reaction is close to an illitic end member composition in the montmorillonite-mixed layer illite solid solution series (Hower and Mowatt, 1966). [j] Computed using the heat capacity of cryptocrystalline gibbsite to represent that of crystalline gibbsite. [k] Idealized end members in the beidellite solid solution series. [l] The entropy of crystalline gibbsite at 25°C was assumed to be equivalent to that of cryptocrystalline gibbsite in the calculations. [m] Computed using $C^\circ_P(T_r)$ for halloysite and dickite (58.86 and 57.24 cal mole^{-1} deg^{-1}, respectively, King and Weller, 1961) as constants. [n] Computed using the heat capacity of antigorite to represent that of chrysotile. [p] These values are consistent with those reported by Hostetler and Christ (1968). [q] Computed using average heat capacities for high albite—see footnote c above. [r] Owing to the significant effect of crystallinity on the thermodynamic behavior of the clay minerals, the actual hydrolysis of these minerals in geochemical processes cannot necessarily be described in terms of the log K values shown in this table; the hydrolysis constants given in the table are "idealized" values. [s] Hydrolysis constants are given in this table for a number of minerals that are not stable in the presence of H_2O at the temperatures indicated, (for example, enstatite, forsterite, et cetera). These reactions were included to enable additive calculation of equilibrium constants for stable assemblages and to facilitate extrapolation to higher temperatures. [t] Constant heat capacity fits of the log K values given in the table results in the following estimates of equilibrium constants for the reactions (in the above order) at 0°C: —4.4, 2.1, 2.1, 2.4, 5.1, 6.3, 11.1, 29.4, 10.2, 11.2, 14.2, 21.4, 13.5, 26.4, 16.9, 11.5, 83.3, 27.4, 26.6, 54.5, 54.4, 12.7, 22.0, 62.8, 21.4, 35.7, 19.7, 32.6, 0.1, 9.9, 8.9, —1.9, 18.5, 9.6, 11.0, 10.0.

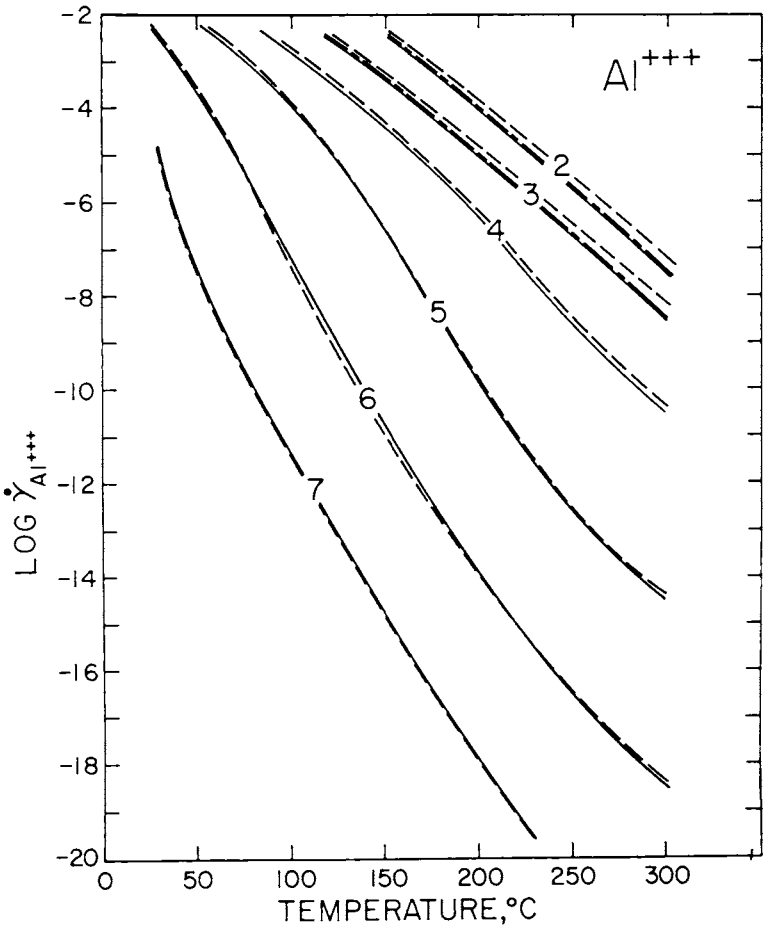

Fig. 9. Stoichiometric individual ion activity coefficients ($\dot{\gamma}_i$) for the aluminum ion as a function of temperature at constant pH (indicated by the numbers on the curves) in 1 (– – –), 2 (— – —), and 3 (——) molal NaCl solutions (see text and table 13.)

charged) complexes were omitted from the calculations represented in the tables.

Distribution diagrams are presented in figures 16 and 17 for aluminum hydroxide species and complexes involving the hydrogen ion and carbonate, sulfide, and sulfate ligands, respectively. Unlike the curves in figure 15, those in figures 16 and 17 represent the equilibrium pH at a given temperature for equal activities of the species shown on either side of the curves. Similar distribution diagrams for sulfur, copper, and iron species in terms of fugacity of oxygen and pH at two temperatures are shown in figures 18 and 19. The relation between fugacity of oxygen and the ratio of the concentration of total sulfate to that of total sulfide

