DETERMINING THE THERMODYNAMIC PROPERTIES OF SOLUTES IN CRUSTAL FLUIDS

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ABSTRACT. The thermodynamic properties of solute species in the complex fluids found at increasing depth within the Earth’s crust, as pressure and temperature increase, can be estimated by considering the changes in electrostatic interactions in the solution. Mineral solubility measurements in pure H₂O allow infinitely dilute aqueous solution Gibbs free energies to be determined. The Born (1920) equation is then used to account for a change in the solute energetics when the solvent is changed from pure H₂O to a mixture of all the uncharged species in solution. The long range electrostatic interactions of charged species can then be evaluated with a Debye-Hückel (1923) type model. The degree of ion pairing, which becomes important at mid- and lower-crustal levels, is determined with a Gilkerson-Fuoss type equation (Brady and Walther, 1990). The approach outlined here relies on determining the dielectric constant of the solution which includes all uncharged species. This is approximated by using the Kirkwood (1939) equation and the Looyenga (1965) mixing rules.

INTRODUCTION

Excluding magmas, the change in composition of volumes of rocks in the Earth’s crust occurs through interactions with a low viscosity fluid phase which generally is composed of H₂O and often contains CO₂ and/or chloride solutes. Equilibrium between minerals and this fluid are important whether one considers the reaction of one assemblage of minerals to another on the thin section scale (Walther and Wood, 1984) or metasomatism on the kilometer scale in metamorphic terrains and ore deposits. At the elevated temperatures of mid- and lower-crustal levels reaction rates are rapid enough that one can generally assume that equilibrium between a fluid and the minerals it contacts is closely maintained on a millimeter scale (Walther and Wood, 1986).

To understand the ability of such fluids to transfer mass between rock volumes, we need to characterize how mineral solubilities and, therefore, how the Gibbs free energies of solutes change as a function of pressure, temperature, and fluid composition in crustal fluids. At the lower temperatures and mineral surface to fluid volume ratios encountered near the Earth’s surface, rates of reaction are dramatically slower. Fluids are often not in equilibrium with the minerals they contact on a local scale. However, characterization of the Gibbs free energy of solute species in equilibrium with minerals in these fluids helps us understand under which conditions minerals will dissolve or precipitate from a particular fluid and the chemical affinity for reaction.

The most widely used model of the thermodynamics of aqueous solutions is that of K. Pitzer (Pitzer, 1973, 1975; Pitzer and Kim, 1974; Pitzer, Peiper, and Busey, 1984). It involves modeling the Gibbs free
energy of multicomponent ionic aqueous fluids by using an electrostatic
term to account for the long range energetics of charged particles at low
species concentrations. A set of paired and, at times, triple interaction
parameters are tabulated corresponding to second and third virial coe-
fficients, respectively, to account for short range specific ion interactions at
high solute concentrations. The model is constructed for empirical use,
allowing accurate characterization of experimental results in simple
systems, which can be interpolated to characterize interactions in more
complex systems. The model is particularly effective at low temperature
where solution compressibility is low. It is, apparently, not effective at
near critical or supercritical pressure-temperature conditions or in extrap-
olating to pressures, temperatures, and fluid components where experi-
mental data are lacking.

The energetics of short range interactions between species at low
temperature in concentrated aqueous solutions are complex and not well
understood. These include electrostatic dipole contributions of hydra-
tion as well as hydrogen and covalent bonding effects and ligand field
stabilization energetics. As temperature increases, the electrostatic effects
of polar H₂O interactions and between oppositely charged species should
begin to dominate.

In this communication I would like to establish a framework for
determining the Gibbs free energy changes for solute species at the
elevated temperatures and pressures of crustal fluids based on electro-
static interactions in a solvent mixture whose dielectric constant departs
from that of pure H₂O.

MINERAL SOLUBILITIES

The Gibbs free energy of formation from the elements of pure single
and multi-oxide mineral phases, ΔG°,min as a function of pressure and
temperature are reasonably well known (Helgeson and others, 1978;
Robie, Hemingway, and Fisher, 1978; Berman, 1988). The largest uncer-
tainties in ΔG°,min generally arise because of solid solution phenomena.
This is particularly true at the Earth’s surface where complex multi-oxide
minerals displaying a wide range of solid solution behavior are present.
The small Gibbs free energy differences between these solid solutions,
such as in clay minerals, often make mineral solubility calculations
difficult. However, in most cases, to obtain the thermodynamic proper-
ties of species in crustal solutions, we can relate the Gibbs free energy of
these species to their mineral counterparts through the equilibrium that
occurs in solubility experiments.

A wide range of other experimental techniques exists for determi-
ning the thermodynamic properties of aqueous solutions. These include
those that relate solute free energies to changes in H₂O free energy such
as vapor pressure, isopiestic concentrations, and freezing or boiling point
changes. Alternatively, one can obtain the free energy temperature
derivative properties through enthalpy and heat capacity measurements.
In this contribution I will emphasize solubility measurements because of
the ability to do these experiments at the pressure and temperature conditions of the middle and lower crust. Also, knowledge of mineral solubilities gives, directly, the information that is needed to model changes in composition of fluids in crustal processes.

