Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of inorganic neutral species

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Abstract—Consideration of interactions between neutral aqueous species and H2O dipoles in terms of effective Born coefficients permits extension of the revised HKF (HELGESON, KIRKHAM and FLOWERS, 1981) equations of state (TANGER and HELGESON, 1988) for the standard partial molal properties of ionic species at high pressures and temperatures to include inorganic gases, acids, and other neutral aqueous species. Correlation algorithms similar to those used to estimate equation of state parameters for ions and electrolytes (SHOCK and HELGESON, 1988) have also been developed for neutral aqueous species. Calculation of the standard partial molal thermodynamic properties of dissolved inorganic gases as well as other neutral aqueous species as a function of pressure and temperature indicates that the standard partial molal volume (\( \overline{V}^0 \)), heat capacity (\( C_P^0 \)), and entropy (\( S^0 \)), together with the apparent standard partial molal enthalpy of formation (\( \Delta H^0 \)) of many of these species in the liquid phase minimize with increasing temperature at \( P_{\text{SAT}}^* \) and approach \( \infty \) at the critical point of H2O. In the case of other neutral aqueous species such as SiO2(aq), \( V^0 \), \( C_P^0 \), \( S^0 \), and \( \Delta H^0 \) behave as functions of temperature and pressure like those of electrolytes in the liquid phase and maximize with increasing temperature at \( P_{\text{SAT}}^* \), approaching \(-\infty \) at the critical point of H2O. Which of these types of behavior is exhibited by \( V^0 \), \( C_P^0 \), \( S^0 \), and \( \Delta H^0 \) for a given neutral aqueous species depends in part on the relative volatility of the aqueous species and the effect of the species on solvent dipole-dipole interaction. Close agreement between predicted and experimentally determined equilibrium constants for gas solubility and inorganic acid dissociation reactions at high temperatures and pressures supports the validity and generality of the equations of state and the predictive algorithms. High temperature/pressure equilibrium constants can be predicted for reactions involving a wide variety of neutral aqueous species for which few or no experimental data are available at temperatures > 25°C. Present capabilities permit such predictions to be made for hydrothermal and magmatic conditions at pressures and temperatures to 5 kb and 1000°C.

INTRODUCTION

Mineral stabilities in weathering, hydrothermal, and metamorphic processes are commonly influenced by dissolved gases such as CO2 and H2S, which react with H2O to form acids. These acids and their dissociation products have a profound effect on mineral hydrolysis. The accuracy of radiogenic age dating techniques involving noble gases depends on the degree to which the noble gas has been retained in the rock, which in hydrothermal systems depends in turn on the solubility of the gas in the aqueous phase, the degree of diffusional transfer of the dissolved gas molecules, and the extent to which the fluid flows through the system. Calculation of the chemical consequences of fluid/rock interaction thus requires thermodynamic data for both dissolved gases and acid dissociation reactions.

The solubility of a gas and its subsequent dissociation can be represented by reactions like

\[
\text{H}_2\text{S}_{(v)} = \text{H}_2\text{S}_{(aq)} \tag{1}
\]

and

\[
\text{H}_2\text{S}_{(aq)} = \text{HS}^- + \text{H}^+ , \tag{2}
\]

respectively, where the subscripts (v) and (aq) refer to the vapor and aqueous phases. Numerous methods have been proposed to calculate the high temperature and pressure thermodynamic properties of acid dissociation reactions (HELGESON, 1967, 1969; LINDSAY, 1980; MURRAY and COBBLE, 1980; SMITH et al., 1986) and gas solubility reactions (VALENTINER, 1927; BUTLER, 1937; ELEY, 1939a,b; FRANK and EVANS, 1945; GLEW and MOELWYN-HUGHES, 1953; MORRISON and JOHNSTONE, 1954; HIMMELBLAU, 1959; WAUCOPE and HAQUE, 1972; HAYDUK and LAUDIE, 1973; PIEROTTI, 1976; BENSON and KRAUSE, 1976; WILHELM et al., 1977; WEISENBERG and GUINASSO, 1979; CLEVER and HAN, 1980; SCHULZE and PRAUSNITZ, 1981; CROVETTO et al., 1982b; BIGGERSTAFF, 1986). Some of these constitute little more than polynomial fits to experimental data, but others are based on attempts to describe interactions among solute species and the surrounding H2O dipoles. Although the latter approach possesses greater predictive capabilities than the others, most of the equations that have been proposed to describe these interactions as a function of pressure and/or temperature cannot be used to predict with confidence the temperature and pressure dependence of the standard partial molal heat capacities and volumes of neutral aqueous species at high temperatures and pressures. Such is not the case with the revised HKF (HELGESON, KIRKHAM and FLOWERS, 1981) equations of state proposed by TANGER and
HELGESON (1988), which can be used to calculate the standard partial molal thermodynamic properties of aqueous species at pressures and temperatures to 5 kb and 1000°C (SHOCK et al., 1989). Furthermore, correlation algorithms can be used to estimate species-dependent equation of state parameters for aqueous species for which experimental data are available only at 25°C (SHOCK and HELGESON, 1988). The purpose of the present communication is to describe application of the revised HKF equations of state and correlation algorithms to calculation of the thermodynamic properties of neutral inorganic aqueous species at supercritical temperatures and pressures.

CONVENTIONS, UNITS, AND STANDARD STATES FOR NEUTRAL SPECIES

Gas solubilities are commonly expressed in terms of Henry's law constants ($k_H$) given by

$$k_H = \frac{f_{j(v)}}{X_{j(aq)}} = \frac{X_{j(v)}P_{j(v)}}{X_{j(aq)}}$$

where $X_{j(aq)}$ stands for the mole fraction of the $j$th aqueous species and $f_{j(v)}$, $X_{j(v)}$ and $P_{j(v)}$ correspond to the fugacity, fugacity coefficient and partial pressure of the $j$th species in the vapor phase. The Henry's law constant corresponds to the product of the rational activity coefficient of the dissolved gas ($\lambda_{j(aq)}$) and the equilibrium constant for a reaction of the form

$$A_{j(aq)} = A_{j(v)}$$

where $A_{j(v)}$ and $A_{j(aq)}$ represent symbolically a gas molecule in the vapor and aqueous phase, respectively. The equilibrium constant ($K$) for reaction (4) can thus be expressed as

$$K = \frac{k_H}{\lambda_{j(aq)}} = \frac{P_{j(v)}}{X_{j(aq)}\lambda_{j(aq)}}$$

which corresponds to the reciprocal of the equilibrium constant for

$$A_{j(v)} = A_{j(aq)}$$

where $a_{j(aq)}$ refers to the activity of the $j$th aqueous species. The molal analog of Eqn. (5) for reaction (6) is given by

$$K = \frac{k_H}{\lambda_{j(aq)}} = \frac{f_{j(v)}}{a_{j(aq)}}$$

Table 1. Summary of equations used to convert experimental gas solubility measurements to the standard state adopted in the present study.

<table>
<thead>
<tr>
<th>Henry's Law Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_H = 55.51$ for $k_H$ in bars,</td>
</tr>
<tr>
<td>$k_H = 54.78$ for $k_H$ in atmospheres,</td>
</tr>
<tr>
<td>$k_H = 3.4007 \times 10^{-2}$ for $k_H$ in mm of Hg</td>
</tr>
</tbody>
</table>

The units referred to by Drummond (1981) as Henry's Law Constant is not equivalent to $k_H$ defined by Eqn (3) because molal units are used rather than the mole fraction of the dissolved gas. Accordingly, the relation between Drummond's solubility constant ($k_D$) and $K$ is given by

$$K = \frac{k_D}{k_H}$$

<table>
<thead>
<tr>
<th>Bunsen Absorption Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta = \frac{600 - P_s}{600}$,</td>
</tr>
<tr>
<td>$\kappa_s = \frac{RT\rho}{LM_s} - P$,</td>
</tr>
</tbody>
</table>

where $\rho_s$ and $M_s$ refer to the density and molecular weight of the solvent, respectively, $T$, and $P_s$ stand for the reference temperature and pressure, and $R$ designates the gas constant in the units appropriate to the choice of $T$, and $P_s$, and the units used to express $\alpha$. Although not the case in the present study, the second term on the right side of Eqn. (13) is often neglected. Relations between $\kappa$ and $\beta$ may be obtained by substituting Eqn. (13) into Eqs. (A), (B), or (C), depending on the units in which the Bunsen absorption coefficients are reported.

<table>
<thead>
<tr>
<th>Oswald Coefficient</th>
</tr>
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<tbody>
<tr>
<td>$L = \frac{T}{T}$,</td>
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</table>

where $T$ refers to the temperature of the measurement. Substituting Eqs. (13) into Eqn. (14) yields

$$\kappa = \frac{RT\rho_s}{LM_s} - P$$

which can be substituted into Eqs. (A), (B), or (C) to obtain values of $K$ for various units of $L$ and $P$, using appropriate values of $R$.

<table>
<thead>
<tr>
<th>Standard Cubic Feet per Barrel</th>
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| These units are often used to express the solubility of various natural gas components. The conversion factor from standard cubic feet per barrel to mole fraction is $1.311 \times 10^{-3}$ (Price, 1979), and the conversion factor to molality is $7.278 \times 10^{-3}$.

Values of molality obtained in this manner were used together with Eqn. (13) to generate values of $K$ for use in the present study by Shock and Helgeson (1989).
where $\gamma_j^{(\text{aq})}$ and $m_j^{(\text{aq})}$ stand for the molal activity coefficient and molality of the $j$th species in the aqueous phase and $K$ denotes the equilibrium constant for reaction (6).

Because the standard state for aqueous species adopted in the present study calls for unit activity of the solute in a hypothetical 1 molal solution referenced to infinite dilution, rational equilibrium constants computed from Henry’s law constants were converted to their molal counterparts using the relevant equations shown in Table 1. Conversion factors for Bunsen coefficients, Ostwald coefficients and other expressions of gas solubility found in the literature are also given in Table 1. Fugacity coefficients for the pure gases were calculated from the modified Redlich-Kwong equation of state using coefficients given by Holloway (1977).

Let us now review the revised HKF equations of state for ions and electrolytes, which are extended below to include neutral aqueous species.