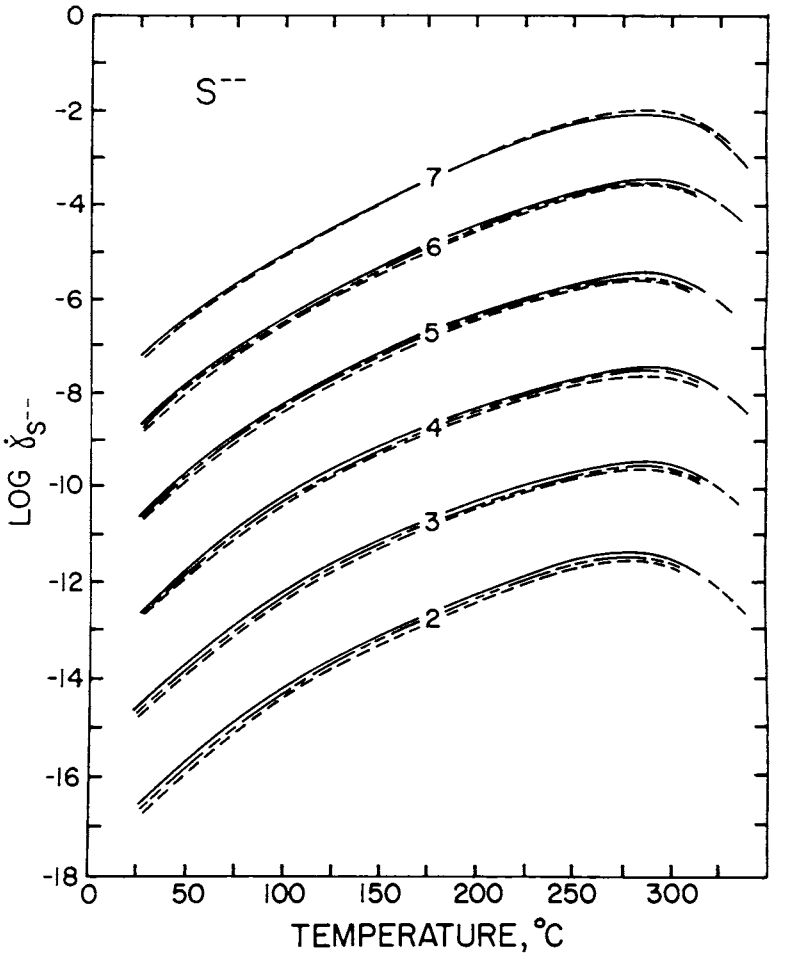

Figure 10. Stoichiometric individual ion activity coefficients ($\dot{\gamma}_i$) for the sulfide ion as a function of temperature at constant pH (indicated by the numbers of the curves) in 1 (– – –), 2 (— – —), and 3 (——) molal NaCl solutions (see text and table 13).

in a 3 molal NaCl solution with a pH of 5 at elevated temperatures is depicted in figure 20. The curves shown in figures 16 to 20 were computed from data given in tables 4, 6, and 9.

CONCLUDING REMARKS

Although many equilibria are considered in the preceding pages, all hydrothermal reactions of interest in hydrothermal geochemistry could not be included in this communication. On the other hand, the data and equations summarized above permit other high temperature equilibrium constants to be calculated to suit the requirements of one or another investigation. In many instances, a desired equilibrium constant can be

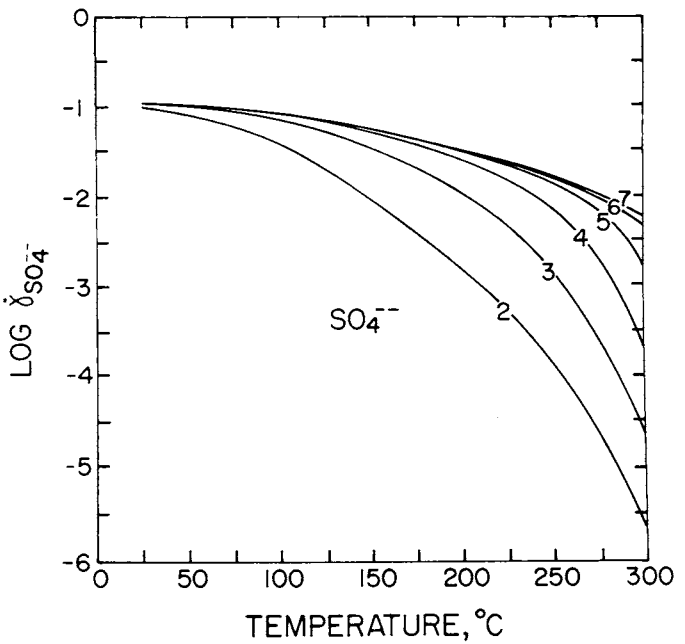

Fig. 11. Stoichiometric individual ion activity coefficients ($\dot{\gamma}_i$) for the sulfate ion as a function of temperature at constant pH (indicated by the numbers on the curves) in 3 molal NaCl solutions (see text and table 13).

obtained by combining various reactions for which log K(T) values are given in the tables. Values of $\dot{\gamma}_i$ can be taken directly from the tables and graphs, and values of y^*_i can be computed as needed from the data and equations given in the foregoing discussion.

The information contained in the tables permits quantitative calculations for hydrothermal systems and processes at high temperatures without the aid of a computer. As an example, calculated sulfide solubilities are plotted against temperature in figure 21. Note that with the exception of metacinnibar, the computed solubilities of the individual sulfides in a 3 molal NaCl solution with a pH of 5 are more than sufficient at high temperatures to account for hydrothermal ore deposits of the metals considered. It can also be seen in figure 21 that the solubilities of a number of the sulfides are similar at high temperatures, but change differentially with decreasing temperatures. Many other conclusions, observations, and implications of considerable geologic significance can be drawn from similar calculations involving the thermodynamics of hydrothermal reactions summarized above. Discussion of these is beyond the scope of the present paper, but in future communications the thermodynamic relations presented here will be used to define phase relations among silicates in hydrothermal systems and to evaluate polyphase equilibrium states and the mass transfer involved in hydrothermal vein for-