For our solubility analysis we need to use a mineral or mineral assemblage that is stable at the pressure, temperature, and fluid composition of the experiment. Because of the complexities of multicomponent experiments, it is generally best to start with the measurement of pure single oxides in pure H₂O solutions (Anderson and Burnham, 1965; Ragnarsdóttir and Walther, 1985). However, for alkali and alkaline earth elements the single oxide phase is not stable in H₂O at crustal pressures and temperatures. For alkaline earths like Ca and Mg we can use the stable hydroxides instead (Walther, 1986). In the case of the alkalis the solubility of the hydroxides is quite large which makes extrapolation to standard state conditions difficult (see below). Also the thermodynamic properties of alkali hydroxides are not accurately known at elevated pressures and temperatures. For alkalis we can use a stable alkali bearing multi-oxide mineral and buffer the other oxide components with minerals of these oxides. For instance, the solubility of the assemblage albite, paragonite, and quartz buffers the Gibbs free energy of the oxides of Na along with Si and Al and is the stable over large regions of crustal pressure and temperature (Woodland and Walther, 1987).

STANDARD STATE PROPERTIES

We define our standard state for minerals as the pure oxide or hydroxide phase at the temperature and pressure of interest. For aqueous species the standard state is a hypothetical one molal solution that has the properties of the species at infinite dilution in pure H₂O at the pressure and temperature of interest. We use conventional properties so the standard state Gibbs free energy and other thermodynamic properties of H⁺ are defined to be zero at all temperatures and pressures.

If we measure the solubility of a single cation oxide of cation A with a positive charge z in pure water, assuming there is only one dominant aqueous species and that polymeric species are not important, we can write the equilibrium for a positively or neutrally charged species as:

\[ \text{AO}_{z/2}^+ + n\text{H}^+ = (\text{AO}_{z/2}^+\text{H}_n)^n \]

A-oxide A-aqueous species

where n is the number of charges on the aqueous species. It should be noted that reaction (1) takes implicit rather than explicit account of any solvation by H₂O. Thus, for instance, the monomer uncharged Si species in solution would be written as SiO₂(aq) rather than H₄SiO₄ as is commonly done at low temperatures. Writing the Si species as H₄SiO₄ implies a structural configuration of associated H₂O dipoles. Because, by convention, the standard state thermodynamic properties of:

\[ \text{SiO}_2(aq) + 2\text{H}_2\text{O} = \text{H}_4\text{SiO}_4 \]
are taken as zero, the two representations of monomer uncharged aqueous Si species are thermodynamically identical (Walther and Helgeson, 1977).

For negatively charged species we can write:

$$\text{AO}_{2/2} + n\text{OH}^- = (\text{AO}_{(2/2+n)}\text{H}_n)^-n$$

$\text{A-oxide} \quad \text{A-aqueous species}$ (3)

For hydroxides in equilibrium with a positively or neutrally charged species we have:

$$\text{A(OH)}_z + n\text{H}^+ = (\text{AO}_z\text{H}_{n+z})^n$$

$\text{A-hydroxide} \quad \text{A-aqueous species}$ (4)

and for negatively charged species:

$$\text{A(OH)}_z + n\text{OH}^- = (\text{AO}_{n+z}\text{H}_{n+z})^-n$$

(5)

The equilibrium constant for reaction (1), $K_{(1)}$, can be written as:

$$\log K_{(1)} = \log a_{A-aq} - \log a_{\text{oxide}} + npH$$

(6)

where $a$ is the activity of the subscripted species. Similar equilibrium constants can be written for reactions (3) to (5).

Because $K_{(1)}$, $K_{(3)}$, $K_{(4)}$, and $K_{(5)}$ are constant as a function of composition at constant temperature and pressure and $a_{\text{oxide}}$ and $a_{\text{hydroxide}}$ are unity for the pure solid phase, we can obtain $n$ and therefore the charge of the aqueous complex from eq (6) or its equivalent for reactions (3) to (5) by determining how $a_{A-aq}$ changes with changing pH. Obviously, we need to add solutes to the solution to change pH at constant pressure and temperature. It is not a priori possible to determine the effects of this addition precisely. However, in these simple systems the uncertainties are small for the concentrations of HCl or NaOH, for instance, that need to be added. If problems develop, other acids or bases can be used for comparison. With a pure mineral phase the conventional standard molal Gibbs free energy of the aqueous complex of element $A$, $\Delta G_{A-aq}^o$, can be computed from the molar standard state Gibbs free energy of formation of the element $A$ oxide mineral phase, $\Delta G_{f,\text{min}}^o$, using:

$$\Delta G_{A-aq}^o = -2.303R T \log \left( \frac{\gamma_{A-aq} m_{A-aq}}{a_{H^+}^n} \right) + \Delta G_{f,\text{min}}^o$$

(7)

where $R$ is the gas constant, $T$ is the temperature in Kelvin, and $a$, $\gamma$, $m$ are the activity, activity coefficient, and molality of the subscripted species, respectively.