**SUMMARY OF THE REVISED HKF EQUATIONS OF STATE FOR IONS AND ELECTROLYTES**

All standard partial molal properties of electrolytes and ions are considered in the revised HKF model to be sums of structural and solvation contributions. The revised HKF equations for the standard partial molal volume ($\bar{V}^0$), heat capacity ($\bar{C}_p^0$) and entropy ($\bar{S}^0$), together with the apparent standard partial molal enthalpy ($\bar{H}_p^0$) and Gibbs free energy of formation ($\bar{G}_f^0$), are given by (Tanger and Helgeson, 1988)

$$
\bar{V}^0 = \Delta \bar{V}_p^0 + \Delta \bar{V}_s^0
$$

$$
= a_1 + \frac{a_2}{\Psi + P} + \frac{a_3}{\Psi + P} \left( \frac{1}{T - \Theta} \right) - a_4 \ln \left( \frac{\Psi + P}{\Psi + P} \right)
$$

$$
\bar{C}_p^0 = \Delta \bar{C}_p^0 + \Delta \bar{C}_p^s
$$

$$
= c_1 + \frac{c_2}{(T - \Theta)^2} - \frac{2T - \Theta}{(T - \Theta)^3} \left( \frac{a_3}{P - P_r} \right) + a_4 \ln \left( \frac{\Psi + P}{\Psi + P} \right) + a_5 \ln \left( \frac{T}{T - \Theta} \right)
$$

$$
\bar{S}^0 = \Delta \bar{S}_s^0 + \Delta \bar{S}_s^0
$$

$$
= S_{p,T}^0 + c_1 \ln \left( \frac{T}{T_r} \right) - \frac{c_1}{\Theta \left( \frac{1}{T - \Theta} \right)} + \frac{a_5 \ln \left( \frac{T_r(T - \Theta)}{T_r(T - \Theta)} \right)}{a_5 \ln \left( \frac{T_r(T - \Theta)}{T_r(T - \Theta)} \right)}
$$

$$
\Delta \bar{H}_p^0 = \Delta \bar{H}_p^s + \left( \bar{H}_{p,T}^0 - \bar{H}_{p,T_r}^0 \right)
$$

$$
= \Delta \bar{H}_p^s + c_1 \left( T - T_r \right) - c_2 \left[ \left( \frac{1}{T - \Theta} \right) \right] + a_1 \left( T - T_r \right) + a_2 \ln \left( \frac{\Psi + P}{\Psi + P} \right)
$$

$$
\Delta \bar{G}_f^0 = \Delta \bar{G}_f^s + \left( \bar{G}_{f,T}^0 - \bar{G}_{f,T_r}^0 \right)
$$

$$
= \Delta \bar{G}_f^s + c_1 \left( T - T_r \right) - c_2 \left[ \left( \frac{1}{T - \Theta} \right) \right] - a_1 \left( T - T_r \right) - a_2 \ln \left( \frac{\Psi + P}{\Psi + P} \right)
$$

where $\Delta \bar{V}_p^0$, $\Delta \bar{C}_p^s$, and $\Delta \bar{S}_s^0$ stand for the nonsolvation (or structural) contributions to $\bar{V}^0$, $\bar{C}_p^0$, and $\bar{S}^0$, respectively, $\Delta \bar{H}_p^s$, $\Delta \bar{C}_p^s$, and $\Delta \bar{S}_s^0$ represent the solvation contributions to $\bar{V}^0$, $\bar{C}_p^0$, and $\bar{S}^0$, $a$, $c$, $a_1$, $a_2$, $a_3$, $a_4$, $c_1$, and $c_2$ represent species-dependent nonsolvation parameters, $T_r$, $P_r$, $T$, and $P$ designate the reference temperature of 298.15 K, the reference pressure of 1 bar, and the temperature and pressure of interest, respectively, $\Delta \bar{H}_p^0$ and $\Delta \bar{G}_f^0$ denote the standard partial molal enthalpy and Gibbs free energy of formation from the elements in their stable form at $P$ and $T$, and those at $P_r$, $T_r$, $\epsilon$ stands for the dielectric constant of H2O, $\Psi$ and $\Theta$ refer to solvent parameters equal to 2600 bars and 228 K, respectively, $Q$, $X$, and $Y$ denote Born functions given by

$$
Q = \frac{1}{\epsilon} \left( \frac{\Psi + P}{\Psi + P} \right)
$$

(13)
X = \frac{1}{\epsilon} \left( \left( \frac{\partial^2 \ln \epsilon}{\partial T^2} \right)_T - \left( \frac{\partial \ln \epsilon}{\partial T} \right)_p \right), \quad (14)

and

Y = \frac{1}{\epsilon} \left( \frac{\partial \ln \epsilon}{\partial T} \right)_p, \quad (15)

and \omega stands for the conventional Born coefficient, which is defined for the jth aqueous species by

\omega_j = \omega_j^{\text{Born}} - Z_j \omega_j^{\text{intr}} \quad (16)

where Z_j stands for the formal charge on the jth aqueous species, \omega_j^{\text{Born}} refers to the absolute Born coefficient of the hydrogen ion, which is taken to be 0.5387 \times 10^-3 cal mol^-1 at 25°C and 1 bar (Helgeson and Kirkham, 1976), and \omega_j^{\text{intr}} designates the absolute Born coefficient of the jth species given by

\omega_j^{\text{intr}} = \frac{N^0 \rho J^2 z_j^2}{2 k_i} = \frac{n z_j^2}{r_{e,j}} \quad (17)

where \(N^0\) represents Avogadro’s number (6.02252 \times 10^{23} \text{ mol}^-1), \rho stands for the absolute electronic charge (4.80289 \times 10^{-10} \text{ esu}), \eta = 1.66027 \times 10^{-3} \text{ A cal mol}^{-1}, and \(r_{e,j}\) denotes the effective electrostatic radius of the jth species given by

r_{e,j} = r_{x,j} + |Z_j| \Gamma_x \quad (18)

where

\Gamma_x = k_x + g \quad (19)

where \(k_x\) represents a charge-dependent constant equivalent to 0.0 for anions and 0.94 for cations, and \(g\) designates a solvent function of temperature and density. The \(g\) function has been characterized at temperatures up to 450°C by fitting orthogonal temperature-density polynomials to values of the Born coefficient (\(\omega_j\)) and its partial derivatives computed from fits of Eqs. (8) and (9) to experimentally determined partial molal properties of NaCl (Tanger and Helgeson, 1988). At higher temperatures the \(g\) function is represented by a temperature-density polynomial fit of \(g\) values calculated from Eqn. (12) using apparent standard partial molal Gibbs free energies of formation of NaCl\(\text{OH}\) generated from supercritical dissociation constants (Shock et al., 1989). At low temperatures and pressures the \(g\) function and its partial derivatives approach 0. As a consequence, \(\Gamma_x\), and therefore \(r_{x,j}\), are essentially constant at temperatures below 170°C, and pressures corresponding to the vapor-liquid saturation curve for H$_2$O (\(P_{\text{sat}}\)). \(\Gamma_x\) and \(r_{x,j}\) are also essentially constant at (Shock et al., 1989)

\[ T < 175^\circ \text{C} \text{ if } P \leq 2450 \text{ bars} \quad (20a) \]

and

\[ P > 1.0 \text{ gm cm}^{-2} \text{ if } 2450 \text{ bars} < P \leq 5000 \text{ bars}. \quad (20b) \]

Values of \(\epsilon\) and the Born functions defined by Eqs. (13)-(15) can be obtained for temperatures and pressures to 1000°C and 5 kb from Shock et al. (1989).

**Theoretical Considerations**

In theoretical models of gas solubility, the overall solution process is described by summing two major contributions: 1) a structural term accounting for cavity formation and 2) solute-solvent interactions (Eley, 1939a,b; Frank and Evans, 1945; Himelfbaul, 1959; Riess et al., 1959; Prussottz and Shahe, 1961; Nemethy and Scheraga, 1962a,b; Ben-Naim, 1963, 1965a,b,c, 1975, 1978, 1980, 1987; Ben-Naim and Egel-Thal, 1965; Nemethy, 1967; Wilkinson and Battino, 1971, 1972; Tiefel and Gubbins, 1972; Lucas, 1973, 1976; Neff and McQuarrie, 1973; Stillinger, 1973; Wilkinson, 1973, 1986; Reynolds et al., 1974; Vaucor and Ben-Naim, 1974; de Light and van der Veen, 1975; Terasawa et al., 1975; Benson and Krause, 1976; Franks et al., 1976; Lucas and Bury, 1976; Clark et al., 1977; Lucas and Carlill, 1977; Pratt and Chandler, 1977; Wilkinson et al., 1977; Shinoda, 1977; Denoysers, 1982; Crovetto et al., 1982b; Alvarez et al., 1983; Lee, 1983; Hu et al., 1985; Fernandez-Prini et al., 1985; Pratt, 1985; Fernandez-Prini and Japas, 1980; Muller, 1988). A similar division into structural and solvation contributions forms the basis for the revised HKF model for aqueous electrolytes. The similarities in the concepts on which these approaches are based suggests that the revised HKF equations of state summarized above for aqueous electrolytes can be used to describe the temperature and pressure dependence of the standard partial molal properties of neutral aqueous species. As shown below, predictions of this kind afford highly accurate reproduction of available experimental data for reactions involving these species. Despite the fact that many neutral species have no formal charge, the success of this approach strongly supports theoretical division of contributions to the standard partial molal properties of neutral aqueous species into structural and electrostatic terms. The electrostatic effects arise from the interaction of polar species with solvent dipoles (Kirkwood, 1939), as well as from the effect of both polar and nonpolar species on dipole-dipole interaction in the vicinity of the species. The structural contributions arise primarily from the process of cavity formation.

**Structural contributions**

The concept that a neutral species dissolves in water in part by the formation of a cavity is consistent with the relatively large positive standard partial molal volumes and heat capacities observed for these species at low temperatures, several of which are plotted in Figs. 1 and 2. The symbols in these figures represent experimental measurements taken from the literature, but the curves were generated by regression of the data with equations summarized below. Whether the standard partial molal properties of neutral aqueous species at low temperatures and pressures increase or decrease with increasing temperature depends on the structural consequences of cavity formation, which can be described in terms of the work required to establish and maintain a cavity within the water structure. At low temperatures the size of the cavity tends to increase with increasing temperature, which results in a corresponding increase in the standard partial molal volume. In contrast, the calorimetric consequences of the relative contributions to cavity formation by the intrinsic size and volatility of the neutral species and its hydrophobic effect on the three-dimensional packing arrangement of H$_2$O dipoles may result in either increasing or decreasing standard partial molal heat capacities with increasing temperature at low temperatures. It can be seen in Figs. 1 and 2 that at temperatures less than ~50°C, the standard partial molal volumes of B(OH)$_n$Na$_{n-1}$ and H$_2$S$_{n-1}$ at $P_{\text{sat}}$ all increase with increasing temperature, which is also true of the standard partial molal heat capacity of NH$_4$Cl at $P_{\text{sat}}$. In contrast, the standard partial molal heat capacities of NaCI at 172 bars and H$_2$S$_{n-1}$ at $P_{\text{sat}}$ decrease with increasing temperature at low temperatures (Fig. 2).

Electrostatic contributions to the standard partial molal properties of aqueous species appear to dominate their behavior at high temperatures and low pressures. These contributions are described in the revised HKF model in terms of electrostatic theory consistent with the Born transfer equation. This approach has been extended in the present study to include species with a formal charge of zero that nevertheless behave as though they have a nonzero effective charge arising from the disruptive effect of the species on dipole-dipole interactions and the local dielectric constant of the solvent.
the critical point of $H_2O$ (WHEELER, approach 00 as temperature increases at the density of the solvent is much higher that hydrophobic molecules disrupt the water structure at high temperature. This is apparently not the case at lower temperatures, where static properties of the solvent in terms of a hypothetical species with dipoles and disrupt solvent dipole-dipole interaction. It thus seems water and dilute aqueous solutions of hydrocarbons, which indicate low and of the solvent in the vicinity of the neutral species. This observation the liquid phase approach -or) as temperature increases at $H_2O$. In contrast, ii', pp, so, and $A_{PSAT}$ of aqueous electrolytes in critical region of the system $H_2O$ can be attributed to increasing re-

Electrostatic contributions.