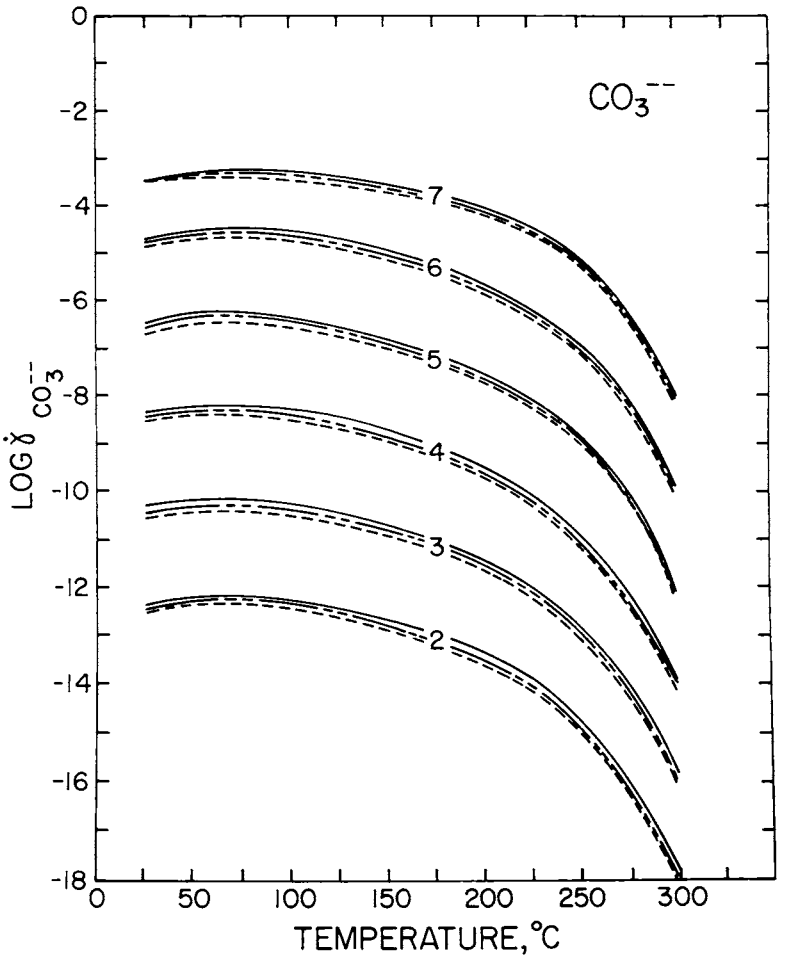

Fig. 12. Stoichiometric individual ion activity coefficients ($\dot{\gamma}_i$) for the carbonate ion as a function of temperature at constant pH (indicated by the numbers on the curves) in 1 (– – –), 2 (— – —), and 3 (——) molal NaCl solutions (see text and table 13).

mation. Such calculations make it possible to characterize quantitatively the mutual solubilities of sulfides and silicates at high temperatures. Irreversible reactions responsible for metasomatism and the paragenesis, replacement, and zoning of hydrothermal minerals have been programmed for machine evaluation. The methods employed in the calculations and idealized models of the mass transfer involved in various geochemical processes have been presented elsewhere (Helgeson, 1968b; Helgeson, Garrels, and Mackenzie, 1969; Helgeson and Garrels, 1968).

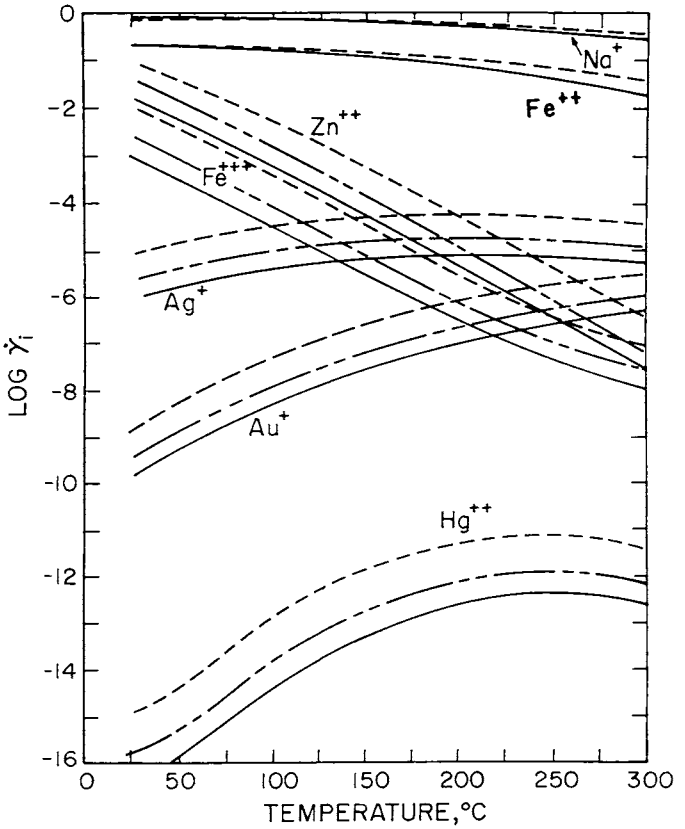

Fig. 13. Stoichiometric individual ion activity coefficients ($\dot{\gamma}_i$) for metal ions in 1 (– – –), 2 (— – —), and 3 (——) molal NaCl solutions at elevated temperatures (see text and table 14).

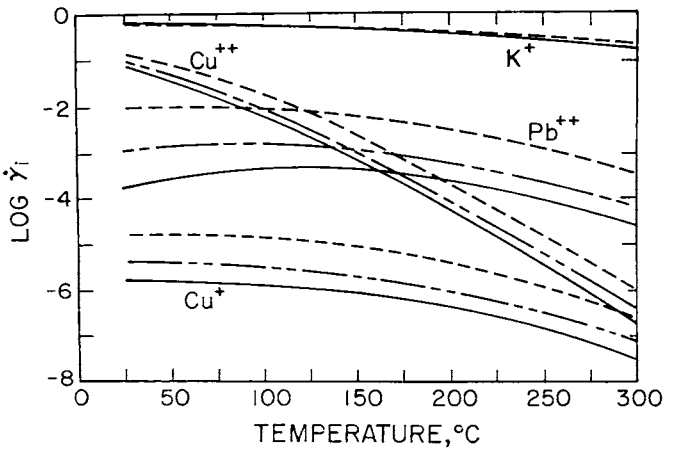

Fig. 14. Stoichiometric individual ion activity coefficients ($\dot{\gamma}_i$) for metal ions in 1 (– – –), 2 (— – —), and 3 (——) molal NaCl solutions at elevated temperatures (see text and table 14).

