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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 H_2O 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 ($\bar{V}^0$), heat capacity ($\bar{C}_P^0$), and entropy ($\bar{S}^0$), together with the apparent standard partial molal enthalpy of formation ($\Delta\bar{H}^0$) of many of these species in the liquid phase minimize with increasing temperature at P_{SAT}* and approach ∞ at the critical point of H_2O. In the case of other neutral aqueous species such as $SiO_{2(aq)}$, $\bar{V}^0$, $\bar{C}_P^0$, $\bar{S}^0$, and $\Delta\bar{H}^0$ behave as functions of temperature and pressure like those of electrolytes in the liquid phase and maximize with increasing temperature at P_{SAT}, approaching $-\infty$ at the critical point of H_2O. Which of these types of behavior is exhibited by $\bar{V}^0$, $\bar{C}_P^0$, $\bar{S}^0$, and $\Delta\bar{H}^0$ 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 CO_2 and H_2S, which react with H_2O 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

$$H_2S_{(v)} = H_2S_{(aq)} \quad (1)$$

and

$$H_2S_{(aq)} = HS^- + H^+, \quad (2)$$

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; WAUCHOPE 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 H_2O 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

* P_{SAT} represents pressures corresponding to liquid-vapor equilibrium for the system H_2O, except at temperatures < 100°C where it refers to the reference pressure of 1 bar.

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

$$k_H \equiv \frac{f_{j(v)}}{X_{j(aq)}} = \frac{\chi_{j(v)} p_{j(v)}}{X_{j(aq)}} \quad (3)$$

where $X_{j(aq)}$ stands for the mole fraction of the jth aqueous species and $f_{j(v)}$, $\chi_{j(v)}$ and $p_{j(v)}$ correspond to the fugacity, fugacity coefficient and partial pressure of the jth 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

$$A_{(aq)} = A_{(v)} \quad (4)$$

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

$$K = \frac{k_H}{\lambda_{j(aq)}} = \frac{f_{j(v)}}{a_{j(aq)}} = \frac{\chi_{j(v)} p_{j(v)}}{X_{j(aq)} \lambda_{j(aq)}} \quad (5)$$

which corresponds to the reciprocal of the equilibrium constant for

$$A_{(v)} = A_{(aq)} \quad (6)$$

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

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

Henry's Law Constant

Henry's Law constants (k_H) are referenced either to pressures in atmospheres, bars, or mm of Hg. The relations between these values of k_H and K can be expressed as

$$K = \frac{55.51}{k_H} \quad \text{for } k_H \text{ in bars.} \quad (A)$$

$$K = \frac{54.78}{k_H} \quad \text{for } k_H \text{ in atmospheres.} \quad (B)$$

and

$$K = \frac{7.4007 \times 10^{-2}}{k_H} \quad \text{for } k_H \text{ in mm of Hg.} \quad (C)$$

The unit 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

$$K = \frac{0.9869}{k_D} \quad (D)$$

Bunsen Absorption Coefficient

There are numerous Bunsen absorption coefficients in the literature, all of which refer to gas solubility on a volumetric basis. Although the symbols α and β are used by most authors, there are a variety of definitions, and care must be taken in converting these Bunsen absorption coefficients to the standard state used in the present study. Strictly, the Bunsen absorption coefficient designated by the symbol α refers to the volume of gas (reduced to 0°C and 760 mm of Hg by the ideal gas law) which is absorbed by a unit volume of liquid under a *partial pressure of the gas* of 760 mm of Hg. In contrast, the Bunsen absorption coefficient β designates the volume of gas (reduced to 0°C and 760 mm of Hg by the ideal gas law) which is absorbed by a unit volume of liquid under a *total pressure* of 760 mm Hg. The relation between α and β can be written as

$$\beta = \alpha \frac{760 - P_s}{760} \quad (E)$$

where P_s stands for the partial pressure of the solvent. The relation between k_H and α is given by

$$k_H = \frac{RT_r P_r \rho_s}{\alpha M_s} + P_r \quad (F)$$

where ρ_s and M_s refer to the density and molecular weight of the solvent, respectively, T_r and P_r stand for the reference temperature and pressure, and R designates the gas constant in the units appropriate to the choice of T_r and P_r, and the units used to express α. Although not the case in the present study, the second term on the right side of Eqn. (F) is often neglected. Relations between α and K can be obtained by substituting Eqn. (F) into Eqns. (A), (B), or (C), depending on the units in which the Bunsen absorption coefficients are reported.