Minerals composed of the major rock-forming oxides typically have low solubility in pure water solutions. We can, therefore, usually use the Debye-Hückel limiting law for charged dissolved species (Debye and
Hückel, 1923) to estimate the decrease in $\gamma_{A-aq}$ due to long range electrostatic interactions:

$$\log \gamma_{A-aq} = -A_z Z_{A-aq}^2 \Gamma^{1/2}$$  \hspace{1cm} (8)

where $A_z = 1.8248 \times 10^6 \rho_{H_2O}^{1/2}/(\varepsilon_{H_2O} T)^{3/2}$ and $Z_{A-aq}$, $\rho_{H_2O}$, and $\varepsilon_{H_2O}$ are the ionic charge of the aqueous species, the density of $H_2O$ in g cm$^{-3}$ and the dielectric constant of $H_2O$, respectively, at the pressure and temperature of interest. $I$, the ionic strength, is summed over all the charged species, $i$, in solution:

$$I = 0.5 \sum m_i Z_i^2.$$

(9)

With the absence of long range electrostatic interactions one can assume $\gamma_{A-aq}$ is unity for uncharged species in these dilute solutions. This is consistent with the analysis of silicate solubility behavior involving the uncharged silica species as a function of silica molality in supercritical aqueous fluids over a wide range of temperature and pressure conditions (Walther and Helgeson, 1977). Therefore, $\Delta G_{A-aq}^o$ can be obtained from solubilities of the pure oxide knowing $\Delta G_{A-aq}^o_{\text{min}}$ and $n$. We can obtain the solution pH from the dissociation constant of $H_2O$ (Quist, 1970; Sweeton, Mesmer, and Baes, 1974; and below) by using the charge balance equation for the solution.

**ELECTROSTATIC PROPERTIES OF $H_2O$**

Because crustal fluids are electrolyte solutions, we want to consider the solution dielectric properties to characterize element stability as a function of composition. The electrostatic force, $F$, between two charged species, $+$ and $-$, from Coulomb's law is:

$$F = \frac{1}{P_0} \left( \frac{Z_+ Z_-}{4\pi \Gamma^2} \right)$$  \hspace{1cm} (10)

where $Z$ is the charge of the subscripted species, $r$ is their distance of separation, and $P_0$ is the permittivity at unit force for unit charge at unit distance in a vacuum. If we replace the vacuum with a dielectric like $H_2O$, a decrease in $F$ occurs because of an increase in the permittivity to a value of $P$. The dielectric constant is then the relative permittivity defined as:

$$\varepsilon = \frac{P}{P_0}$$  \hspace{1cm} (11)

and Coulomb's law becomes:

$$F = \frac{1}{\varepsilon} \left( \frac{Z_+ Z_-}{4\pi \Gamma^2} \right).$$  \hspace{1cm} (12)

In water, it is the alignment of the positive and negative charges of the $H_2O$ dipoles (moment = $1.87 \times 10^{-18}$ e.s.u.) due to coulombic attrac-
tion that causes an opposing electrical field which increases P. This opposing field in H₂O will lower the force acting between charged solute species and, therefore, stabilizes the species in a H₂O solution.

At Earth surface temperatures and pressures, the structure of liquid H₂O can be described by a simple model of a mixture of two species (Davis and Jarzynski, 1972). One is an open tetrahedron of H₂O dipoles hydrogen bonded to four nearest neighbors, and the other a close packed structure with a center molecule surrounded by more than four nearest neighbors and lacking strong hydrogen bonding. The mutual positive interaction of the electrostatic fields generated by the dipole moments in the tetrahedral structure creates an orientation polarization which gives rise in H₂O to a high relative permittivity, that is, dielectric constant, ε_H₂O, of 78.3 at 25°C and 1 bar.

In figure 1 are plotted values of 1/ε for H₂O from 25 to 550°C and at pressures to 5 kb at constant density. The densities were obtained from Helgeson and Kirkham’s (1974a) fit to the data of Burnham, Holloway, and Davis (1969). The values of 1/ε were calculated from the Kirkwood (1939) equation using Pitzer’s (1983) expression for the Kirkwood correlation factor based on the dielectric constants of Heger (1969) to 5 kb and 550°C. As seen in figure 1, 1/ε is nearly a linear function of temperature at constant density. Because H₂O densities have been measured to 10 kb and 1000°C and can be extrapolated to even greater pressures and

![Graph](image)

**Fig. 1.** The inverse of the dielectric constant of H₂O as a function of temperature at the indicated density, ρ, in g/cm³ to 5 kb. For the method of obtaining the dielectric constant, see the text. The solid lines are linear fits to the data.
temperatures, $1/\varepsilon$ can be estimated with some reliability above the measurements of Heger (1969). Note that above the $\mathrm{H}_2\mathrm{O}$ critical temperature, $1/\varepsilon$ increases at constant temperature to an increasing extent as density decreases. These correlations demonstrate why changes in solution density are such a good proxy for changes in $1/\varepsilon$ when electrostatic interactions such as the degree of ion pair formation are analyzed (Marshall and Mesmer, 1984).

**ELECTROSTATIC PROPERTIES OF STRONG ELECTROLYTES**

Introduction of a strong electrolyte causes collapse of the tetrahedral $\mathrm{H}_2\mathrm{O}$ structure due to the coulombic interaction of the charged species with the $\mathrm{H}_2\mathrm{O}$ dipoles. A decrease in orientation polarization and, therefore, dielectric constant results. Generally, as shown by Helgeson, Kirkham, and Flowers (1981), there is a proportionality between $I$ and the inverse of the dielectric constant of a completely dissociated electrolyte (cde) solution, $\varepsilon_{\text{cde}}$:

$$b_{\text{cde}}I = \frac{\varepsilon_{\text{H}_2\text{O}}}{\varepsilon_{\text{cde}}} - 1 \quad (13)$$

where $b_{\text{cde}}$ is a constant that depends on the electrolyte, pressure, and temperature. The reason that $I$ at constant temperature and pressure is a linear function of $1/\varepsilon_{\text{cde}}$ can be related to the fact that $I$ is a charge concentration factor in solution which is directly related to the electrostatic potential of charging the solution, whereas $\varepsilon_{\text{cde}}$ is inversely related to it.