TABLE 13

Stoichiometric individual ion activity coefficients ($\dot{\gamma}_i$) for aluminum, sulfide, carbonate, sulfate, and calcium ions present in relatively small concentrations in 3.0 molal sodium chloride solutions

Ion	pH	log $\dot{\gamma}_i$[a]						
		25°C	50°C	100°C	150°C	200°C	250°C	300°C
Al^{+++} (assuming the presence of $Al(OH)^{++}$ and $Al(OH)_4^-$)	2	—1.17	—1.22	—1.46	—2.49	—4.07	—5.71	—7.55
	3	—1.17	—1.25	—1.94	—3.45	—5.04	—6.71	—8.56
	4	—1.21	—1.47	—2.83	—4.45	—6.27	—8.65	—10.50
	5	—1.49	—2.18	—3.94	—6.72	—9.83	—12.60	—14.45
	6	—2.26	—3.54	—7.34	—10.70	—13.83	—16.60	—18.45
	7	—4.87	—7.33	—11.34	—14.70	—17.83	—20.60	—22.45
	8	—8.86	—11.33	—15.34	—18.70	—21.83	—24.60	—26.45
	9	—12.86	—15.33	—19.34	—22.70	—25.83	—28.60	—30.45
	10	—16.86	—19.33	—23.34	—26.70	—29.83	—32.60	—34.45
	11	—20.86	—23.33	—27.34	—30.70	—33.83	—36.60	—38.45
	12	—24.86	—27.33	—31.34	—34.70	—37.83	—40.60	—42.45
S^{--} (assuming the presence of HS^- and $H_2S_{(aq)}$)	2	—16.60	—15.64	—14.17	—13.11	—12.29	—11.69	—11.42
	3	—14.60	—13.64	—12.17	—11.11	—10.29	—9.69	—9.42
	4	—12.61	—11.65	—10.17	—9.11	—8.29	—7.69	—7.42
	5	—10.62	—9.66	—8.20	—7.13	—6.30	—5.70	—5.42
	6	—8.71	—7.81	—6.39	—5.30	—4.43	—3.78	—3.47
	7	—7.20	—6.39	—5.04	—3.93	—2.98	—2.27	—2.11
CO_3^{--} (assuming the presence of HCO_3^-, $H_2CO_{3(aq)}$ and $CO_{2(aq)}$)[b]	2	—12.38	—12.22	—12.37	—12.79	—13.52	—14.79	—17.88
	3	—10.38	—10.22	—10.37	—10.79	—11.52	—12.79	—15.88
	4	—8.39	—8.23	—8.37	—8.79	—9.52	—10.79	—13.88
	5	—6.43	—6.28	—6.41	—6.81	—7.53	—8.79	—11.88
	6	—4.73	—4.58	—4.65	—4.97	—5.62	—6.83	—9.88
	7	—3.50	—3.35	—3.38	—3.58	—4.08	—5.10	—7.93
SO_4^{--} (assuming the presence of HSO_4^- in the absence of calcium)	2	—1.01	—1.09	—1.43	—2.03	—2.77	—3.79	—5.62
	3	—0.96	—1.00	—1.14	—1.42	—1.92	—2.82	—4.62
	4	—0.95	—0.99	—1.10	—1.26	—1.51	—2.07	—3.64
	5	—0.95	—0.99	—1.10	—1.25	—1.43	—1.79	—2.77
	6	—0.95	—0.99	—1.10	—1.24	—1.43	—1.75	—2.33
	7	—0.95	—0.99	—1.10	—1.24	—1.43	—1.75	—2.25
	$a_{Ca^{++}}$							
SO_4^{--} (assuming the presence of HSO_4^- and $CaSO_{4(aq)}$ at a pH of 5)	0.001	—0.95	—1.0	—1.1	—1.3	—1.5		
	0.01	—1.04	—1.1	—1.2	—1.4	—1.7		
	$a_{SO_4^{--}}$							
Ca^{++} (assuming the presence of $CaSO_{4(aq)}$ and $CaCO_{3(aq)}$ at a pH of 5)[c]	0.001	—0.67	—0.7	—0.8	—0.9	—1.2		
	0.01	—0.75	—0.8	—1.0	—1.2	—1.5		

[a] Computed from equation (49) or expressions for anions analogous to equation (49) using data given in tables 2 and 4 (see text). [b] If the total molality of calcium present in the solution is one or less, the computed values of $\dot{\gamma}_{CO_3^{--}}$ are not affected by the formation of $CaCO_{3(aq)}$. [c] Where total $CO_{2(aq)}$ is less than 1 molal, the $CaCO_{3(aq)}$ species has a negligible effect on $\dot{\gamma}_{Ca^{++}}$ at pH 6 and below.