Ample evidence indicates that neutral aqueous species such as alcohols and aqueous silica interact to a significant degree with the solvent in aqueous solution (BUTLER and RAMCHANDANI, 1935; BUTLER and REID, 1935; BUTLER et al., 1935; ELLIS, 1966; FRIEDMAN and KRISHNAN, 1973; FRANKS, 1973, 1975; MALININ, 1974; WALTHER and HELGESON, 1977; ABRAHAM, 1979; BEN-NAIM, 1980; PRATT, 1985; SCHOTT and DANDURAND, 1987; DANDURAND and SCHOTT, 1987). It can be seen in Fig. 2 that the high-temperature standard partial molal heat capacity of aqueous argon at 172 bars (BIGGERSTAFF and WOOD, 1988a) increases to an increasing degree with increasing temperature above $-100°C$. Recent experimental evidence (BIGGERSTAFF and WOOD, 1985b; GATFIS 1972; HELGESON and KIRKHAM, 1977; COBBLE and MURRAY, 1976; BEN-NAIM, 1980; RAMCHANDANI, 1935; ELLIS, 1966; FRIEDMAN and KRISHNAN, 1973; FRANKS, 1973, 1975; MALININ, 1974; WALTHER and HELGESON, 1977; ABRAHAM, 1979; BEN-NAIM, 1980; PRATT, 1985; SCHOTT and DANDURAND, 1987; DANDURAND and SCHOTT, 1987). The latter behavior is consistent with MULLER'S (1988) recent model calculations for the effective Born coefficients of neutral aqueous molecules as a function of temperature at $P_{SAT}$. The symbols represent experimental data taken from the sources shown in the figure, but the curves were generated from Eqsns. (22) and (25) using parameters given in Table 2.

FIG. 1. Standard partial molal volumes ($\bar{P}$) of inorganic neutral aqueous species as a function of temperature at $P_{SAT}$. The symbols represent experimental data taken from the sources shown in the figure, but the curves were generated from Eqsns. (22) and (25) using parameters given in Table 2.

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Taking account of Eqsns. (16) and (17), the effective Born coefficient of the $j$th neutral aqueous species ($\omega_{n,j}$) is defined by

$$\omega_{n,j} = \frac{Z_{e,j}^2}{r_{e,j}}$$

(21)

where $Z_{e,j}$ and $r_{e,j}$ refer to the effective charge and effective electrostatic radius of the $j$th neutral species, respectively (HELGESON et al., 1981). At present, values of $Z_{e,j}$ and $r_{e,j}$ for neutral aqueous species cannot be assessed with confidence, which precludes independent calculation of $\omega_{n,j}$ from Eqn. (21). However, values of $\omega_{n,j}$ can be obtained by regression of experimental data or calculated from correlation algorithms (see below).

Because the magnitude of the second term on the right side of Eqn. (18) depends on the formal charge of the $j$th aqueous species, the assumption was made in the present study that the effective Born coefficients of neutral aqueous species can be regarded in a first approximation as pressure/temperature-independent parameters. It follows from the revised HKF model that the solvation contributions to the standard partial molal volumes, heat capacities and entropies of neutral aqueous species are then given by

$$\Delta V_s^0 = V^0 - \Delta V_n^0 = -\omega_Q Q$$

(22)

$$\Delta C_{PSAT}^0 = C_P^0 - \Delta C_{PSAT}^0 = \omega_Q X$$

(23)

$$\Delta S_{s}^0 = S^0 - \Delta S_{s}^0 = \omega_Y Y$$

(24)

where $Q$, $X$, and $Y$ stand for Born functions defined by Eqsns.

FIG. 2. Standard partial molal heat capacities ($C_P^0$) of inorganic neutral aqueous species as a function of temperature at $P_{SAT}$, or in the case of $Ar_{PSAT}$ at $172$ bars. The symbols represent experimental data taken from the sources shown in the figure, but the curves were generated from Eqsns. (23) and (26) using parameters given in Table 2.
The temperature dependence of $\Delta P_n^0$ can be expressed as

$$\Delta P_n^0 = \sigma + \xi \left( \frac{1}{T - \Theta} \right)$$

(25)

where

$$\sigma = a_1 + a_2 \left( \frac{1}{\Psi + P} \right)$$

(25a)

and

$$\xi = a_3 + a_4 \left( \frac{1}{\Psi + P} \right)$$

(25b)

and that of $\Delta C_{p,n}^0$ at $P = P_r$ as

$$\Delta C_{p,n}^0 = c_1 + c_2 \left( \frac{1}{T - \Theta} \right)^2$$

(26)

Equations (25) and (26) can also be used together with values of $\sigma$ and $\xi$ for $P = P_r$ to represent closely the nonsolvation standard partial molar volumes and heat capacities of neutral aqueous species as a function of temperature at $P_{sat}$ to ~200°C, where the vapor pressure of H$_2$O is only 15.537 bars (HAAK et al., 1984). Complete expressions of the temperature and pressure dependence of the standard partial molar volumes and heat capacities of neutral species analogous to Eqs. (8) and (9) are given by

$$\theta^0 = a_1 + a_2 \left( \frac{1}{\Psi + P} \right)$$

$$+ \left( a_3 + a_4 \left( \frac{1}{\Psi + P} \right) \right) \left( \frac{1}{T - \Theta} \right) - \omega_0 Q$$

(27)

and

$$\tilde{C}_p^0 = c_1 + c_2 \left( \frac{1}{T - \Theta} \right)^2$$

$$\times \left( \frac{2T \left( \frac{1}{T - \Theta} \right)^3}{\left( 1 - \frac{1}{T - \Theta} \right)^2} \right)$$

$$\times \left( \frac{1}{T - \Theta} \right)$$

(28)

Integration of Eqn. (28) with respect to temperature results in

$$S^0 = S_{p,n, T}^0 + c_1 \ln \left( \frac{T}{T_r} \right) - c_2 \left( \frac{1}{T - \Theta} \right) - \left( \frac{1}{T_r - \Theta} \right)$$

$$\frac{1}{\Theta} \ln \left( \frac{T_r (T - \Theta)}{T_r (T_r - \Theta)} \right) + \left( \frac{1}{T - \Theta} \right)^2$$

$$\times \left[ \frac{a_3 (P - P_r) + a_4 \ln \left( \frac{\Psi + P}{\Psi + P_r} \right) + \omega_0 (Y - Y_{p,n,T})}{T - \Theta} \right]$$

(29)

Expressions analogous to Eqs. (11) and (12) for the apparent standard partial molar enthalpy and Gibbs free energy of formation can now be written as

$$\Delta H^0_n = \Delta H^0_{p,n} + (\tilde{H}_{p,n}^0 - \tilde{H}_{p,n}^0)$$

$$= \Delta H^0_{p,n} + c_1 (T - T_r) - c_2 \left( \frac{1}{T - \Theta} \right) - \left( \frac{1}{T_r - \Theta} \right)$$

where

$$\Delta H^0_{p,n} = a_1 (P - P_r) + a_2 \ln \left( \frac{\Psi + P}{\Psi + P_r} \right)$$

$$+ \left( \frac{2T - \Theta}{(T - \Theta)^2} \right) \left( \frac{a_3 (P - P_r) + a_4 \ln \left( \frac{\Psi + P}{\Psi + P_r} \right) + \omega_0 \left( T Y_{p,n,T} - T_r Y_{p,n,T} \right)}{T - \Theta} \right)$$

$$= \left( \frac{T - \Theta}{(T - \Theta)^2} \right) \left( \frac{a_3 (P - P_r) + a_4 \ln \left( \frac{\Psi + P}{\Psi + P_r} \right) + \omega_0 \left( T Y_{p,n,T} - T_r Y_{p,n,T} \right)}{T - \Theta} \right)$$

$$+ \left( \frac{1}{\epsilon_{p,n,T}} - 1 \right)$$

(30)

and

$$\Delta G^0_n = \Delta G^0_{p,n} + (\tilde{G}_{p,n}^0 - \tilde{G}_{p,n}^0)$$

$$= \Delta G^0_{p,n} - S_{p,n,T}^0 (T - T_r) \ln \left( \frac{T_r}{T} \right) - T_r$$

$$\frac{T}{\Theta} \ln \left( \frac{T_r (T - \Theta)}{T_r (T_r - \Theta)} \right) + \left( \frac{1}{T - \Theta} \right) \left( \frac{a_3 (P - P_r) + a_4 \ln \left( \frac{\Psi + P}{\Psi + P_r} \right) + \omega_0 (Y - Y_{p,n,T})}{T - \Theta} \right)$$

$$+ \left( \frac{1}{\epsilon_{p,n,T}} - 1 \right)$$

(31)

REGRESSION OF EXPERIMENTAL DATA

The experimentally determined isobaric standard partial molar heat capacities of aqueous argon represented by the symbols in Fig. 2 were regressed in the present study with Eqs. (23) and (26) to obtain the $c_1$, $c_2$ and $\omega_0$ parameters for Ar$_{sat}$ given in Table 2. The results of these regression calculations are represented by the curve shown in Fig. 2. The value of $\omega_{ar} (-0.3073 \times 10^4$ cal mol$^{-1}$) is opposite in sign but similar in magnitude to that of $\omega_{p,n} (0.3306 \times 10^4$ cal mol$^{-1}$) given by SHOCK and HELGESON (1988). This observation is consistent with the relatively high volatility of dissolved argon, which repels the surrounding H$_2$O dipoles and disrupts their interaction in the vicinity of the argon molecule. In contrast, the attractive forces characteristic of Na$^+$ solvation lead to the positive value of $\omega_{p,n}$.

Table 2. Summary of equations of state parameters generated by regression of nonsolvent contributions to the standard partial molar volumes and heat capacities of neutral aqueous Ar species as a function of temperature at 1 bar with Eqs. (25) and (26).

<table>
<thead>
<tr>
<th>Species</th>
<th>$c_1 \times 10^{12}$</th>
<th>$c_2 \times 10^{12}$</th>
<th>$\epsilon_{p,n,T}$</th>
<th>$\omega_{p,n} \times 10^{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$<em>2$S$</em>{sat}$</td>
<td>32.3</td>
<td>4.73</td>
<td>38.13</td>
<td>2.37</td>
</tr>
<tr>
<td>N$<em>2$S$</em>{sat}$</td>
<td>20.3</td>
<td>-1.17</td>
<td>25.8</td>
<td>-0.98</td>
</tr>
<tr>
<td>Ar$_{sat}$</td>
<td>35.65</td>
<td>7.316</td>
<td>43.8</td>
<td>-0.3073</td>
</tr>
<tr>
<td>BOH$_{sat}$</td>
<td>-3.2</td>
<td>3.5</td>
<td>-0.2</td>
<td>-0.3073</td>
</tr>
</tbody>
</table>

a. Cal mol$^{-1}$ K$^{-1}$. b. Cal K mol$^{-1}$. c. Cm$^{-1}$ mol$^{-1}$. d. Cm$^2$ K mol$^{-1}$. e. Cal mol$^{-1}$. 