We can consider differences in $\varepsilon_{\text{cde}}$ of different electrolyte solutions with the same anion species at the same concentration by considering the electrolyte's cation radius, $r_{\text{cat}}$, obtained from crystallographic measurements. $1/r_{\text{cat}}$ should be proportional to the relative differences of the electric potential in solution. Therefore, the decrease in the dielectric constant below that of $\varepsilon_{\text{H}_2\text{O}}$ to $\varepsilon_{\text{cde}}$ for different electrolyte solutions of a common anion and concentration should be directly related to $r_{\text{cat}}$. Figure 2A shows this relationship between $\varepsilon_{\text{cde}}$ and $r_{\text{cat}}$ for one molar one-to-one metal-chloride solutions at 25°C. The dashed line is given by:

$$\varepsilon_{\text{cde}} = 5.7r_{\text{cat}} + 60.85 \quad (14)$$

Clearly the smaller the cation radius the greater its surface charge density and therefore its ability to disrupt the orientation polarization of the $\mathrm{H}_2\mathrm{O}$ dipoles and decrease the dielectric constant of the solution. We can calculate $b_{\text{cde}}$ at 25°C and 1 bar for 1:1 electrolyte solutions at 1 molal by combining eqs (13) and (14):

$$b_{\text{cde}} = \frac{78.3}{5.7r_{\text{cat}} + 60.85} - 1 \quad (15)$$

knowing the electrolyte's cation radius. The results plotted for the electrolytes shown in figure 2A are given in figure 2B. While eq (15) is
Fig. 2. The dielectric constant (A) and $b_{cde}$ (B) of the indicated electrolyte solution at 1 molar and 25°C as a function of the cation radius of the electrolyte in angstroms. Data from Pottel (1973) for dielectric constants.
hyperbolic, it is nearly linear in the region of interest. The line in figure 2B is given by:

$$b_{cde} = -0.1r_{cat} + 0.28$$  \hspace{1cm} (16)

Because I and $1/\epsilon_{cde}$ are linearly related, $b_{cde}$ and the coefficient of the Brönsted-type (1922) term, $b_\gamma I$, should also be directly related. $b_\gamma I$ is often added to the Debye-Hückel activity coefficient model to account for short range interactions. The relation between the two is calculated to be:

$$b_{cde} = b_\gamma + 0.115$$  \hspace{1cm} (17)

In figure 3 are shown the Brönsted-type coefficients for chloride electrolytes calculated by Helgeson, Kirkham, and Flowers (1981). The solid line computed from eqs (16) and (17) is given by:

$$b_\gamma = -0.1r_{cat} + 0.165$$  \hspace{1cm} (18)

![Graph showing the relationship between $b_\gamma$ and cation radius.](image)

Fig. 3. Extended term coefficients of the Debye-Hückel equation at 25°C and 1 bar from Helgeson, Kirkham, and Flowers (1981) as a function of cation radius for the indicated chloride electrolyte.
Therefore, the Br"{o}nsted-type extended term coefficients in the Debye-H"{u}ckel equation for chloride electrolytes can be estimated from the cation radius, and the term could be written in terms of changes in $1/\varepsilon_{\text{cd}}$ rather than $1$.

**NON-STANDARD STATE SPECIES PROPERTIES**

Crustal solutions can often contain large concentrations of other species besides $\text{H}_2\text{O}$. In order to calculate the Gibbs free energy of $A$-species in a concentrated solution, $\Delta G_{A\text{-aq}}^\circ$ besides $\Delta G_{A\text{-aq}}^\circ$, the molal Gibbs free energy at infinite dilution with $\text{H}_2\text{O}$, we also require the molal non-standard state Gibbs free energy change as a function of solution composition, $\Delta G_{A\text{-aq}}^\ast$. We will calculate $\Delta G_{A\text{-aq}}^\ast$ by considering separately the effects of changes in the Gibbs free energy of adding charged (electrostatic) species, $\Delta G_{A\text{-aq}}^{\text{el}}$, and uncharged (solvent) species, $\Delta G_{A\text{-aq}}^{\text{sol}}$, to $\text{H}_2\text{O}$ on our $A$-aqueous species so that:

$$
\Delta G_{A\text{-aq}} = \Delta G_{A\text{-aq}}^\circ + \Delta G_{A\text{-aq}}^\ast = \Delta G_{A\text{-aq}}^\circ + \Delta G_{A\text{-aq}}^{\text{sol}} + \Delta G_{A\text{-aq}}^{\text{el}}
$$

Besides $\text{H}_2\text{O}$ dipoles the uncharged species are various associated uncharged ion pairs and dissolved molecular gas species. The charged species are generally dissociated electrolyte species.

To partition the changes in $\Delta G_{A\text{-aq}}^\ast$ between $\Delta G_{A\text{-aq}}^{\text{sol}}$ and $\Delta G_{A\text{-aq}}^{\text{el}}$ we require the speciation at the composition, temperature, and pressure of interest. In order to do this calculation we need to solve a set of $k$ equations for the chemical potential of $k$ unknown components at the specified pressure and temperature in our heterogeneous system by solving a set of Gibbs-Duhem equations for each phase (compare Van Zeggeren and Storey, 1970; Wolery, 1979). We can use solubility, charge, and total element mass constraints. To relate the chemical potentials to solubilities we require the equilibrium constants for the mass action equations for formation of all the aqueous complexes and need to evaluate their non-standard state Gibbs free energy in solution.