TABLE 14

Stoichiometric individual ion activity coefficients ($\dot{\gamma}_i$) for Na^+ and cations present in relatively small concentrations in 1.0, 2.0, and 3.0 molal sodium chloride solutions

Ion	$m_{t,NaCl}$	log $\dot{\gamma}_i$[a]						
		25°C	50°C	100°C	150°C	200°C	250°C	300°C
Ag^+	1.0	— 5.07	— 4.8	— 4.5	— 4.3	— 4.3	— 4.2[b]	— 4.5[b]
	2.0	— 5.68	— 5.5	— 5.1	— 4.8	— 4.8	— 4.7[b]	— 5.0[b]
	3.0	— 6.06	— 5.8	— 5.5	— 5.2	— 5.1	— 5.0[b]	— 5.3[b]
Cu^+[c]	1.0	— 4.75	— 4.8	— 4.9	— 5.0	— 5.4	— 6.0[b]	— 6.6[b]
	2.0	— 5.36	— 5.4	— 5.5	— 5.6	— 6.0	— 6.5[b]	— 7.1[b]
	3.0	— 5.75	— 5.8	— 5.9	— 6.0	— 6.3	— 6.8[b]	— 7.5[b]
Cu^{++}	1.0	— 0.91	— 1.0	— 1.7	— 2.6	— 3.7[b]	— 4.8[b]	— 6.0[b]
	2.0	— 1.03	— 1.2	— 2.0	— 3.0	— 4.1[b]	— 5.2[b]	— 6.4[b]
	3.0	— 1.10	— 1.3	— 2.2	— 3.2	— 4.3[b]	— 5.4[b]	— 6.7[b]
Pb^{++}	1.0	— 2.07	— 2.0	— 2.2	— 2.3	— 2.5	— 2.9[b]	— 3.5[b]
	2.0	— 2.99	— 2.6	— 2.8	— 3.0	— 3.2	— 3.5[b]	— 4.2[b]
	3.0	— 3.75	— 3.1	— 3.3	— 3.4	— 3.6	— 3.9[b]	— 4.6[b]
Zn^{++}	1.0	— 1.00	— 1.4	— 2.3	— 3.2	— 4.3	— 5.2[b]	— 6.5[b]
	2.0	— 1.43	— 1.9	— 2.9	— 3.8	— 5.0	— 5.8[b]	— 7.2[b]
	3.0	— 1.84	— 2.4	— 3.4	— 4.3	— 5.4	— 6.3[b]	— 7.6[b]
Hg^{++}	1.0	—14.98	—14.4	—12.8	—11.8	—11.3	—11.1[b]	—11.4[b]
	2.0	—15.90	—15.3	—13.7	—12.7	—12.1	—11.9[b]	—12.2[b]
	3.0	—16.50	—15.9	—14.3	—13.3	—12.6	—12.3[b]	—12.6[b]
Fe^{+++}[d]	1.0	— 2.02	— 2.5	— 3.4	— 4.4	— 5.5[b]	— 6.6[b]	— 7.1[b]
	2.0	— 2.60	— 3.1	— 4.1	— 5.1	— 6.1[b]	— 7.2[b]	— 7.6[b]
	3.0	— 2.98	— 3.5	— 4.5	— 5.5	— 6.5[b]	— 7.5[b]	— 8.0[b]
Fe^{++}[e]	1.0	— 0.64	— 0.67	— 0.7	— 0.8	— 1.0	— 1.2[b]	— 1.4[b]
	2.0	— 0.68	— 0.71	— 0.8	— 0.9	— 1.0	— 1.2[b]	— 1.6[b]
	3.0	— 0.67	— 0.70	— 0.8	— 0.9	— 1.0	— 1.3[b]	— 1.7[b]
Au^+[f]	1.0	— 8.8	— 8.2	— 7.3	— 6.6	— 6.0	— 5.6[b]	— 5.5[b]
	2.0	— 9.4	— 8.9	— 7.9	— 7.2	— 6.6	— 6.2[b]	— 6.0[b]
	3.0	— 9.8	— 9.2	— 8.3	— 7.5	— 6.9	— 6.5[b]	— 6.3[b]
Au^{+++}[f]	1.0	—25.4	—24.0	—21.7	—20.1	—19.1	—18.7[b]	—19.2[b]
	2.0	—26.7	—25.2	—23.0	—21.3	—20.2	—19.8[b]	—20.2[b]
	3.0	—27.5	—26.0	—23.8	—22.0	—20.9	—20.4[b]	—20.8[b]
Na^+	1.0	— 0.18	— 0.19	— 0.21	— 0.25	— 0.31	— 0.41[b]	— 0.61[b]
	2.0	— 0.17	— 0.18	— 0.20	— 0.25	— 0.33	— 0.46[b]	— 0.68[b]
	3.0	— 0.15	— 0.15	— 0.17	— 0.24	— 0.33	— 0.49[b]	— 0.73[b]
K^+	1.0	— 0.22	— 0.22	— 0.25	— 0.29	— 0.35	— 0.44[b]	— 0.62[b]
	2.0	— 0.22	— 0.23	— 0.25	— 0.30	— 0.37	— 0.49[b]	— 0.71[b]
	3.0	— 0.20	— 0.21	— 0.24	— 0.28	— 0.37	— 0.51[b]	— 0.76[b]

[a] The dissociation constants for the metal chloride complexes used in calculating the values of $\dot{\gamma}_i$ in this table from equation (49) are shown in table 5. To insure minimal uncertainty and conservative values (see text), divalent and trivalent metal chloride complexes were not considered in the calculations; that is, q in equation (49) was assigned a value of $Z_i + 1$ for each metal ion. Because all the metal ions considered above, with the exception of Fe^{++}, associate with the chloride ion to a significant degree, the individual ion activity coefficients for the ions themselves have no significant effect, except in the case of Na^+, K^+, and Fe^{++}, on the $\dot{\gamma}_i$ values shown above. [b] These values have a higher uncertainty than the others given in the table owing to extrapolation of equilibrium constants and activity coefficients used

in the calculations. [c] No log K(T) data are available for $CuCl_{(aq)}$ so this species was not considered specifically in the calculations. [d] The term for $FeCl^{++}$ was omitted from equation (49) to eliminate the influence of the divalent charge on this species, which is the most stable of the ferric chloride complexes. The degree of formation achieved by this species is represented by the magnitude of the overall dissociation constants for the higher order ferric chloride complexes considered in the calculations. [e] There is little indication that chloride complexes of Fe^{++} form to significant degrees, at least at low temperatures. The values shown for Fe^{++} are thus equivalent to individual ion activity coefficients. Because the ion is divalent and a 25°C å was used in the calculations, the activity coefficients shown for this species at high temperatures are probably too small. On the other hand, there are indirect indications from solubility data that Fe^{++} may form stable complexes with chloride in the region of 300°, and that the overall stability constant is of the order of 10^{-2} or 10^{-3}. In view of these uncertainties, the activity coefficients shown above for Fe^{++} should be considered provisional estimates. [f] The values shown for these ions are based on the dissociational reactions for the gold species shown in table 5.