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Summary of equations of state parameters generated by regression of nonsolvent contributions to the standard partial molar volumes and heat capacities of neutral aqueous Ar species as a function of temperature at 1 bar with Eqs. (25) and (26).
As emphasized above, the electrostatic contributions to the standard partial molal properties of aqueous species become dominant at high temperatures. Of the experimentally determined standard partial molal properties of neutral aqueous species depicted in Figs. 1 and 2, only the heat capacity data for aqueous argon extend to high enough temperatures (>250°C) for these effects to be discernible. In contrast, experimental equilibrium constants (K) for solubility and dissociation reactions involving neutral aqueous species have been reported over wide ranges of high temperature and pressure, extending well into the supercritical region of the system H2O. These data can be regressed simultaneously with experimental standard partial molar volumes and heat capacities at low temperatures like those shown in Figs. 1 and 2 to obtain equation of state parameters for the neutral species by taking account of Eqn. (31) and the relation

$$\log K = \frac{-\Delta G^0}{2.303 RT}$$

where \( K \) stands for the gas constant (1.98719 cal mol\(^{-1}\) K\(^{-1}\)) and \( \Delta G^0 \) denotes the standard partial molar Gibbs free energy of the \( r \)th reaction given by

$$\Delta G^0_r = \sum r_i \Delta G^0$$

where \( r_i \) stands for the reaction coefficient of the \( i \)th species in the reaction, which is positive for products and negative for reactants.

Experimental equilibrium constants for reactions involving \( \text{NH}_3(aq) \) and \( \text{H}_2\text{S}(aq) \) at temperatures and pressures along the vapor-liquid saturation curve for \( \text{H}_2\text{O} \) have a negligible effect on the apparent standard partial molar Gibbs free energies of formation (\( \Delta G^0 \)) of aqueous species at temperatures \( \leq 350°C \) (HELGESON et al., 1981; TANGER and HELGESON, 1988), the data for \( \text{H}_2\text{O} \) and \( \text{NH}_3(aq) \) shown in Figs. 2 and 3 were regressed with Eqns. (28) and (31)-(33) after setting \( a_1 = a_2 = a_3 = a_4 = 0 \) to obtain the values of \( c_1 \), \( c_2 \) and \( \omega_0 \) given in Table 2. The values of \( \omega_0 \) obtained in this manner were then used to calculate the values of \( \Delta P^0 \) and \( \Delta P^0_\text{a} \) shown in Table 3 from Eqn. (22) using experimental values of \( \bar{P} \) taken from Table 3. The \( \sigma \) and \( \xi \) parameters for \( \text{H}_2\text{O} \) and \( \text{NH}_3(aq) \) shown in Table 2 were obtained by graphical fits of Eqn. (25) to the values of \( \Delta P^0 \) in Table 3. The resulting regression curves correspond to the two lower left curves in Fig. 4. The effective Born coefficients for these species were also used to calculate values of \( \Delta C^0_v \) from Eqn. (23). These values were then used to compute corresponding values of \( \Delta C^0_v \) from the first identity in Eqn. (9) using the experimental values of \( C^0_v \) listed in Table 2.

Taking account of Eqn. (26), plots of \( \Delta C^0_v \) against \( 1/(T - \theta) \) should fall on linear curves. Plots of this type, generated using the values of \( \Delta C^0_v \) given in Table 3, are shown for \( \text{Ar}(aq) \), \( \text{NH}_3(aq) \), and \( \text{H}_2\text{O} \) on the right side of Fig. 4. The values of \( c_1 \) and \( c_2 \) obtained from the regression procedure described above were used to calculate the curves shown. Also shown in Fig. 4 is a plot of \( \Delta P^0(q) \) against \( 1/(T - \theta) \) for \( \text{B(OH)}_3(aq) \), which was generated by regression of the experimental \( P^0 \) data for \( \text{B(OH)}_3(aq) \) in Table 3 with Eqn. (25) to obtain the values of \( \sigma_1 \), \( \xi \) and \( \omega_0 \) for this species shown in Table 2.

**CORRELATIONS AMONG EQUATION OF STATE PARAMETERS**

Correlations among equation of state parameters in the revised HKF model and various standard partial molar properties of aqueous ions at 25°C and 1 bar (SHOCK and HELGESON, 1988) are depicted in Fig. 5. The linear curves in these correlation plots are consistent with

$$a_1 = 1.3684 \times 10^{-2} \Delta P^0 + 0.1765,$$

$$a_2 = 17.19 \Delta P^0 \times 10^4 + 421.1,$$

$$\sigma = 1.11 \Delta P^0 + 1.8,$$

and

$$c_1 \times 10^{-4} = 0.203/C^0 \quad c_2 \times 10^{-4} = 0.0346$$

where \( \Delta P^0 = -\frac{\partial \Delta \tilde{P}}{\partial \rho} \). Equation (36) represents the linear correlation of \( \sigma \) with \( \Delta P^0 \) for both aqueous ions and neutral aqueous species in Figs. 5 and 6. The \( c_2 \) parameters shown in Table 2 are plotted in Fig. 7 against the corresponding values of \( C^0_v \) at 25°C and 1 bar in Table 3. Values of \( c_2 \) and \( C^0_v \) for \( \text{Cl}^- \) for \( \text{H}_2\text{O(aq)} \) (SHOCK and HELGESON, 1989) are also shown in Fig. 7. The curve in Fig. 7 is consistent with Eqn. (38), which applies also to the curve shown in the lower left diagram in Fig. 5. Hence, Figs. 6 and 7 reinforce observations that Eqns. (36) and (38) are independent of charge (SHOCK and HELGESON, 1988). The charge-independence of these relations suggests that other correlations observed among volumetric equation of state parameters for ions can also be used for neutral aqueous species. Although there are no reports in the literature of experimental compressibility data for neutral aqueous species which can be used to directly test this observation, indirect supporting evidence is provided by the close agreement between the experimental measurements and the independently predicted curves in Fig. 8. Equilibrium constants are shown in this figure for the reaction

$$\text{NH}_3(aq) + \text{H}^+ = \text{NH}_4^+$$

as a function of temperature at pressures of 1, 2, 3 and 4 kb.
The curves were generated from Eqns. (12) and (31)-(33) using parameters for NH$_2$ and H$^+$ taken from SHOCK and HELGESON (1988) and those for NH$_3$(aq) given in Table 4. The values of $a_1$, $a_2$, $a_3$, and $a_4$ for NH$_3$(aq), as well as those for all of the other aqueous species except SiO$_2$(aq), shown in Table 4 were estimated from the correlations for aqueous neutral species at various temperatures and pressures for reactions involving He(0), H$_2$, PO$_4$(aq), and NZ$_2$(aq) taken from the references given in Figs. 1 and 2, but the curves correspond to regression values (see text). Experimental equilibrium constants at temperatures above 250°C are reported in the literature for reactions involving a number of aqueous neutral species for which experimental values of $S^\theta$ and $C_p^\theta$, at 25°C and 1 bar are available. These include CO$_2$(aq), HNO$_3$(aq), Xe(aq), H$_2$(aq), O$_2$(aq), He(aq), and H$_2$PO$_4$(aq). Equilibrium constants for various reactions involving these species are shown in Fig. 9, where the symbols represent experimental measurements, but the curves were generated by regression of the experimental data with Eqns. (12) and (31)-(33) using parameters and data taken from Table 4 and those for aqueous ions given by SHOCK and HELGESON (1988) to obtain the values of $\omega_1$ given in Table 4. In the case of the reaction involving B(OH)$_3$(aq), the values of $S^\theta$ shown in Table 4 for this species was obtained by regression of the experimental log $K$ values for the reaction in Fig. 9. It can be seen in this figure that the regression calculations using independently generated values of all of the equation of state parameters except $\omega_1$ closely represent all of the experimental data shown in the figure.

Other experimental data that are closely consistent with the curves shown in Figs. 3, 8, and 9 (but not shown in the figures) have been reported or summarized by WINKLER (1981a), Cady et al. (1982), Nims (1934), Owen (1934), Pitzer (1937), Owen and King (1943), Manov et al. (1944), Bates and Pinching (1949, 1950), Bates (1951), Buchanan and Hamann (1953), Everett and Landsman (1954), Hamann and Strauss (1955), Yeh and Peterson (1964), de Wet (1964), Haase et al. (1965), Hepler (1965), Carpenter (1966), Larson and Hepler (1969), Nakayama (1971), Murray and Riley (1971), Fisher and Barnes (1972), Vanderzee et al. (1972), Stokes (1975), Pitzer and Silvester (1976), Lee and Matther (1977), Gordon et al. (1977), Berg and Vanderzee (1978), Hepler and Hopkins (1979), Yasunishi and Yoshida (1979), Gill and Wadso (1982), Moore et al. (1982), Perrin (1982), Plummer and Buesenberg (1982), Bignell (1984), Kutsche et al. (1984), Dec and Gill (1985), Postigo and Katz (1987), and Versteeg and van Swaai (1988).

The curves were generated from Eqns. (12) and (31)-(33) using parameters for NH$_2$ and H$^+$ taken from SHOCK and HELGESON (1988) and those for NH$_3$(aq) given in Table 4. The values of $a_1$, $a_2$, $a_3$, and $a_4$ for NH$_3$(aq), as well as those for all of the other aqueous species except SiO$_2$(aq), shown in Table 4 were estimated from the correlations for aqueous ions in Fig. 5 assuming that these correlations are charge-independent like those for $\sigma$ and $c_2$ in Figs. 6 and 7. This assumption is strongly supported by the remarkably close agreement in Fig. 8 between the independently predicted equilibrium constants and their experimental counterparts for reaction (39) over the entire temperature and pressure range from 0 to 600°C and 1 to 4 kb. This and similar agreement between experimental equilibrium constants at elevated pressures for reactions involving He$_{eq}$, H$_2$PO$_4$$_{aq}$, and N$_2$(aq) (see below) provide strong supporting evidence that the correlations among equation of state parameters and standard partial molal properties represented by Eqns. (34)-(38) apply equally well to ionic and neutral aqueous species. These observations, together with the curves shown in Figs. 6 and 7 permit one-parameter regression of experimental equilibrium constants at temperatures $\geq$ 250°C to obtain values of $\omega_1$ from a combined statement of Eqns. (22), (25)-(27), (31)-(34), and (36)-(38).

Experimental equilibrium constants at temperatures above 250°C are reported in the literature for reactions involving a number of aqueous neutral species for which experimental values of $S^\theta$ and $C_p^\theta$, at 25°C and 1 bar are available. These include CO$_2$(aq), HNO$_3$(aq), Xe(aq), H$_2$(aq), O$_2$(aq), He(aq), and H$_2$PO$_4$(aq). Equilibrium constants for various reactions involving these species are shown in Fig. 9, where the symbols represent experimental measurements, but the curves were generated by regression of the experimental data with Eqns. (12) and (31)-(33) using parameters and data taken from Table 4 and those for aqueous ions given by SHOCK and HELGESON (1988) to obtain the values of $\omega_1$ given in Table 4. In the case of the reaction involving B(OH)$_3$(aq), the value of $S^\theta$ shown in Table 4 for this species was obtained by regression of the experimental log $K$ values for the reaction in Fig. 9. It can be seen in this figure that the regression calculations using independently generated values of all of the equation of state parameters except $\omega_1$ closely represent all of the experimental data shown in the figure.

![Fig. 4. Graphic representation of Eqns. (25) and (26) for the non solvation contributions to the standard partial molal volume ($\Delta V^\theta$) and heat capacity ($\Delta C_p^\theta$) of neutral aqueous species at various temperatures and $P_{sat}$. The symbols represent experimental data taken from the references given in Figs. 1 and 2, but the curves correspond to regression values (see text).](image-url)
In the case of many aqueous neutral species for which equilibrium constants have been measured experimentally at high pressures and temperatures, no experimental values of $\tilde{\mathcal{V}}^0_j$ and/or $C^0_{p,j}$ at 25°C and 1 bar are available in the literature. Given an independent means of estimating $a$, Eqs. (12) and (31)-(33) can be used together with the correlation algorithms represented by Eqs. (34)-(38) to regress equilibrium constant data for values of $\tilde{\mathcal{V}}^0_j$ and/or $C^0_{p,j}$ at 25°C and 1 bar. The requisite estimates of $a_{x,j}$ for neutral aqueous species can be made by first considering the relation between $a_{x,j}$ and $S^p_j$ for aqueous ions.