In order to solve this set of equations for a heterogeneous equilibrium we will address the calculation of mass action equilibrium constants and non-standard state Gibbs free energy changes of species separately. To relate composition to chemical potential we first consider changes in the energetics of $A$-species when changing the solvent from pure $\text{H}_2\text{O}$ to a solvent mixture containing all the uncharged species. This approach differs from those of Pitzer (1973) and Helgeson, Kirkham, and Flowers (1981) in calculating the thermodynamic effects of neutral species before the electrostatic effects of charged species are considered.

**UNCHARGED AQUEOUS SPECIES**

The effects of uncharged species on the thermodynamics of our system and in particular $A$-aqueous species can be calculated as a change in the dielectric properties in diluting $\text{H}_2\text{O}$ dipoles with other uncharged species in a solvent mixture. In other words, we want to calculate the change in Gibbs free energy of $A$-species from our pure $\text{H}_2\text{O}$ standard state to this solvent mixture of uncharged species.
We can use the Born (1920) equation which gives the change in Gibbs free energy for electrostatic interaction in going from one dielectric state to another. In our case going from our pure H\textsubscript{2}O standard state to that of the uncharged solvent mixture.

\[
\Delta G_{\text{sol}}^{\text{A-aq}} = \frac{N^0 Z_{A-aq}^2 e}{2r_{A-aq}} \left( \frac{1}{\epsilon_{\text{mix}}} - \frac{1}{\epsilon_{\text{H}_2\text{O}}} \right)
\]  

(20)

where N\textsuperscript{0}, Z\textsubscript{A-aq}, e, r\textsubscript{A-aq}, \epsilon_{\text{mix}}, and \epsilon_{\text{H}_2\text{O}} are Avogadro’s number, the ionic charge of A-aq, the electronic charge \((4.803 \times 10^{-10}\text{ e.s.u.})\), the electrostatic radius of A-aq, the dielectric constant of the H\textsubscript{2}O solvent with the uncharged species, and that of pure H\textsubscript{2}O, respectively. Because the dipole moments of neutral ion pairs like NaCl \((9.0 \times 10^{-18}\text{ e.s.u.})\) and KCl \((10.3 \times 10^{-18}\text{ e.s.u.})\) are larger than H\textsubscript{2}O, these species have the tendency to increase the dielectric constant of the solution. In general, at constant composition a greater fraction of neutral ion pairs are formed with increasing temperature. Therefore this effect becomes more important at elevated temperatures.

In H\textsubscript{2}O rich solutions species like CO\textsubscript{2} and CH\textsubscript{4} which possess no dipole moment but only a small polarization due to distortion of their electron configuration have a much lower polarizability than H\textsubscript{2}O. Addition of these gas species to H\textsubscript{2}O decreases the dielectric constant of the solution. These species also become more important at greater crustal depth because increasing temperature causes a decreased immiscibility with H\textsubscript{2}O, and they, therefore, can occur in greater concentration. If we can characterize the changes in the dielectric constant of the solution with these changes in the solvent, we can evaluate changes in their effect on the energetics of A-species through the Born equation.

For the purposes of calculating the change in energetics of A-species on addition of uncharged species; we will consider the solvent as a mixture of H\textsubscript{2}O dipoles with salt dipoles (NaCl uncharged aqueous complex) and molecular gas species. Following the approach of Looyenga (1965) we can obtain the dielectric constant of the mixture by using a truncated Taylor expansion for the volume of mixing on the permittivities of the endmembers: This has been shown to work well for calculating the dielectric properties of mixtures of C\textsubscript{6}H\textsubscript{6} and H\textsubscript{2}O at high pressures and temperatures (Deul, ms). In our case this would be H\textsubscript{2}O and the other uncharged species in solution. For a binary mixture we have:

\[
\epsilon_{\text{mix}} = (\epsilon_{\text{uc}}^{1/3} + V_f (\epsilon_{\text{H}_2\text{O}}^{1/3} - \epsilon_{\text{uc}}^{1/3}))^3
\]

(21)

where \epsilon_{\text{uc}} and \epsilon_{\text{H}_2\text{O}} are the dielectric constant of uncharged (uc) pure associated electrolyte or gas and H\textsubscript{2}O, respectively. \(V_f\) is the volume fraction of H\textsubscript{2}O in the solution. We can use the Kirkwood (1939) equation to calculate the dielectric constant of the endmember fluid species:

\[
\frac{(2\epsilon + 1)(\epsilon - 1)}{9\epsilon} = \frac{4\pi N^0 \rho (\alpha + \mu^2g)}{3M} \left( \frac{3\kappa\Gamma}{3\kappa T} \right)
\]

(22)
where $\rho$ and $M$ are the density and molecular weight of the fluid endmember, respectively, $k$ is Boltzman’s constant, and $T$ is temperature in Kelvin. $\alpha$ and $\mu$ are the molecular polarizability and dipole moment respectively. $g$ is the “Kirkwood orientation factor” accounting for the orientational dipole correlation. For pure H$_2$O we can obtain $g$ from Pitzer’s (1983) formulation:

$$g_{H_2O} = 1 + 2.68\rho_{H_2O} + 6.69\rho_{H_2O}^5 \left( \frac{565}{T} \right)^{0.5} - 1$$

(23)

Shown in table 1 are $\alpha$ and $\mu$ and also $\rho$ at 2 kb and 500°C for H$_2$O and hypothetical pure associated electrolyte and gas fluid phases needed to calculate the pure endmember $\varepsilon$ from the Kirkwood equation. Values of $\alpha$ and $\mu$ were obtained from Böttcher and others (1973).