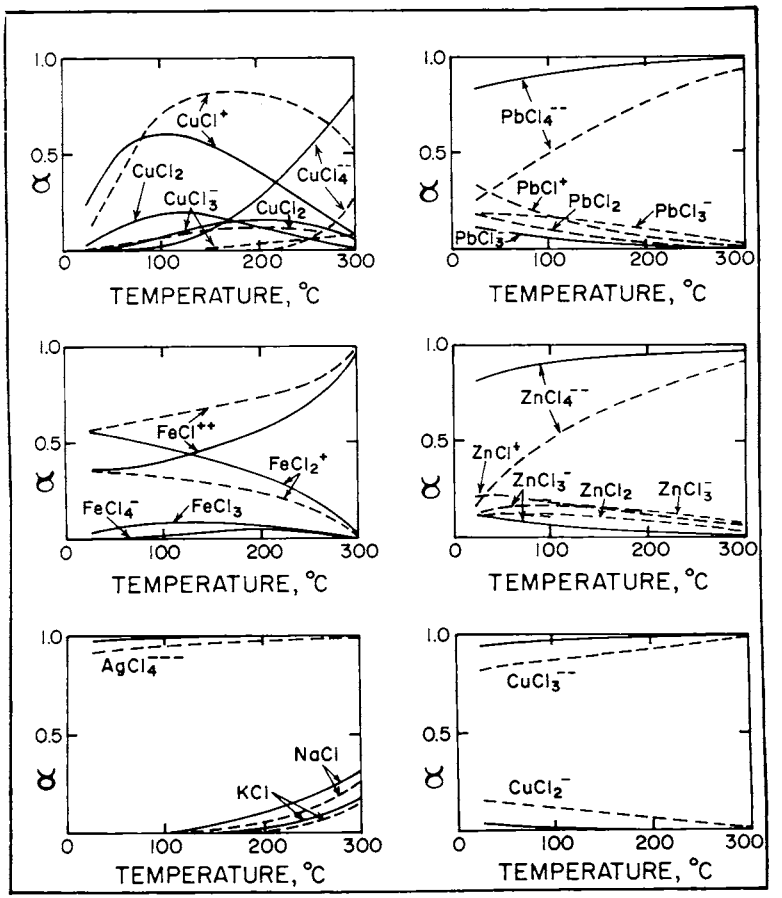

Fig. 15. Degrees of formation (α) for metal chloride complexes in 1 (– – –) and 3 (——) molal NaCl solutions at elevated temperatures (see text—eq 54). Mercury is not shown because the species $HgCl_3^-$ accounts for >98 percent of the mercury in solution. Complexes that form to less than a few percent have been omitted from the diagrams. Unlike the $\dot{\gamma}_i$ values shown in table 14 and figures 13 and 14, the α values shown above were calculated (eq 54) assuming the presence of all chloride complexes (of each cation) in table 5 (see text).

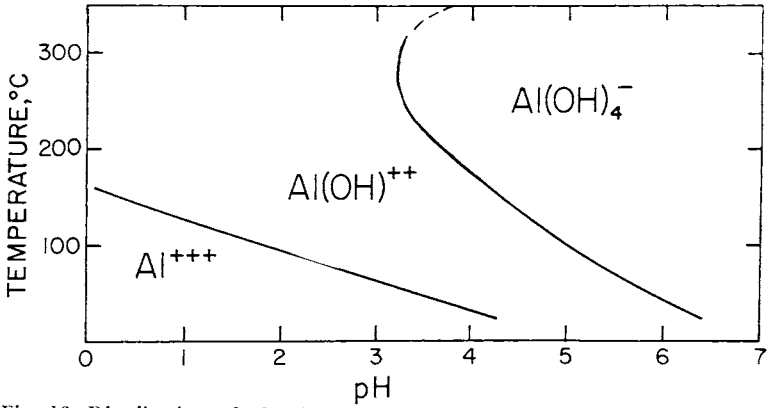

Fig. 16. Distribution of aluminum species in aqueous solution as a function of temperature and solution pH. The curves represent equal activities of the species shown in adjoining fields in the diagram. The positions of the curves are defined by dissociation constants in table 4.