Correlation of $a_j$ and $S^p_j$

The effective electrostatic radius of an aqueous ion is related to its crystallographic counterpart by Eqn. (18). This equation cannot be directly applied to aqueous neutral species because there is no unambiguous way to compute $r_{x,j}$ for these species and $Z_j$ is unknown for $Z_i = 0$. As emphasized elsewhere (Hegeson and Kirkham, 1976; Shock and Hegeson, 1988), $r_{x,j}$ is also ambiguous for polyatomic ionic species. However, estimates of $r_{x,j}$ at 25°C and 1 bar for polyatomic ionic species can be made from their standard partial molar entropies using the relation (Shock and Hegeson, 1988)

$$r_{x,j} = \frac{Z_j^2(yY - 100)}{S^p_j - \alpha Y},$$

where $\alpha Y$ represents a charge-dependent constant. Values of $r_{x,j}$ computed from Eqn. (40) permit calculation of $a_{x,j}^\text{th}$ from Eqn. (17), which can in turn be used to compute values of $a_j$ from Eqn. (16) and the standard partial molar solvation...
properties of aqueous polyatomic ionic species at 25°C and 1 bar. As shown below, a similar approach can be used to estimate these properties for neutral aqueous species.

Combining the definition of the absolute Born coefficient given by Eqn. (17) with Eqn. (40) leads to

\[
\frac{S_0^0}{\omega_z} = \omega_j \left( Y - \frac{100}{\eta} \right)
\]

where

\[
\beta_z = \frac{-\alpha_2 \eta}{Y \eta} - \frac{Z_j \omega_j^0}{Y}.
\]  (43)

Values of \(\beta_z\) for charged species computed from Eqn. (43) using values of \(\alpha_2\) taken from SHOCK and HELGESON (1988) are given in Table 5. These values were used together with Eqn. (42) to generate the curves depicted in Fig. 10, where it can be seen that they compare favorably with the symbols representing values of \(S_0^0\) and \(\omega_j\) for monatomic ions at 25°C and 1 bar taken from SHOCK and HELGESON (1988).

It follows from Eqn. (43) that for a formal charge of zero, where \(\alpha_2 = 0\), \(\beta_z\) will also equal 0, and therefore Eqn. (42) reduces to

\[
\omega_j = \omega_{w,j} = -1514.4S_0^0,
\]  (44)

which was used to generate the lower curve in Fig. 11. The solid symbols shown in this figure represent values of \(S_0^0\) and \(\omega_{w,j}\) taken from Table 4, which were obtained by regression of experimental standard partial molal volume and heat capacity data (see above). With the exception of that for \(\text{SiO}_2\), the open symbols in Fig. 11 represent species in Table 4 for which \(\omega_{w,j}\) was obtained in the present study by regression of high-temperature equilibrium constant data. The open symbol for \(\text{SiO}_2\) denotes the value of \(\omega_{w,j}\) given by WALTHER and HELGESON (1977) and the value of \(S_0^0\) obtained in the present study (see below).

It can be seen in Fig. 11 that the points representing \(\text{Ar}_{(at)}\), \(\text{He}_{(aq)}\), \(\text{Xe}_{(aq)}\), \(\text{H}_2\text{O}_{(aq)}\), and \(\text{O}_2\text{O}_{(aq)}\) fall along the curve predicted independently from Eqn. (44). The symbols representing \(\text{SiO}_2\), \(\text{H}_2\text{S}_{(aq)}\), \(\text{NH}_3\text{O}_{(aq)}\), \(\text{CO}_2\text{O}_{(aq)}\), \(\text{HNO}_3\text{O}_{(aq)}\), \(\text{B(OH)}_3\text{O}_{(aq)}\), and \(\text{H}_3\text{PO}_4\text{O}_{(aq)}\) lie at more positive values of \(\omega_{w,j}\), but the curve drawn through them has the same slope as the curves in Fig. 10 and the lower curve in Fig. 11. The equation of the upper curve in Fig. 11 is given by

\[
\omega_{w,j} = -1514.4S_0^0 + 0.34 \times 10^3. \quad (45)
\]

Note that the upper curve in Fig. 11 crosses \(\omega_{w,j} = 0\) at \(S_0^0 = 22.45\), which leads to positive values of \(\omega_{w,j}\) for this group of neutral aqueous species at lower values of \(S_0^0\). It can be deduced from the values of \(\log K\) for the gas solubility reactions depicted on the left side of Fig. 9, together with those for other similar reactions, that, of the symbols shown in Fig. 11, only those representing the more volatile neutral aqueous species corresponding to the noble and diatomic gases are the ones in agreement with the lower curve. In contrast, values of \(\omega_{w,j}\) for polyatomic and polar neutral aqueous species fall along the upper curve in Fig. 11, which lies between the curves for formal charges of 0 (the lower curve in Fig. 11) and 1 (the lower curve in Fig. 10). Estimates of \(\omega_{w,j}\) for 32 neutral inorganic aqueous species generated from Eqs. (44) and (45) using these criteria (see below) and values of \(S_0^0\) taken from the literature are listed in Table 6.

The intercepts corresponding to \(\beta_z\) in Fig. 10 are given by appropriate statements of Eqn. (43) for 25°C and 1 bar, which can be written as

\[
\beta_z = 0.54 \times 10^5 |Z_j| \quad (46)
\]

for cations and

\[
\beta_z = 1.62 \times 10^5 |Z_j| \quad (47)
\]

for anions. Equations (46) and (47) are represented by the curves in Fig. 12, which converge at the origin. As indicated above, the origin in Fig. 12 corresponds to the intercept of
Fig. 8. Logarithm of the equilibrium constant for reaction (39) as a function of temperature at pressures of 1, 2, 3, and 4 kilobars. The symbols represent experimental data, but the curves were generated from Eqsns. (12) and (31)-(33) using parameters and thermodynamic data for NH₃ taken from Table 4 and those for H⁺ and NH₄⁺ from Shock and Helgeson (1988) (see text).

the lower curve representing the more volatile aqueous species shown in Fig. 11. Hence, in calculating the values of \( \omega_{e,i} \), shown in Table 6, Eqn. (44) was used for all neutral aqueous species with the stoichiometry \( A \) or \( A_2 \), where \( A \) represents a given element. The values of \( \omega_{e,i} \) for the other neutral aqueous species shown in Table 6 were generated from Eqn. (45), which is consistent with the upper curve in Fig. 11. The factors controlling the position of this curve have yet to be determined.

COMPARISON OF CALCULATED AND EXPERIMENTAL EQUILIBRIUM CONSTANTS AT HIGH TEMPERATURES AND Pressures

The sign of the second derivative of \( \log K \) with respect to temperature at \( P_{\text{SAT}} \) for solubility reactions involving the liquid phase in the system H₂O depends on the volatilities of the aqueous species participating in the reaction (Helgeson, 1989). If the dissolving phase is more soluble in the liquid phase than in the coexisting vapor, which is the case for minerals and electrolytes, \( (\delta^2 \log K/\delta T^2)_{P_{\text{SAT}}} \), for reactions involving the liquid phase is negative and \( \log K \) at \( P_{\text{SAT}} \) maximizes with increasing temperature. Under these circumstances, \( (\delta \log K/\delta T)_{P_{\text{SAT}}} \) in the liquid phase region approaches \(-\infty\) at the critical point of H₂O. In contrast, if the solubility of the dissolving phase is greater in H₂O vapor than in the coexisting liquid phase, which is generally true of gas solubilities, then \( (\delta^2 \log K/\delta T^2)_{P_{\text{SAT}}} \), for the liquid phase is positive and \( \log K \) minimizes with increasing temperature at \( P_{\text{SAT}} \). As a consequence, \( (\delta \log K/\delta T)_{P_{\text{SAT}}} \), for the liquid phase approaches \( \infty \) at the critical point of H₂O. For intermediate cases in which the solubility of the dissolving phase is higher in liquid H₂O at low temperatures and in the coexisting vapor at high temperatures, or vice versa, \( \log K \) for the solubility reaction in the liquid phase region exhibits a reverse sigmoidal or sigmoidal configuration with increasing temperature at \( P_{\text{SAT}} \). Nevertheless, in all instances the logarithm of the equilibrium constant for a reaction representing the solubility of a phase in liquid or supercritical aqueous solutions can be calculated from Eqsns. (31)-(33) using values of \( \Delta G^\circ \) for the gases or solids involved in the reaction.

Gas solubilities

Numerous measurements of gas solubilities at elevated temperatures and pressures are reported in the literature (Boyle, 1911; Kofler, 1912; Hudson, 1925; Wright and Maass, 1932; Wiebe et al., 1933; Wiebe and Gaddy, 1934, 1935; Johnstone and Leppla, 1934; Markham and Kobe,
Table 4. Summary of experimental and retrieved partial molar thermodynamic properties of aqueous neutral species at 25°C and 1 bar, together with the parameters required to calculate the corresponding properties at high pressures and temperatures from Eqs. (21) through (31). The values of $u_c$ shown below were obtained by regression of experimental data, but those for $a_1$, $a_2$, $a_3$, $u_c$, and $e_1$ were estimated with the aid of Eqs. (22), (23), (25)-(28), (34), and (36)-(38)—see text.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta G^\circ$</th>
<th>$\Delta H^\circ$</th>
<th>$\Delta S^\circ$</th>
<th>$u_c$</th>
<th>$e_1$</th>
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<tbody>
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<td>Ne</td>
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<td>-8990.0</td>
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<td>58.7</td>
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<td>H$_2$SO$_4$</td>
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<td>-900.4</td>
<td>30.0</td>
<td>42.7</td>
<td>34.9</td>
</tr>
<tr>
<td>BO$_3$H$_2$O</td>
<td>-2168.50</td>
<td>-25682.03</td>
<td>37.0</td>
<td>12.0</td>
<td>39.22</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>-24730.8</td>
<td>-45410.7</td>
<td>42.5</td>
<td>18.0</td>
<td>10.0</td>
</tr>
<tr>
<td>SO$_3$H$_2$O</td>
<td>-195910.8</td>
<td>-209775.7</td>
<td>18.0</td>
<td>-76.7</td>
<td>16.0</td>
</tr>
<tr>
<td>H$_2$PO$_4$</td>
<td>273100.9</td>
<td>307920.1</td>
<td>38.0</td>
<td>23.4</td>
<td>48.19</td>
</tr>
</tbody>
</table>

At $25$ °C and 1 bar, $K$ is expressed as $K = 1.65$; for solubility and/or dissociation equilibria $K$ is expressed as $K = 10$. The values of $K$ from Table 2. y. Generated by regression (see text). z. Taken from the literature. 