Ostwald Coefficient

The Ostwald coefficient is defined as the ratio of the volume of the absorbed gas to the volume of the solvent and is generally designated L. It is related to the α Bunsen absorption coefficient by

$$L = \frac{\alpha T}{T_r} \quad (G)$$

where T refers to the temperature of the measurement. Substituting Eqn. (G) into Eqn. (F) yields

$$k_H = \frac{RT_r P_r \rho_s}{LM_s} + P_r \quad (H)$$

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

Standard Cubic Feet per Barrel

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 1.311×10^{-4} (Price, 1979), and the conversion factor to molality is 7.278×10^{-3}. Values of molality obtained in this manner were used together with Eqn. (7) to generate values of K for use in the present study and by Shock and Helgeson (1989).

$$K = \frac{a_{j(\mathrm{aq})}}{f_{j(\mathrm{v})}} = \frac{\gamma_{j(\mathrm{aq})} m_{j(\mathrm{aq})}}{\chi_{j(\mathrm{v})} p_{j(\mathrm{v})}} \tag{7}$$

where $\gamma_{j(\mathrm{aq})}$ and $m_{j(\mathrm{aq})}$ stand for the molal activity coefficient and molality of the jth 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 ($\bar{C}^0_P$) and entropy ($\bar{S}^0$), together with the apparent standard partial molal enthalpy ($\Delta\bar{H}^0$) and Gibbs free energy of formation ($\Delta\bar{G}^0$), are given by (TANGER and HELGESON, 1988)

$$\begin{aligned}\bar{V}^0 &= \Delta\bar{V}^0_{\mathrm{n}} + \Delta\bar{V}^0_{\mathrm{s}} \\ &= \sigma + \frac{\xi}{T-\Theta} - \omega Q + \left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial\omega}{\partial P}\right)_T \\ &= a_1 + \frac{a_2}{\Psi + P} + \left(a_3 + \frac{a_4}{\Psi + P}\right)\left(\frac{1}{T-\Theta}\right) \\ &\quad - \omega Q + \left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial\omega}{\partial P}\right)_T, \end{aligned} \tag{8}$$

$$\begin{aligned}\bar{C}^0_P &= \Delta\bar{C}^0_{P,\mathrm{n}} + \Delta\bar{C}^0_{P,\mathrm{s}} \\ &= c_1 + \frac{c_2}{(T-\Theta)^2} - \left(\frac{2T}{(T-\Theta)^3}\right)\left(a_3(P-P_{\mathrm{r}}) \right. \\ &\quad \left. + a_4 \ln\left(\frac{\Psi + P}{\Psi + P_{\mathrm{r}}}\right)\right) + \omega T X + 2TY\left(\frac{\partial\omega}{\partial T}\right)_P \\ &\quad - T\left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial^2\omega}{\partial T^2}\right)_P, \end{aligned} \tag{9}$$

$$\begin{aligned}\bar{S}^0 &= \Delta\bar{S}^0_{\mathrm{n}} + \Delta\bar{S}^0_{\mathrm{s}} \\ &= \bar{S}^0_{P_{\mathrm{r}},T_{\mathrm{r}}} + c_1 \ln\left(\frac{T}{T_{\mathrm{r}}}\right) - \frac{c_2}{\Theta}\left[\left(\frac{1}{T-\Theta}\right)\right. \\ &\quad \left. - \left(\frac{1}{T_{\mathrm{r}}-\Theta}\right) + \frac{1}{\Theta}\ln\left(\frac{T_{\mathrm{r}}(T-\Theta)}{T(T_{\mathrm{r}}-\Theta)}\right)\right] \\ &\quad + \left(\frac{1}{T-\Theta}\right)^2\left(a_3(P-P_{\mathrm{r}}) + a_4 \ln\left(\frac{\Psi + P}{\Psi + P_{\mathrm{r}}}\right)\right) \\ &\quad - \omega Y - \left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial\omega}{\partial T}\right)_P - \omega_{P_{\mathrm{r}},T_{\mathrm{r}}} Y_{P_{\mathrm{r}},T_{\mathrm{r}}}, \end{aligned} \tag{10}$$