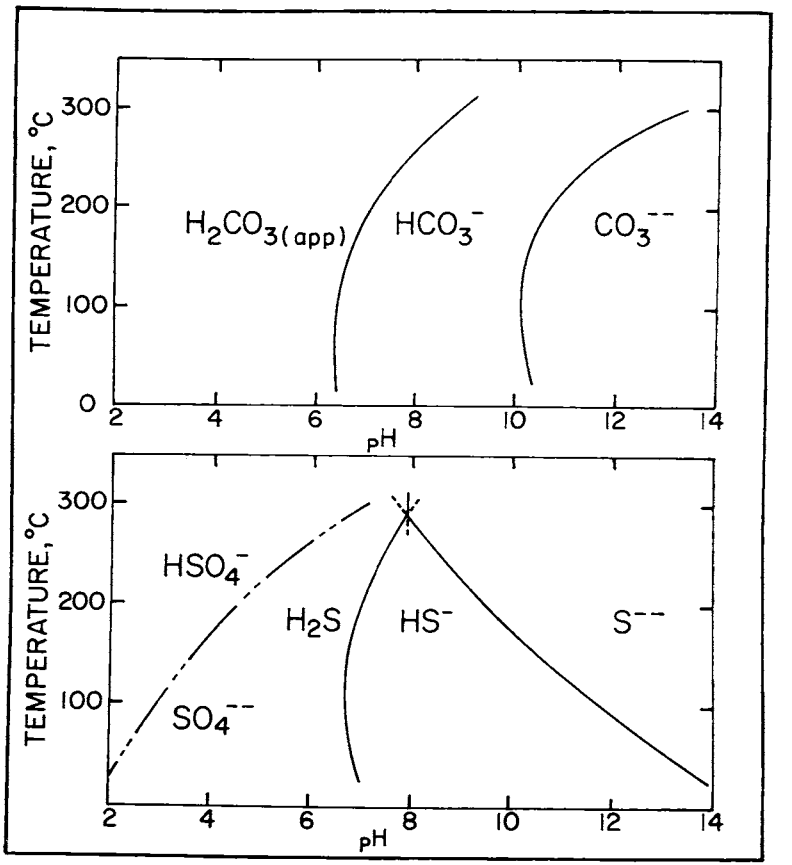

Fig. 17. Distribution of carbonate, sulfide, and sulfate species in aqueous solution as a function of temperature and solution pH. The curves represent equal activities of the species shown in adjoining fields in the diagrams. The positions of the curves are defined by dissociation constants in table 4. The subscript (app) indicates that the species referred to is the undifferentiated sum of H_2CO_3 and $CO_{2(aq)}$.

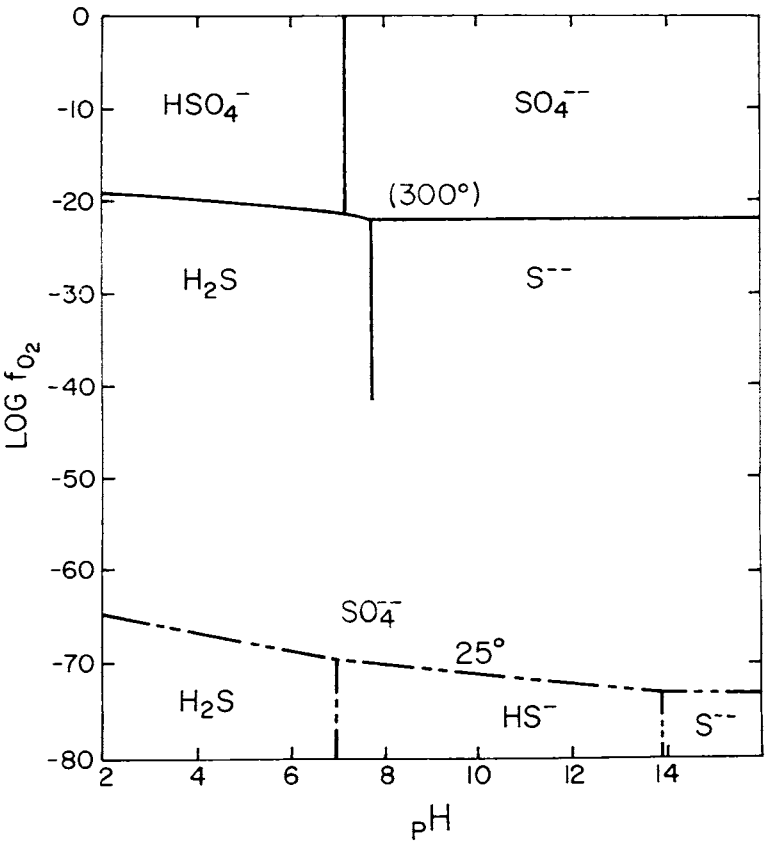

Fig. 18. Distribution of sulfur species at 25°C (— - - —) and 300°C (——) as a function of f_{O_2} and solution pH. The curves, which define the positions of equal activities of the species in adjoining fields in the diagram, were computed from the equilibrium constants given in table 9. The field for HSO_4^- at 25°C lies to the left of the diagram.

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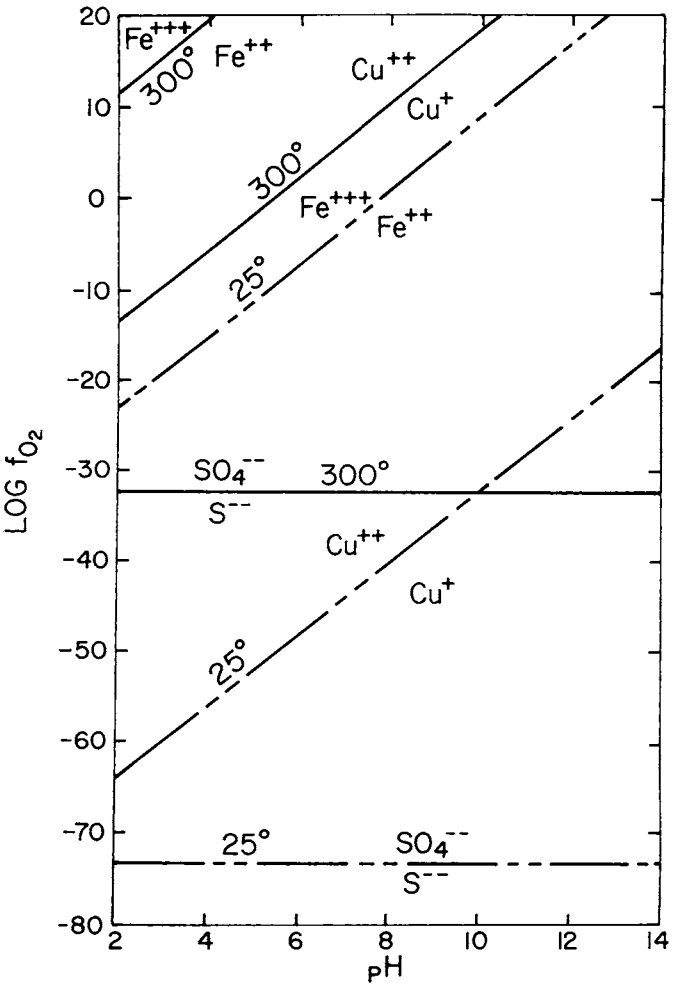

Fig. 19. Distribution of iron, copper, and sulfur species at 25°C (— - - —) and 300°C (——) as a function of f_{O_2} and solution pH. The curves, which define the positions of equal activities of the species in adjoining fields in the diagram, were computed from the equilibrium constants given in table 9.