**Table 4.** Summary of experimental and retrieved partial molar thermodynamic properties of aqueous neutral species at 25°C and 1 bar, together with the parameters required to calculate the corresponding properties at high pressures and temperatures from Eqs. (21) through (31). The values of $u_c$ shown below were obtained by regression of experimental data, but those for $a_1$, $a_2$, $a_3$, $u_c$, and $e_1$ were estimated with the aid of Eqs. (22), (23), (25)-(28), (34), and (36)-(38)—see text.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta G^\circ$</th>
<th>$\Delta H^\circ$</th>
<th>$\Delta S^\circ$</th>
<th>$u_c$</th>
<th>$e_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>-4658.6</td>
<td>-150.9</td>
<td>14.22</td>
<td>37.3</td>
<td>13.6</td>
</tr>
<tr>
<td>Ar</td>
<td>9503.0</td>
<td>-2870.3</td>
<td>14.5</td>
<td>31.7</td>
<td>17.1</td>
</tr>
<tr>
<td>Ne</td>
<td>3225.7</td>
<td>-4515.0</td>
<td>14.6</td>
<td>44.8</td>
<td>37.5</td>
</tr>
<tr>
<td>H$_2$</td>
<td>4236.2</td>
<td>-1300.9</td>
<td>13.8</td>
<td>36.9</td>
<td>25.2</td>
</tr>
<tr>
<td>O$_2$</td>
<td>3954.8</td>
<td>-2900.0</td>
<td>26.5</td>
<td>56.0</td>
<td>30.3</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>-6393.7</td>
<td>-19440.8</td>
<td>25.7</td>
<td>17.9</td>
<td>24.4</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>9225.0</td>
<td>-8990.0</td>
<td>28.1</td>
<td>58.7</td>
<td>32.2</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>6073.9</td>
<td>-900.4</td>
<td>30.0</td>
<td>42.7</td>
<td>34.9</td>
</tr>
<tr>
<td>BO$_3$H$_2$O</td>
<td>-2168.50</td>
<td>-25682.03</td>
<td>37.0</td>
<td>12.0</td>
<td>39.22</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>-24730.8</td>
<td>-45410.7</td>
<td>42.5</td>
<td>18.0</td>
<td>10.0</td>
</tr>
<tr>
<td>SO$_3$H$_2$O</td>
<td>-195910.8</td>
<td>-209775.7</td>
<td>18.0</td>
<td>-76.7</td>
<td>16.0</td>
</tr>
<tr>
<td>H$_2$PO$_4$</td>
<td>273100.9</td>
<td>307920.1</td>
<td>38.0</td>
<td>23.4</td>
<td>48.19</td>
</tr>
</tbody>
</table>

a. Cal mol$^{-1}$. b. Cal mol$^{-1}$ K$^{-1}$. c. cm$^3$ mol$^{-1}$. d. Cal mol$^{-1}$ bar$^{-1}$. e. Cal K mol$^{-1}$ bar$^{-1}$. f. Cal mol$^{-1}$ K$^{-1}$ bar$^{-1}$. g. Calculated from values of log $K$ at 25 °C and 1 bar for solubility and/or dissociation reactions using values of $\Delta G^\circ$ of the gas species taken from Wagman et al. (1982) and those of $\Delta G^\circ$ for aqueous ions from Shock and Helgeson (1980). h. Uhde et al. (1985). i. Calculated from values of $\Delta G^\circ$ and $\Delta H^\circ$ using $S^\circ$ of the elements taken from Wagman et al. (1982). j. Calculated from a fit of high-pressure solubility data (see text and Fig. 13), k. Tropel and Grahinski (1977). l. Biggert et al. (1986). m. Wagman et al. (1982). n. Calculated from the value of $\Delta C^\circ$ given by Clever and Han (1980) and that of $C^\circ$ of the gas taken from Wagman et al. (1982). o. Vanderveen and King (1972). p. Allred and Woolley (1981). q. Barbero et al. (1983). r. Calculated from the temperature dependence of log $K$ for solubility and/or dissociation reactions using $S^\circ$ of the elements taken from Wagman et al. (1982). s. Calculated from values of $\Delta G^\circ$ and $\Delta S^\circ$ using $S^\circ$ of the elements taken from Wagman et al. (1982). t. Barbero et al. (1982). u. Ward and Miller (1976). v. Calculated from the temperature dependence of log $K$ for solubility and/or dissociation reactions using the parameters in Table 4. w. Taken from Table 6. x. Generated by regression (see text). y. Waithier and Helgeson (1977). z. Larson et al. (1982).
Fig. 9. Logarithm of the equilibrium constants for several gas solubility and acid dissociation reactions as a function of temperature at $P_{\text{sat}}$, and in the case of the He solubility reaction at 1 kb. The symbols represent experimental data taken from the references shown in the figure, but the curves were generated by regression of the data to obtain values of $v_{inj}$ using Eqs. (12) and (31)-(38).
Table 5. Values of \( \beta_2 \) calculated from Eqn. (43) for aqueous ions of various charges.

<table>
<thead>
<tr>
<th>( Z_i )</th>
<th>( \beta_2 \times 10^{-5} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>0.5517</td>
</tr>
<tr>
<td>+2</td>
<td>1.0579</td>
</tr>
<tr>
<td>+3</td>
<td>1.5793</td>
</tr>
<tr>
<td>+4</td>
<td>2.1764</td>
</tr>
<tr>
<td>-1</td>
<td>3.2127</td>
</tr>
<tr>
<td>-2</td>
<td>5.8115</td>
</tr>
<tr>
<td>-3</td>
<td>7.6831</td>
</tr>
<tr>
<td>-4</td>
<td>15.5860</td>
</tr>
</tbody>
</table>

with the other data represented by the symbols in the figure.

In the case of Rn\(_{aq}\) and N\(_2\)\(_{aq}\), for which no \( C_p^R \) values at 25°C and 1 bar are available in the literature, the curves in Fig. 13 were generated by regression of the log \( K \) data using predicted values of the equation of state parameters to obtain \( C_p^R \) for the aqueous species at 25°C and 1 bar in the manner described above. The standard partial molal volumes and heat capacities at 25°C and 1 bar for all of the aqueous species shown in Fig. 13 are given in Tables 4 and 7, together with corresponding values of \( \Delta G^R_i, \Delta H^R_i, S^R_i, \omega_i, \) and the equation of state parameters that were used in the calculations.

It can be seen in Fig. 13 that the calculated equilibrium constants represented by the curves are in close agreement with the bulk of their experimental counterparts. The agreement for the curves representing the solubilities of Ar\(_{aq}\), Ne\(_{aq}\), Kr\(_{aq}\), and SO\(_2\)\(_{aq}\) is particularly remarkable because the curves were generated independently of the experimental data represented by the symbols at temperatures > 25°C. The calculated values corresponding to the curves in Fig. 13 fall within the experimental uncertainty (indicated by the symbol size) of all the available experimental data, except some of the log \( K \) values generated from solubility measurements of noble gases reported by Potter and Clynne (1978). As noted by Crovett\( et\) \( al.\) (1982a), Potter and Clynne’s (1978) measurements yield systematically high solubilities relative to all other experimental determinations at low temperatures. Above \(~200°C\), Potter and Clynne’s (1978) values of log \( K \) for these reactions tend to be systematically low, and differ by as much as 40% from the more recent measurements by Crovett\( et\) \( al.\) (1982a). Furthermore, in a number of cases they fail to exhibit a smooth distribution with increasing temperature. This is particularly true of Potter and Clynne’s (1978) solubility data for argon.

Although the logarithms of the equilibrium constants for all of the gas solubility reactions in Figs. 3, 9, and 13 exhibit minima with increasing temperature, the temperature at the minimum is not the same for all of the reactions. For example, the minimum values of log \( K \) for the solubilities of He and

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**FIG. 10.** Correlation of the Born coefficients \( (\omega_i) \) of aqueous ions with their standard partial molal entropies \( (S^R_i) \) at 25°C and 1 bar. The solid symbols represent regression values of \( \omega_i \) derived from standard partial molal properties, but the open symbols for species other than SiO\(_2\) correspond to values of \( \omega_i \) obtained in the present study by regression of log \( K \) data (see text).

**Table 6.** Experimental standard partial molal entropies \( (S^R_i) \) and effective Born coefficients \( (\omega_i) \) for neutral aqueous species calculated from Eqsns. (44) and (45).

<table>
<thead>
<tr>
<th>Aqueous Species</th>
<th>( S^R )</th>
<th>( \omega_i \times 10^{-1} )</th>
<th>Aqueous Species</th>
<th>( S^R )</th>
<th>( \omega_i \times 10^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>16.74</td>
<td>-0.2545</td>
<td>O(_2)</td>
<td>34.4</td>
<td>-0.1985</td>
</tr>
<tr>
<td>Kr</td>
<td>15.06</td>
<td>-0.2221</td>
<td>H(_2)O(_2)</td>
<td>34.4</td>
<td>-0.1810</td>
</tr>
<tr>
<td>Rn</td>
<td>16.00</td>
<td>-0.2423</td>
<td>HF</td>
<td>22.5</td>
<td>-0.0007</td>
</tr>
<tr>
<td>Cl(_2)</td>
<td>28.95</td>
<td>-0.4377</td>
<td>HClO(_2)</td>
<td>44.0</td>
<td>-0.1749</td>
</tr>
<tr>
<td>ClO(_2)</td>
<td>39.13</td>
<td>-0.2526</td>
<td>HClO(_2)</td>
<td>45.0</td>
<td>-0.3415</td>
</tr>
<tr>
<td>Br(_2)</td>
<td>31.22</td>
<td>-0.4725</td>
<td>HBrO(_2)</td>
<td>33.9</td>
<td>-0.1724</td>
</tr>
<tr>
<td>I(_2)</td>
<td>22.80</td>
<td>-0.4967</td>
<td>HIO</td>
<td>22.6</td>
<td>-0.0053</td>
</tr>
<tr>
<td>N(_2)</td>
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<td>-0.3463</td>
<td>HIO(_2)</td>
<td>39.9</td>
<td>-0.2642</td>
</tr>
<tr>
<td>NO</td>
<td>28.43</td>
<td>-0.0905</td>
<td>HCN</td>
<td>29.8</td>
<td>-0.1113</td>
</tr>
<tr>
<td>N(_2)O</td>
<td>28.94</td>
<td>-0.0846</td>
<td>HN(_2)</td>
<td>34.0</td>
<td>-0.1885</td>
</tr>
<tr>
<td>N(_2)H(_4)</td>
<td>33.07</td>
<td>-0.1598</td>
<td>HNO(_2)</td>
<td>32.4</td>
<td>-0.1507</td>
</tr>
<tr>
<td>NF(_2)</td>
<td>37.52</td>
<td>-0.2009</td>
<td>H(_2)PO(_4)</td>
<td>64.1</td>
<td>-0.5307</td>
</tr>
<tr>
<td>PH(_2)</td>
<td>26.47</td>
<td>-0.0598</td>
<td>H(_2)AsO(_4)</td>
<td>50.0</td>
<td>-0.5763</td>
</tr>
<tr>
<td>CO</td>
<td>24.53</td>
<td>-0.0315</td>
<td>H(_2)AsO(_4)</td>
<td>30.1</td>
<td>-0.1158</td>
</tr>
<tr>
<td>SF(_6)</td>
<td>37.22</td>
<td>-0.2237</td>
<td>H(_2)SiO(_2)</td>
<td>11.1</td>
<td>-0.1719</td>
</tr>
<tr>
<td>SO(_2)</td>
<td>38.77</td>
<td>-0.2461</td>
<td>H(_2)Se</td>
<td>39.1</td>
<td>-0.2521</td>
</tr>
<tr>
<td>AsH(_3)</td>
<td>30.21</td>
<td>-0.1175</td>
<td>H(_2)S(_2)O(_5)</td>
<td>49.7</td>
<td>-0.4127</td>
</tr>
</tbody>
</table>

---

*a* Cal. mol\(^{-1}\) K\(^{-1}\). *b* Cal. mol\(^{-1}\). Calculated from equation (45) unless indicated otherwise. *c* Wagman et al. (1982). *d* Taken from table 7. *e* Wilhelm et al. (1977). *f* Calculated from equation (44).
Regardless of the temperatures at which the minima occur, the other cases for which $\omega_{eq}$ is less negative (like the dissolution of $H_2S$, $CO_2$, and $SO_2$) the log $K$ curves exhibit broad curvature and the minima occur at temperatures $>100^\circ C$. Regardless of the temperatures at which the minima occur, the calculated values of log $K$ in every case increase dramatically at temperatures above $350^\circ C$ (not shown in Figs. 3, 9, and 13). As in the case of aqueous argon, this high-temperature behavior is consistent with the approach to infinity of $C_p^S$ for aqueous dissolved gases in the liquid phase with increasing temperature at $P_{SAT}$.