$$\begin{aligned}\Delta\bar{H}^0 &\equiv \Delta\bar{H}^0_{\mathrm{f}} + (\bar{H}^0_{P,T} - \bar{H}^0_{P_{\mathrm{r}},T_{\mathrm{r}}}) \\ &= \Delta\bar{H}^0_{\mathrm{f}} + c_1(T - T_{\mathrm{r}}) - c_2\left(\left(\frac{1}{T-\Theta}\right) - \left(\frac{1}{T_{\mathrm{r}}-\Theta}\right)\right) \\ &\quad + a_1(P - P_{\mathrm{r}}) + a_2 \ln\left(\frac{\Psi + P}{\Psi + P_{\mathrm{r}}}\right) \\ &\quad + \left(\frac{2T-\Theta}{(T-\Theta)^2}\right)\left(a_3(P-P_{\mathrm{r}}) + a_4 \ln\left(\frac{\Psi + P}{\Psi + P_{\mathrm{r}}}\right)\right) \\ &\quad + \omega\left(\frac{1}{\epsilon} - 1\right) + \omega T Y - T\left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial\omega}{\partial T}\right)_P \\ &\quad - \omega_{P_{\mathrm{r}},T_{\mathrm{r}}}\left(\frac{1}{\epsilon_{P_{\mathrm{r}},T_{\mathrm{r}}}} - 1\right) - \omega_{P_{\mathrm{r}},T_{\mathrm{r}}} T_{\mathrm{r}} Y_{P_{\mathrm{r}},T_{\mathrm{r}}} \end{aligned} \tag{11}$$

and

$$\begin{aligned}\Delta\bar{G}^0 &\equiv \Delta\bar{G}^0_{\mathrm{f}} + (\bar{G}^0_{P,T} - \bar{G}^0_{P_{\mathrm{r}},T_{\mathrm{r}}}) \\ &= \Delta\bar{G}^0_{\mathrm{f}} - \bar{S}^0_{P_{\mathrm{r}},T_{\mathrm{r}}}(T - T_{\mathrm{r}}) - c_1\left(T \ln\left(\frac{T}{T_{\mathrm{r}}}\right) - T + T_{\mathrm{r}}\right) \\ &\quad + a_1(P - P_{\mathrm{r}}) + a_2 \ln\left(\frac{\Psi + P}{\Psi + P_{\mathrm{r}}}\right) - c_2\left[\left(\left(\frac{1}{T-\Theta}\right)\right.\right. \\ &\quad \left.\left. - \left(\frac{1}{T_{\mathrm{r}}-\Theta}\right)\right)\left(\frac{\Theta - T}{\Theta}\right) - \frac{T}{\Theta^2}\ln\left(\frac{T_{\mathrm{r}}(T-\Theta)}{T(T_{\mathrm{r}}-\Theta)}\right)\right] \\ &\quad + \left(\frac{1}{T-\Theta}\right)\left(a_3(P-P_{\mathrm{r}}) + a_4 \ln\left(\frac{\Psi + P}{\Psi + P_{\mathrm{r}}}\right)\right) \\ &\quad + \omega\left(\frac{1}{\epsilon} - 1\right) - \omega_{P_{\mathrm{r}},T_{\mathrm{r}}}\left(\frac{1}{\epsilon_{P_{\mathrm{r}},T_{\mathrm{r}}}} - 1\right) \\ &\quad + \omega_{P_{\mathrm{r}},T_{\mathrm{r}}} Y_{P_{\mathrm{r}},T_{\mathrm{r}}}(T - T_{\mathrm{r}}) \end{aligned} \tag{12}$$