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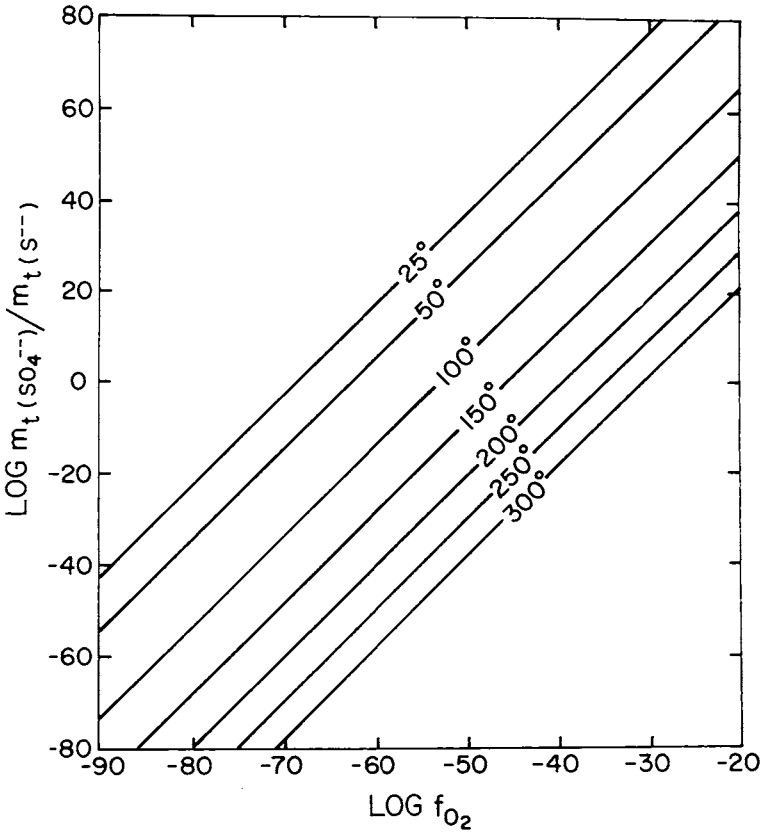

Fig. 20. Ratio of the total concentration of sulfate to sulfide in a 3.0 molal NaCl solution as a function of f_{O_2} from 25° to 300°C at a pH of 5. The positions of the isotherms were computed from the data given in tables 9 and 13.

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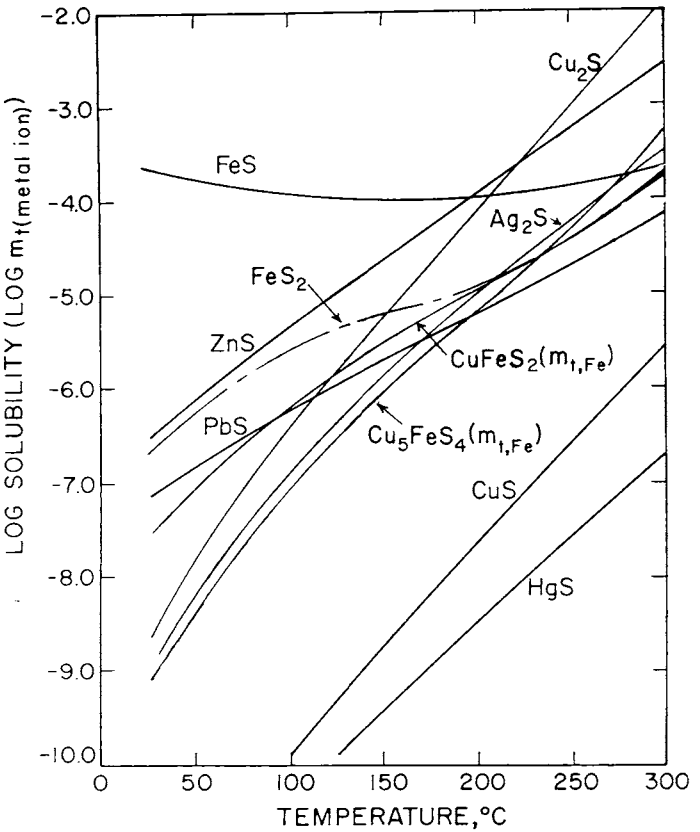

Fig. 21. Calculated stoichiometric solubilities (in terms of the total molality of the metal ion) of various individual sulfides in a 3 molal sodium chloride solution with a pH of 5 at elevated temperatures. HgS refers to metacinnabar. Except for pyrite, chalcopyrite, and bornite, the solubilities were computed from equation (51) and the data presented in tables 11, 13, and 14. Pyrite solubilities were calculated by evaluating $4FeS_2 + 8H^+ + 4H_2O \rightleftarrows 8H_2S + 4Fe^{++} + SO_4^{--}$ and $4FeS_2 + 7H^+ + 4H_2O \rightleftarrows 7H_2S + 4Fe^{++} + HSO_4^-$ with the aid of the data in tables 10, 13, and 14. The solubilities of chalcopyrite and bornite were computed from oxidation-reduction equations analogous to those given above for pyrite, which are written in terms of the predominant species in the aqueous phase. This procedure permits the molalities of all species in the reactions to be defined in terms of the molality of Fe^{++}, and therefore the solubilities of the minerals can be computed directly from the Law of Mass Action equations for the reactions. Owing to the limitation imposed by the computed stoichiometric individual ion activity coefficients (see footnote a, table 14), all solubilities depicted above should be regarded as minimal approximations of the true mineral solubilities.

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