For molecular gases where $\mu$ equals zero the value of $g$ is not needed. In the case of the associated electrolyte where $\mu$ can be large, we can assume as a first approximation that $g = 1$, which it must as the ideal gas state is approached. The value of $g$ is closely tied to the extent of hydrogen bonding in the fluid and, therefore, decreases as temperature increases. Even in the case of H$_2$O where hydrogen bonding is strong, $g_{H_2O}$ decreases from 5.1 at 25°C and 1 bar to 2.8 at 400°C and 1 kb.

The values of $\rho$ given for NaCl and KCl pure fluid are those of the pure fused salt assuming it is supercooled to the temperature of interest. While this is an approximation, the uncertainties in these values when they are used to calculate $\varepsilon$ from eq (22) are small. The volume fraction of these species is, generally, quite small relative to that of H$_2$O and molecular gases in solution. Therefore, uncertainties will be further minimized when calculating $\varepsilon_{\text{mix}}$ from eq (21). What one surmises is the density of the hypothetical pure electrolyte fluid should be significantly greater than H$_2$O which is consistent with using the pure fused salt densities. The densities of the molecular gases, CH$_4$ and CO$_2$, were computed with the Redlich-Kwong equation; a corresponding states expression of a modified van der Waals type equation (Holloway, 1977).

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\alpha^*$</th>
<th>$\mu^{**}$</th>
<th>$\rho^{***}$</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
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<td>1.87</td>
<td>0.69</td>
<td>14.16</td>
</tr>
<tr>
<td>NaCl</td>
<td>3.24</td>
<td>9.0</td>
<td>1.72</td>
<td>86.09</td>
</tr>
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<td>KCl</td>
<td>4.15</td>
<td>10.3</td>
<td>1.69</td>
<td>86.83</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>2.63</td>
<td>0.0</td>
<td>0.77</td>
<td>1.43</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>2.60</td>
<td>0.0</td>
<td>0.27</td>
<td>1.37</td>
</tr>
</tbody>
</table>

* cm$^3$ × 10$^{24}$ (Böttcher and others, 1973; Johnson, Subbaswamy, and Senatore, 1987).

** e.s.u. × 10$^{19}$ (McClellan, 1970).

*** g/cm$^3$. 

TABLE 1

Polarizability, dipole moment, density, and dielectric constant at 500 °C and 2 kb for pure substance
The computed dielectric constants at 2 kb and 500°C are also given in table 1.

**CHARGED AQUEOUS SPECIES**

Having outlined the approach to obtain the effects of the uncharged species, we now need to consider the long range electrostatic interactions between the charged species in solution. That is, we need to consider the effects of adding charged species to our solvent mixture of neutral species. The Debye-Hückel limiting law gives the interactions of charged species as the charge species concentration changes from an infinitely dilute state:

\[
\Delta G_{A_{aq}}^{el} = -(2.303RT)AZ^2I^{1/2}
\]

where

\[
A = \frac{(1.8248 \times 10^6)\rho_{mix}^{1/2}}{(\epsilon_{mix}T)^{3/2}}.
\]  

(24)

Note that we need to use the mixed solvent density, \(\rho_{mix}\), and its dielectric constant, \(\epsilon_{mix}\), in the analysis and compute molalities and the ionic strength per 1000 g of the solvent mixture. At somewhat higher charged species concentrations we would need to consider the effects of the electrostatic distance of closest approach of oppositely charged species, \(a\). In this case the energetics can be accurately modeled for charged species mole fractions as high as \(2 \times 10^{-3}\). The Debye-Hückel equation then becomes:

\[
\Delta G_{A_{aq}}^{el} = \frac{(2.303RT)AZ^2I^{1/2}}{(1 + Ba^{1/2})} + \Gamma_G
\]

where

\[
B = \frac{50.291 \times 10^8\rho_{mix}^{1/2}}{(\epsilon_{mix}T)^{1/2}} \quad \text{and} \quad \Gamma_G = -2.203RT\log\left(\frac{1 + m^*}{m_{mix}}\right)
\]

(25)

\(\Gamma_G\) is the mole fraction to 1000 g of solvent conversion factor. Charged species total molality is given by \(m^*\), and the moles of mixed solvent in 1000 g is given by \(m_{mix}\). \(\Gamma_G\) becomes important at very high charged species concentrations (compare Helgeson, Kirkham, and Flowers, 1981). Note that \(\rho_{mix}\) and \(\epsilon_{mix}\) need to be similar for all A-aqueous species in this analysis. If the concentration of charged species affects the density or dielectric constant as shown earlier for \(\epsilon_{sde}\) then this must also be accounted for. Also, more recent work has demonstrated the problems with the assumptions used in the Debye-Hückel treatment of charged species thermodynamics (Anderson, 1975). Because at elevated temperatures these assumptions are generally more reasonable, we can use the Debye-Hückel treatment for most analyses.
It is clear from the analysis at 25°C that $a$ is not related to an ion's crystallographic size but to the cation surface charge potential $\omega$:

$$\omega = \frac{Z_{\text{cat}}}{r_{\text{cat}}}$$  \hspace{1cm} (26)