where $\Delta\bar{V}^0_{\mathrm{n}}$, $\Delta\bar{C}^0_{P,\mathrm{n}}$, and $\Delta\bar{S}^0_{\mathrm{n}}$ stand for the nonsolvation (or structural) contributions to $\bar{V}^0$, $\bar{C}^0_P$, and $\bar{S}^0$, respectively, $\Delta\bar{V}^0_{\mathrm{s}}$, $\Delta\bar{C}^0_{P,\mathrm{s}}$, and $\Delta\bar{S}^0_{\mathrm{s}}$ represent the solvation contributions to $\bar{V}^0$, $\Delta\bar{C}^0_P$, and $\bar{S}^0$, σ, ξ, 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, $\Delta\bar{H}^0_{\mathrm{f}}$ and $\Delta\bar{G}^0_{\mathrm{f}}$ denote the standard partial molal enthalpy and Gibbs free energy of formation from the elements in their stable form at P_{r} and T_{r}, $(\bar{H}^0_{P,T} - \bar{H}^0_{P_{\mathrm{r}},T_{\mathrm{r}}})$ and $(\bar{G}^0_{P,T} - \bar{G}^0_{P_{\mathrm{r}},T_{\mathrm{r}}})$ correspond to the difference in the conventional standard partial molal enthalpy and Gibbs free energy of formation of an aqueous species at P and T and those at P_{r}, T_{r}, ϵ stands for the dielectric constant of H_2O, Ψ and Θ refer to solvent parameters equal to 2600 bars and 228 K, respectively, Q, X, and Y denote Born functions given by

$$Q \equiv \frac{1}{\epsilon}\left(\frac{\partial \ln \epsilon}{\partial P}\right)_T, \tag{13}$$

$$X \equiv \frac{1}{\epsilon}\left(\left(\frac{\partial^2 \ln \epsilon}{\partial T^2}\right)_P - \left(\frac{\partial \ln \epsilon}{\partial T}\right)_P^2\right), \quad (14)$$

and

$$Y \equiv \frac{1}{\epsilon}\left(\frac{\partial \ln \epsilon}{\partial T}\right)_P, \quad (15)$$

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

$$\omega_j \equiv \omega_j^{\mathrm{abs}} - Z_j \omega_{\mathrm{H}^+}^{\mathrm{abs}} \quad (16)$$

where Z_j stands for the formal charge on the jth aqueous species, $\omega_{\mathrm{H}^+}^{\mathrm{abs}}$ refers to the absolute Born coefficient of the hydrogen ion, which is taken to be 0.5387×10^5 cal mol^{-1} at 25°C and 1 bar (HELGESON and KIRKHAM, 1976), and ω_j^{abs} designates the absolute Born coefficient of the jth species given by

$$\omega_j^{\mathrm{abs}} \equiv \frac{N^0 e^2 Z_j^2}{2 r_{e,j}} = \frac{\eta Z_j^2}{r_{e,j}} \quad (17)$$

where N^0 represents Avogadro's number (6.02252×10^{23} mol^{-1}), e stands for the absolute electronic charge (4.80298×10^{-10} esu), $\eta = 1.66027 \times 10^5$ Å cal mol^{-1}, and $r_{e,j}$ denotes the effective electrostatic radius of the jth species given by

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

where

$$\Gamma_\pm \equiv k_z + g \quad (19)$$

where k_z 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 (ω_k) and its partial derivatives computed from fits of Eqns. (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^0 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, $\Gamma_\pm$, and therefore $r_{e,j}$, are essentially constant at temperatures below 170°C, and pressures corresponding to the vapor-liquid saturation curve for H_2O (P_{SAT}). $\Gamma_\pm$ and $r_{e,j}$ are also essentially constant at (SHOCK *et al.*, 1989)

$$T < 175°\mathrm{C} \quad \text{if} \quad P \leq 2450 \text{ bars} \quad (20a)$$

and

$$\rho > 1.0 \text{ gm cm}^{-3} \quad \text{if} \quad 2450 \text{ bars} < P \leq 5000 \text{ bars}. \quad (20b)$$