The observations summarized in the preceding paragraph are consistent with recent experimental determinations of the heat capacities of $A_2e(aq)$, $Xe(aq)$, and $C_2H_4(aq)$ at supercritical temperatures (BIGGERSTAFF and WOOD, 1988a,b). As indicated above, the configurations of the curves representing gas solubilities in Figs. 3, 9, and 13 can be attributed to the fact that the solubility of a gas in liquid $H_2O$ at low temperatures and $P_{SAT}$ is much lower than its equilibrium solubility in the coexisting $H_2O$ vapor. However, as temperature and pressure approach those at the critical point of $H_2O$ and the distinction between the liquid and vapor phases diminishes, the solubilities of the gas in the liquid and vapor phases converge and reach an identical value. To the extent that these gases behave ideally, all of the log $K$ values for these reactions should approach $-0.6$ at the critical point of $H_2O$ (BEUTTER and RENON, 1978; BIGGERSTAFF et al., 1985). In addition, all thermodynamic properties of gas solubility reactions involving the liquid phase at high temperatures that depend on the isobaric or isothermal partial derivatives of log $K$ ($\Delta H^0$, $\Delta C_P^S$, $\Delta V^0$, $\Delta S^0$, $(\partial \Delta V^0/\partial T)_P$, and $(\partial \Delta C_P^S/\partial T)_P$) increase with increasing temperature at $P_{SAT}$ and approach $\infty$ at the critical point of $H_2O$. In contrast, the standard partial molal heat capacities, compressibilities, and expansibilities of dissolved gases in steam approach $-\infty$ as the critical point is approached at the critical pressure from higher temperatures. All of this behavior is exactly opposite to that of the corresponding thermodynamic properties of solubility reactions that involve only aqueous species with low volatilities such as electrolytes or aqueous silica (HELGESON, 1989).

### Quartz solubility

The solubility of quartz has been studied experimentally over a wide range of temperature and pressure up to $900^\circ C$ and 9 kb (KENNEDY, 1950; MOREY and HESSELLGESSER, 1951; KHITAROV, 1956; KITAHARA, 1960; VAN LIER et al., 1960; SIEVER, 1962; MOREY et al., 1962; WEILL and FYFE, 1964; ANDERSON and BURNHAM, 1965, 1967; CRERAR and ANDERSON, 1971; HEMLEY et al., 1980; WALTHER and ORVILLE, 1983; and RIMSTIDT, 1984, among others). Values of log $K$ for the reaction

$$SiO_2_{(quartz)} = SiO_2_{(aq)}$$

calculated from experimental quartz solubilities as a function of temperature at $P_{SAT}$, 0.5, and 0.75 kb, 0.6, 1.0 and 1.5 kb, and 2.0, 3.0, 4.0, and 5.0 kb are shown as symbols in Fig. 14A, B, and C, respectively. These data are also shown in Fig. 14D as a function of pressure at temperatures from 100 to $900^\circ C$. The curves in Fig. 14 were generated in the present study by regression of the experimental data. It can be seen in this figure that log $K$ at $P_{SAT}$ for reaction (48) increases with increasing temperature and maximizes at approximately $325^\circ C$.

In contrast to gases, the solubilities of quartz and other minerals at $P_{SAT}$ in the liquid phase region of the system $H_2O$ are much greater than their solubilities in the coexisting vapor phase. However, as temperature increases at $P_{SAT}$ toward the critical point of $H_2O$, the distinction between the two solvent phases diminishes and the solubility of quartz in the vapor phase approaches that in the liquid. The apparent standard partial molal enthalpy of formation and the standard partial molal entropy, volume, and heat capacity of $SiO_2_{(aq)}$ in both the vapor and liquid phases approach $-\infty$ as temperature increases at $P_{SAT}$ toward the critical point of $H_2O$ (HELGESON, 1989). In contrast to the standard partial molal heat capacity, compressibility, and expansibility of a volatile neutral species in steam, those of $SiO_2_{(aq)}$ approach $\infty$ as the critical point of $H_2O$ is approached at the critical pressure from higher temperatures.

The behavior of the standard partial molal thermodynamic properties of reaction (48) discussed in the preceding paragraph is consistent with the positive effective Born coefficient and the low volatility of $SiO_2_{(aq)}$. $SiO_2_{(aq)}$ is apparently present in aqueous solution as $Si(OH)_4$ (2$H_2O$) (WALTHER and ORVILLE, 1983). Hence, hydrogen bonds may be in part responsible for the positive value of $\omega_{eq}$ and the relatively low standard partial molal entropy of aqueous silica at $25^\circ C$ and 1 bar. As indicated above, the value of $\omega_{eq}$ for $SiO_2_{(aq)}$ adopted in the present study is that retrieved by WALTHER and HELGESON (1977) from their regression of the quartz solubility data shown in Fig. 14 with the HFK model. These same data were regressed with the revised HFK equations of state in the pres-
Fig. 13. Logarithms of the equilibrium constants for gas solubility reactions as functions of temperature at $P_{\text{SAT}}$, and in the case of $N_2(g) + N_2(00)$ at 100 bars. The symbols represent experimental data, but the curves were generated from Eqsns. (31)-(33) using parameters and thermodynamic data taken from Table 7. The curves for the reaction involving $\text{Ne}(g), K_3, A_1, \text{Ar}(g),$ and $\text{SO}_2(00)$ correspond to independent predictions at temperatures $> 25^\circ\text{C}$, but those for $\text{N}_2$ and $\text{R}_2$ were produced by regression of the data with Eqsns. (31)-(38) to obtain values of the standard partial molal heat capacities ($C_P$) of the neutral aqueous species at 25$^\circ\text{C}$ and 1 bar.

Acid dissociation reactions

The data and parameters shown in Tables 4, 6, and 7, together with those given by Shock and Helgeson (1988), permit prediction of values of log $K$ for acid dissociation reactions at high temperatures and pressures from Eqsns. (12) and (31)-(33). Predictions of this kind are depicted as curves...
Table 7. Summary of experimental and retrieved standard partial molal thermodynamic properties of aqueous neutral species at 25°C and 1 bar, together with the parameters required to calculate the corresponding properties at high pressures and temperatures from Eqs. (27) through (31). The values of \( \nu \) shown below are estimated.

<table>
<thead>
<tr>
<th>Species</th>
<th>( \Delta G^\circ )</th>
<th>( \Delta G^\circ )</th>
<th>( s^\circ )</th>
<th>( c^\circ )</th>
<th>( \psi^\circ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NaNO}_2 )</td>
<td>-455.4</td>
<td>-870.0</td>
<td>16.74</td>
<td>39.2</td>
<td>20.4</td>
</tr>
<tr>
<td>( \text{KNO}_3 )</td>
<td>-355.4</td>
<td>-3650.0</td>
<td>15.06</td>
<td>57.0</td>
<td>33.5</td>
</tr>
<tr>
<td>( \text{RbNO}_3 )</td>
<td>-770.0</td>
<td>-5000.0</td>
<td>16.0</td>
<td>81.0</td>
<td>64.1</td>
</tr>
<tr>
<td>( \text{Na}_2\text{SO}_4 )</td>
<td>-434.7</td>
<td>-2455.4</td>
<td>22.58</td>
<td>56.0</td>
<td>33.9</td>
</tr>
<tr>
<td>( \text{K}_2\text{SO}_4 )</td>
<td>-1950.0</td>
<td>-7114.8</td>
<td>38.7</td>
<td>60.6</td>
<td>38.5</td>
</tr>
<tr>
<td>( \text{NaF}_2 )</td>
<td>-1766.6</td>
<td>-7683.5</td>
<td>22.5</td>
<td>14.0</td>
<td>12.5</td>
</tr>
</tbody>
</table>

Species \( \Delta x_{10} \) \( \Delta x_{10}^{-2} \) \( \Delta x_{10}^{-3} \) \( \Delta x_{10}^{-4} \) \( \Delta x_{10}^{-5} \)

\( \text{NaNO}_2 \) 4.6709 3.1352 4.5177 -2.9086 27.0977 5.0523 -0.2535
\( \text{KNO}_3 \) 6.2721 7.5333 2.7891 -3.0904 37.8262 8.6985 -0.2281
\( \text{RbNO}_3 \) 9.0862 14.4045 0.0884 -3.3745 52.5774 13.8725 -0.2423
\( \text{Na}_2\text{SO}_4 \) 6.2046 7.3468 2.8539 -3.0306 35.7911 8.3726 -0.2468
\( \text{K}_2\text{SO}_4 \) 6.9502 9.1890 2.1383 -3.1589 31.2101 6.4578 -0.2461
\( \text{NaF}_2 \) 3.4753 0.7042 5.4732 -2.8081 14.3647 -0.1828 -0.0007

The thermodynamics of aqueous solutions at high \( T \) and \( P \) is described in Figs. 15 and 16, where the values can be compared with the experimental values represented by the symbols. Figures 17-22 at pressures and temperatures to 5 kb and 1000°C. In these figures, the curves representing the independently predicted values of the first dissociation constant of \( \text{H}_3\text{PO}_4(nq) \) agree closely with the experimental values of \( \log K \) at both 1 and 2 kb. The curves in Figs. 16 are consistent with the regression curve for the dissociation of \( \text{H}_3\text{PO}_4(nq) \) at \( P = \text{PSAT} \) in Fig. 9, where similar agreement between the curve and experimental values of \( \log K \) is apparent. PREDICTION OF EQUILIBRIUM CONSTANTS AND STANDARD PARTIAL MOLAL PROPERTIES OF NEUTRAL AQUEOUS SPECIES TO 5 KB AND 1000°C

Predicted dissociation constants for \( \text{H}_3\text{Si}(aq) \) at high temperatures and pressures can be used to generate curves representing equal activities of \( \text{HS}^- \) and \( \text{H}_2\text{Si}(aq) \) as a function of \( \text{pH} \) and temperature at constant pressure. Curves of this kind are shown in Fig. 17, together with analogous curves generated for equal activities of \( \text{H}_3\text{PO}_4(nq), \text{H}_2\text{PO}_4^-, \text{and HPO}_4^{2-} \) using data and parameters taken from Table 4 and those for the ion species from \textit{SHOCK} and \textit{HELGESON} (1988). Diagrams and calculations of this kind facilitate considerably identification of predominant aqueous species in hydrothermal solutions. It can be seen in Fig. 17 that the curves representing equal activities of \( \text{H}_3\text{Si}(aq) \) and \( \text{H}_2\text{Si}(aq) \), as well as those for \( \text{H}_3\text{PO}_4^-, \text{and HPO}_4^{2-} \), exhibit \( \text{pH} \) minima in the vicinity of 100°C. In contrast, those representing equal activities of \( \text{H}_3\text{PO}_4(nq) \) and \( \text{H}_2\text{PO}_4^- \) do not. The latter behavior is typical of reactions for which the dissociation constant is \( \approx -2 \) at 25°C and 1 bar. Otherwise, \( \Delta H^\circ \) is common positive at low temperatures and a minimum \( \text{pH} \) occurs in curves like those shown in Fig. 17.