where $Z_{\text{cat}}$ and $r_{\text{cat}}$ are the charge and crystallographic radius of the cation, respectively. Values of $\omega$ determined at 25°C are plotted as a function of $a$ in figure 4 for a number of chloride electrolytes of varying size and charge. One can see that there is a reasonable linear correlation between $a$ and $\omega$, particularly considering $a$ is tabulated to $\pm 0.5\text{Å}$ (Kielland, 1937; Klotz, 1964). To calculate $\Delta G^d_{\text{aq}}$ in mixed electrolyte solutions $a$ should be averaged over all charged species in solution. It then is reasonable to use a Güntelburg (1926) type approach and set $a$ to a constant independent of concentration. Perhaps an arithmetic mean over the various charge types as suggested by Helgeson, Kirkham, and Flowers (1981) would work well. Often a value of a near 4Å is chosen at 25°C when sodium is the dominant cation in solution.

Unfortunately, at elevated temperatures and pressures there are insufficient data available to do a reasonable analysis of the magnitude of $a$. It may be possible to use an arithmetic mean type approximation in mixed electrolytes but it is not clear what values $a$ should take over 25°C. Clearly, values of $a$ must absorb the problems with the assumptions in the

---

**Fig. 4.** Debye-Hückel ion size parameter in angstroms as a function of the cation surface charge potential for the indicated ions. Ion sizes from Kielland (1937) and Klow (1964). The solid line gives the linear least squares fit to the data.
Debye-Hückel model. For instance, recent work with less stringent assumptions decreases the value of $a$ toward a more crystallographic value (Newman, 1989). In our present state of knowledge the Debye-Hückel limiting law or a Güntelburg type approach with $Ba = 1$ in eq (25) is probably a reasonable first order approximation. This is particularly true for mid to lower crustal solutions where uncharged solvent effects usually dominate the non-standard state properties (Fein and Walther, 1989).

**Properties of $\text{H}_2\text{O}$ at Elevated Temperature and Pressure**

Because of greater thermal agitation of $\text{H}_2\text{O}$ dipoles with increasing temperature above 25°C the pseudo-tetrahedral structure in $\text{H}_2\text{O}$ is destroyed as we break more hydrogen bonds. The proportion of close packed structure increases, and $\varepsilon_{\text{H}_2\text{O}}$ therefore decreases. In the region of 50°C the isothermal compressibility and heat capacity of $\text{H}_2\text{O}$ at constant pressure reach a minimum as a function of temperature at 1 bar (Helgeson and Kirkham, 1974a). Generally standard state volumes and heat capacities of electrolytes maximize with increasing temperature between this temperature and 100°C at $\text{H}_2\text{O}$ saturation pressure (Helgeson, Kirkham, and Flowers, 1981). This behavior suggests the concentration of tetrahedral structure has decreased significantly with increasing temperature, and hydrogen bonding effects, while still important, no longer dominate the $\text{H}_2\text{O}$ structure compared to electrostatic effects on $\text{H}_2\text{O}$ dipoles on introduction of charged solute species.

With increasing temperature $\text{H}_2\text{O}$ self-dissociation, $K_{\text{H}_2\text{O}}$ increases due, in part, to the decrease in hydrogen bonding. The dissociation of $\text{H}_2\text{O}$ also increases at constant temperature and pressure with increasing concentration of strong electrolyte. As indicated earlier the presence of charged species in $\text{H}_2\text{O}$ disrupts the tetrahedral structure and, therefore, the extent of hydrogen bonding. Interestingly as indicated in eq (13) the dielectric constant of the solution decreases with addition of electrolyte which should cause $\text{H}^+$ and $\text{OH}^-$ to be more associated. Clearly the disruption of the hydrogen bonding is the greater effect, at least at low values of ionic strength and temperatures below ~250°C (see below).

Shown in figure 5 are electrical conductance measurements of the self-ionization constant of $\text{H}_2\text{O}$ as a function of $I^{1/2}$ in KCl solutions for the indicated temperatures at $\text{H}_2\text{O}$ saturation pressure (Sweeton, Mesmer, and Baes, 1974). The nearly linear increase of $\text{H}_2\text{O}$ ionization constant with $I^{1/2}$ at low ionic strength stems from long range electrostatic interactions as modeled by the Debye-Hückel limiting law as shown by the solid lines. These activity coefficient effects are not accounted for in the $\text{H}_2\text{O}$ ionization constants shown in figure 5. As predicted by the full Debye-Hückel law which includes a parameter of ion-size, the linearity with $I^{1/2}$ fails at higher ionic strength. As to be anticipated, similar experiments with NaCl show the effect on $\text{H}_2\text{O}$ dissociation to be nearly the same. They are, however, somewhat larger at high salt concentration for NaCl than KCl solutions at the same concentration because of its somewhat greater cation surface potential (Busey and Mesmer, 1978).
For pure $\text{H}_2\text{O}$ at pressures and temperatures above the Joule-Kelvin inversion curve where $(dP/dT)_\text{AH}$ is positive (~250°C at saturation pressure) and the maximum in $\text{H}_2\text{O}$ dissociation as a function of temperature (~220°C at saturation pressure), electrostatic interactions should dominate the thermodynamic properties.