Values of ϵ and the Born functions defined by Eqns. (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; HIMMELBLAU, 1959; REISS *et al.*, 1959; PRAUSNITZ and SHAIR, 1961; NEMETHY and SCHERAGA, 1962a,b; PIEROTTI, 1963, 1965, 1976; BEN-NAIM, 1965a,b,c, 1975, 1978, 1980, 1987; BEN-NAIM and EGEL-THAL, 1965; NEMETHY, 1967; WILHELM and BATTINO, 1971, 1972; TIEPEL and GUBBINS, 1972; LUCAS, 1973, 1976; NEFF and MCQAURRIE, 1973; STILLINGER, 1973; WILHELM, 1973, 1986; REYNOLDS *et al.*, 1974; YAACOBI and BEN-NAIM, 1974; DE LIGNY 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 CARGILL, 1977; PRATT and CHANDLER, 1977; WILHELM *et al.*, 1977; SHINODA, 1977; DESNOYERS, 1982; CROVETTO *et al.*, 1982b; ALVAREZ *et al.*, 1983; LEE, 1983, 1985; HU *et al.*, 1985; FERNANDEZ-PRINI *et al.*, 1985; PRATT, 1985; FERNANDEZ-PRINI and JAPAS, 1986; 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 representation of available experimental data for reactions involving these species. Despite the fact that 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_2O 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 $B(OH)_{3(aq)}$, $NH_{3(aq)}$ and $H_2S_{(aq)}$ at P_{SAT} all increase with increasing temperature, which is also true of the standard partial molal heat capacity of $NH_{3(aq)}$ at P_{SAT}. In contrast, the standard partial molal heat capacities of $Ar_{(aq)}$ at 172 bars and $H_2S_{(aq)}$ at P_{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.

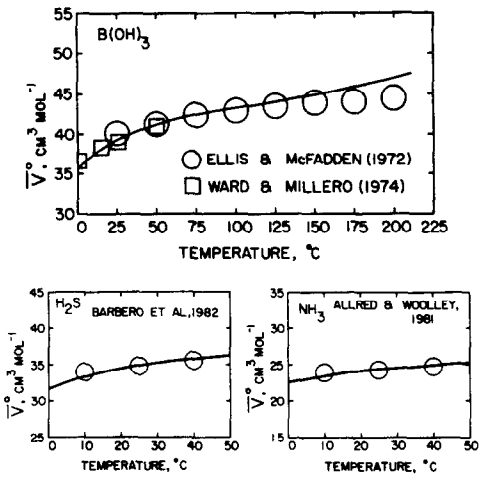

FIG. 1. Standard partial molal volumes ($\bar{V}^0$) of inorganic neutral aqueous species as a function of temperature at P_{SAT}. The symbols represent experimental data taken from the sources shown in the figure, but the curves were generated from Eqns. (22) and (25) using parameters given in Table 2.