The close agreement between the calculated and experimental equilibrium constants depicted in Figs. 3, 8, 9, and 13-17 lends considerable support to the validity and generality of the equations, correlations, and parameters summarized above. Eqs. (27)–(31), together with the equation of state parameters given in Tables 4 and 7, can be used to predict standard partial molal properties of neutral aqueous species at higher temperatures and pressures than those shown in the previous figures. Examples of calculated standard partial molal volumes, heat capacities, and entropies, as well as apparent standard partial molal enthalpies and Gibb's free energies of formation of \( \text{CO}_2(nq), \text{O}_2(nq), \text{H}_2\text{Si}(aq), \text{and SiO}_2(nq) \), are depicted in Figs. 18–22 at pressures and temperatures to 5 kb and 1000°C. It can be seen in these figures that the magnitude of the effect of temperature and pressure changes on the standard partial molal properties of dissolved aqueous gases varies considerably from gas to gas. For example, as shown in Fig. 18, the calculated standard partial molal volume of aqueous \( \text{O}_2 \) increases by \( \approx 350 \text{ cm}^3 \text{ mol}^{-1} \) over the tem-
FIG. 14. Logarithm of the equilibrium constant for reaction (48) as a function of temperature at $P_{\text{SAT}}$ and constant pressure (diagrams A, B, and C) and pressure at constant temperature (diagram D). The symbols represent experimental data, but the curves were generated by regression of the experimental values of log $K$ and their finite difference derivatives with the revised HKF equations of state to obtain values of $a_1$, $a_2$, $a_3$, $a_4$, $c_1$, and $c_2$, as well as $S^0$, $P^0$, and $C^0_p$ of SiO$_2$(aq) at 25°C and 1 bar. The value of $\omega_{aq}$ for SiO$_2$(aq) and the thermodynamic data for quartz used in the regression calculations are the same as those used by WALTHER and HELGESON (1977).

Temperature range 0 to 350°C at $P_{\text{SAT}}$, but those of $\text{H}_2\text{S}(aq)$ and CO$_2$(aq) increase by only $\sim$90 and $\sim$25 cm$^3$ mol$^{-1}$, respectively, at $P_{\text{SAT}}$ over the same range of temperature increase. Similar differences in magnitude for changes of $P^0$, $S^0$ and $\Delta H^0$ for these dissolved gases as functions of temperature and pressure can be observed in Figs. 19–21.

Predictive uncertainties

Uncertainties in calculated standard partial molal properties of neutral aqueous species at high temperatures and pressures arise in part from uncertainties in estimated equation of state parameters. A detailed discussion of the estimation procedure, uncertainties in estimated equation of state parameters, and the extent to which these uncertainties are manifested in calculated standard partial molal properties of aqueous ions and electrolytes is given elsewhere (SHOCK and HELGESON, 1988). This discussion applies also to neutral aqueous species. However, in the case of the latter species, additional uncertainties in predicted equilibrium constants and standard partial molal properties at high temperatures and pressures arise from uncertainties in values of $\omega_{aq}$ obtained either by regression of experimental
Fig. 15. Logarithms of the equilibrium constants for acid dissociation reactions as functions of temperature at $P_{SAT}$, and in the case of carbonic acid at higher pressures (labeled in kb). The symbols represent experimental data, but the curves for all of the reactions except the dissociation of HF correspond to independent predictions at temperatures $> 25^\circ C$, which were generated from Eqs. (12) and (31)-(33) using parameters and thermodynamic data for the neutral aqueous species taken from Tables 4 and 7, and those for the aqueous ions given by SHUCK and HELGESON (1988). The curve shown in the plot for HF dissociation was generated by regression of the data with Eqs. (31)-(38) to obtain a value of $C^\circ$ for the aqueous HF ion pair at $25^\circ C$ and 1 bar.

Fig. 16. Logarithm of the equilibrium constant for the first dissociation of $H_2PO_4^{\circ}$ as a function of temperature at 1 and 2 kb. The symbols represent experimental data, but the curves correspond to independent predictions generated from Eqs. (12) and (31)-(33) using parameters and thermodynamic data taken from Table 4 and SHUCK and HELGESON (1988).

Data or estimated from the correlations represented by Eqs. (44) and (45). The latter uncertainties do not affect $\omega_j$ values for simple ions, which can be calculated from Eqs. (17) and (18). Values of $\omega_j$, generated by regression of experimental values of log $K$ at a series of temperatures are considerably more uncertain than those obtained by regression of experimental standard partial molal volumes or heat capacities. Uncertainties in $\omega_{ij}$ are generally less than $\sim 10^4$ cal mol$^{-1}$. Assuming a "typical" uncertainty in $\omega_{ij}$ of $\pm 5000$ cal mol$^{-1}$ leads to a corresponding uncertainty in $\Delta G^0$ of $\pm 2.6$ cal mol$^{-1}$ at $25^\circ C$ and 1 kb. At $500^\circ C$ and 1 kb, the corresponding uncertainty in $\Delta G^0$ is $\pm 328$ cal mol$^{-1}$. With increasing pressure to 5 kb, the uncertainty in $\Delta G^0$ at $500^\circ C$ decreases to $\pm 61$ cal mol$^{-1}$, but increases with increasing temperature at 5 kb to $\pm 337$ cal mol$^{-1}$ at $1000^\circ C$. It should be noted in this
Fig. 17. pH as a function of temperature and pressure from 0 to 500°C and $P_{\text{SAT}}$ to 5 kb for equal activities of aqueous $\text{H}_2\text{S}$ and $\text{HS}^-$, $\text{H}_3\text{PO}_4$ and $\text{H}_2\text{PO}_4^-$, and $\text{H}_2\text{PO}_4$ and $\text{HPO}_4^{2-}$. The curves were generated with the aid of Eqns. (12) and (31)-(33) using parameters and thermodynamic data taken from Table 4 and SHOCK and HELGESON (1988).

Fig. 18. Standard partial molar volumes ($\bar{V}$) of aqueous $\text{O}_2$, $\text{CO}_2$, $\text{H}_2\text{S}$ and $\text{SiO}_2$ as a function of temperature at $P_{\text{SAT}}$ and constant higher pressures (labeled in kb) calculated from Eqn. (27) using parameters and thermodynamic data taken from Tables 4 and 7.

regard that uncertainties in calculated high-temperature/pressure standard partial molal properties of aqueous species arising from uncertainties in $\bar{v}$ are generally less than those arising from uncertainties in the nonsolvation equation of state parameters discussed by SHOCK and HELGESON (1988).

Because the standard partial molal properties of aqueous species approach either $\infty$ or $-\infty$ at the critical point of $\text{H}_2\text{O}$, uncertainties attending calculation of their standard partial molal properties are greatest in the critical region. However, they decrease dramatically with increasing pressure and/or increasing or decreasing temperature from the critical point. In addition to uncertainties in $\bar{C}_p$ resulting from uncertainties in the nonsolvation equation of state parameters adduced above, a typical uncertainty of $\pm 5000$ cal mol$^{-1}$ in $\bar{v}$ leads to an uncertainty in $\bar{C}_p(\delta\bar{C}_p)$ of $\pm 0.5$ cal mol$^{-1}$ K$^{-1}$ at 25°C and 1 bar, which decreases with increasing pressure to $\pm 0.36$ cal mol$^{-1}$ K$^{-1}$ at 25°C and 1 kb. However, $\delta\bar{C}_p$ then increases with increasing temperature, reaching $\pm 18.2$ cal mol$^{-1}$ K$^{-1}$ in the supercritical region at 500°C and 1 kb. From there the uncertainty in $\bar{C}_p$ decreases with increasing temperature and pressure to $\pm 0.92$ cal mol$^{-1}$ K$^{-1}$.

Fig. 19. Standard partial molar heat capacities ($\bar{C}_p$) of aqueous $\text{O}_2$, $\text{CO}_2$, $\text{H}_2\text{S}$ and $\text{SiO}_2$ as a function of temperature at $P_{\text{SAT}}$ and constant higher pressures (labeled in kb) calculated from Eqn. (28) using equation of state parameters and thermodynamic data taken from Tables 4 and 7.

Fig. 20. Standard partial molar entropies ($\bar{S}$) of aqueous $\text{O}_2$, $\text{CO}_2$, $\text{H}_2\text{S}$ and $\text{SiO}_2$ as a function of temperature at $P_{\text{SAT}}$ and constant higher pressures (labeled in kb) calculated from Eqn. (29) using equation of state parameters and thermodynamic data taken from Tables 4 and 7.
at 1000°C and 5 kb. Similar trends are observed for the other standard partial molal properties. For example, the uncertainty in $\bar{\omega}$ arising from an uncertainty in $\omega_{0}$ of ±5000 cal mol⁻¹ is ±0.12 cm³ mol⁻¹ at 25°C and 1 bar, ±3.4 × 10⁻² cm³ mol⁻¹ at 25°C and 1 kb, ±17.2 cm³ mol⁻¹ at 500°C and 1 kb, and ±5.4 cm³ mol⁻¹ at 1000°C and 5 kb.

CONCLUDING REMARKS

The equations, correlations and parameters summarized above can be employed together with Born functions (Helgeson and Kirkham, 1974a; Shock et al., 1989) to calculate $P^{0}$, $C^{0}$, $S^{0}$, $\Delta H^{0}$ and $\Delta S^{0}$ for many neutral aqueous species at high pressures and temperatures. These calculated values can then be used together with corresponding values for ionic aqueous species (Shock and Helgeson, 1988) and minerals (Helgeson et al., 1978) to predict equilibrium constants and other reaction properties for acid dissociation and solubility reactions to 5 kb and 1000°C. The equations and correlation algorithms summarized above can be extended to include neutral organic aqueous species (Shock and Helgeson, 1989) and neutral inorganic aqueous metal complexes (Sverjensky et al., 1989). Calculated equilibrium constants for various reactions involving these species agree closely with their experimental counterparts, both along the vapor-liquid saturation curve for H₂O and at supercritical temperatures and pressures. These calculations make it possible to characterize both homogeneous and heterogeneous equilibria (Sverjensky, 1987) and diffusional transport (Oelkers and Helgeson, 1988) in a wide variety of geochemical processes at magmatic temperatures and pressures. The revised HKF equations of state, their adaptations to neutral species, and their extension to 5 kb and 1000°C have been incorporated in a revised version of the computer program SUPCRT (SUPCRT 89), which is available together with a new data file including all of the species listed in Tables 4 and 7 from the Laboratory of Theoretical Geochemistry (otherwise known as Prediction Central) at the University of California, Berkeley.

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