Shown in figure 6 are the electrical conduction measurements of $K_{\text{H}_2\text{O}}$ (Quist, 1970; Sweeton, Mesmer, and Baes, 1974) plotted against $1/\epsilon T$ at constant pressure. From the electrostatic theory of ion pair formation $\log K$ of dissociation should be a linear function of $1/\epsilon T$ (Denison and Ramsey, 1955). Note that at low values of $1/\epsilon T$ the effects of hydrogen bonding apparently dominate, but at values of $1/\epsilon T$ above about $8 \times 10^{-5} \degree \text{K}^{-1}$ in pure $\text{H}_2\text{O}$ an electrostatic model seems effective. This is at temperatures greater than about 275°C at $\text{H}_2\text{O}$ saturation, but not until 350°C at 1 kb or 650°C at 5 kb. In fact at 5 kb the data are all at values of $1/\epsilon T$ below $8 \times 10^{-5} \degree \text{K}^{-1}$, and, therefore, $\log K_{\text{H}_2\text{O}}$ has yet to maximize as a function of $1/\epsilon T$ as is indicated by the data at lower pressures. One, however, can reasonably use an electrostatic model to calculate the degree of ion pair formation when $1/\epsilon T$ is greater than $8 \times 10^{-5} \degree \text{K}^{-1}$. Note at values of $1/\epsilon T$ greater than $8 \times 10^{-5} \degree \text{K}^{-1}$, $\log K_{\text{H}_2\text{O}}$ decreases with increasing $1/\epsilon T$ to a greater extent at constant increasing pressure. This implies the projections of the linear trends at constant pressure would cross as $1/\epsilon T$ increases. Thus, $\log K_{\text{H}_2\text{O}}$ changes from
Fig. 6. Log K of the self-dissociation constant of H$_2$O plotted against the inverse of the dielectric constant times temperature in K. Values labeled in kb from Quist (1970) interpolated to constant pressure from constant density measurements. Values at H$_2$O saturation labeled Sat from Sweeton, Mesmer, and Baes (1974). Lines connect values at constant pressure, and the arrows show the predicted behavior as 1/εT increases.

increasing to decreasing with increasing pressure at constant 1/εT at large values of 1/εT. This behavior occurs at quite high temperatures. H$_2$O dissociation at 2 kb would be less than that at 1 kb when temperatures were about 800°C. Interestingly, the log of the dissociation constant of strong electrolytes at supercritical conditions displays a similar linear dependence on 1/εT at constant pressure but shows this crossing behavior at much lower values of 1/εT, that is, temperature (Brady and Walther, 1990).

**SPECIES ASSOCIATION**

With the decrease of ε$_{H_2O}$ with increasing temperature the force of coulombic attraction between oppositely charged solute particles increases. Electrolytes become more associated. As described by Brady and Walther (1990) the extent of association in infinitely dilute supercritical H$_2$O solutions for hard cations like the alkalis and alkaline earths and ligands like Cl$^-$, OH$^-$, F$^-$, and HCO$_3^-$ (Pearson, 1963) can be modeled with a Gilkerson-Fuoss type equation (Gilkerson, 1970). The equilibrium constant of the ith ion pair association reaction, $K_{i}$ assoc, is given by:

$$\log K_{i}^{\text{assoc}} = -2.60 + 3 \log d_i + \frac{72800Z_+Z_-}{T\varepsilon d_i} + \frac{\Delta S_i}{2.303R}$$

(27)
where \(d_i, Z_+, Z_-, \epsilon, \Delta S_i, \) and \(R\) are the center to center distance of the \(i\)th pair in angstroms, the ionic charge on the positive and negative species, the dielectric constant of the solution, the entropy of specific solvation of the pair, and the gas constant, respectively. Brady and Walther also showed that \(d_i\) and \(\Delta S_i\) can be considered to be independent of temperature, thus \(\log K^\text{assoc}\) at constant pressure is a linear function of \(\epsilon T^{-1}\). Additionally they demonstrated how \(d_i\) and \(\Delta S_i\) could be estimated as a function of pressure from the surface charge potential of the complex. That is from:

\[
\frac{Z_+Z_-}{d_i}
\]

(28)

where \(Z\) is the charge of the subscripted species, and \(d_i\) is the sum of the atomic radii of the ion pair.

**CONCLUDING REMARKS**

What is advocated in this contribution is that the thermodynamic properties of solutes in complex crustal fluids at elevated temperatures and pressures can be estimated from standard state properties at infinite dilution in pure H\(_2\)O through solubility experiments. Considering the electrostatic interactions in the solution, a model based on the Born equation can then be used to calculate the change in the solvent due to all the neutral species in solution. Changes in the thermodynamic properties because of the charged nature of the species from this solvent mixture, that is, the effects of long range electrostatic interaction can be obtained using a Debye-Hückel type model knowing the density and dielectric constant of the solvent.

The effects of association of charged species to form lower charged complexes can be determined using a Gilkerson-Fuoss type equation. This is needed to help determine the concentration and nature of the potentially large number of different charged species in solution.

Unfortunately there are only a limited number of thermodynamic measurements at temperatures and pressures above the critical point of H\(_2\)O. We will need to make measurements to obtain algorithms for determining the Debye-Hückel electrostatic size parameter, Born radii, and the dielectric properties of solvent mixtures. At \(1/\epsilon T\) below about \(8 \times 10^{-5} \, \text{°K}^{-1}\), which is less than 275°C at H\(_2\)O saturation pressure, we need to incorporate the effects of hydrogen bonding on our solvent. Also for elements like the transition metals covalent bonding effects need to be considered.

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