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 *et al.*, 1985) increases to an increasing degree with increasing temperature above ~100°C. Recent experimental evidence (BIGGERSTAFF and WOOD, 1988a,b) indicates that $\bar{V}^0$, $\bar{C}_P^0$, $\bar{S}^0$, and $\Delta\bar{H}^0$ of aqueous Ar, Xe, and C_2H_4 in the liquid phase increase and approach ∞ as temperature increases at P_{SAT} to the critical point of H_2O. In contrast, $\bar{V}^0$, $\bar{C}_P^0$, $\bar{S}^0$, and $\Delta\bar{H}^0$ of aqueous electrolytes in the liquid phase approach $-\infty$ as temperature increases at P_{SAT} to the critical point of H_2O (WHEELER, 1972; HELGESON and KIRKHAM, 1974b; WALTHER and HELGESON, 1977; COBBLE and MURRAY, 1977; GATES *et al.*, 1982; WOOD and QUINT, 1982; LEVELT SENGERS *et al.*, 1986). The latter behavior is consistent with increasingly weaker attractive forces between ions and H_2O dipoles as the solvent expands and the dielectric constant diminishes with increasing temperature at high temperatures. In contrast, the behavior of the standard partial molal properties of highly volatile neutral aqueous species in the critical region of the system H_2O can be attributed to increasing repulsion of H_2O molecules by the neutral species as hydrogen bonding among the solvent dipoles becomes weaker with increasing temperature. This is apparently not the case at lower temperatures, where the density of the solvent is much higher (FERNANDEZ-PRINI *et al.*, 1985). However, at the temperatures and pressures in the critical region where the density and dielectric constant of the solvent are low and $(\partial\bar{V}^0/\partial T)_P$, $(\partial\bar{V}^0/\partial P)_T$, $(\partial\epsilon/\partial T)_P$, and $(\partial\epsilon/\partial P)_T$ of H_2O are high, the presence of a volatile neutral molecule would be expected to have a substantial disruptive effect on the electrostatic properties of the solvent in the vicinity of the neutral species. This observation is consistent with MULLER's (1988) recent model calculations for water and dilute aqueous solutions of hydrocarbons, which indicate that hydrophobic molecules disrupt the water structure at high temperatures. Nonvolatile and/or highly polar molecules should attract H_2O dipoles and behave like electrolytes, but their volatile and nonpolar or weakly polar counterparts would be expected to repel water dipoles and disrupt solvent dipole-dipole interaction. It thus seems appropriate to describe the effect of a neutral species on the electrostatic properties of the solvent in terms of a hypothetical species with an effective charge and electrostatic radius. The effective electrostatic radius is positive if attractive forces dominate between the neutral molecules and neighboring H_2O dipoles, but negative if repulsive forces dominate between these species. This formalism permits effective Born coefficients to be defined for neutral aqueous species (see below). Values of these coefficients can be obtained by regression of experimental data with the revised HKF equations of state. In most cases, the effective Born coefficients of neutral aqueous molecules are negative as a consequence of repulsive disruption of electrostatic dipole-dipole interaction in the vicinity of the molecule.

EXTENSION OF THE REVISED HKF MODEL TO INCLUDE NEUTRAL AQUEOUS SPECIES

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

$$\omega_{e,j} = \frac{Z_{e,j}^2 \eta}{r_{e,j}} \tag{21}$$

where $Z_{e,j}$ and $r_{e,j}$ refer to the effective charge and effective electrostatic radius of the jth 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 $\omega_{e,j}$ from Eqn. (21). However, values of $\omega_{e,j}$ 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 jth 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

$$\Delta\bar{V}_s^0 = \bar{V}^0 - \Delta\bar{V}_n^0 = -\omega_e Q \tag{22}$$

$$\Delta\bar{C}_{P,s}^0 = \bar{C}_P^0 - \Delta\bar{C}_{P,n}^0 = \omega_e TX \tag{23}$$

$$\Delta\bar{S}_s^0 = \bar{S}^0 - \Delta\bar{S}_n^0 = \omega_e Y \tag{24}$$

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

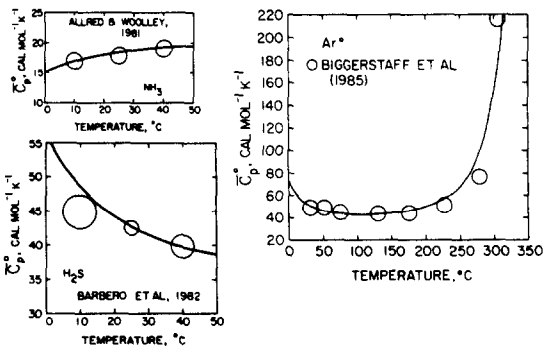

FIG. 2. Standard partial molal heat capacities ($\bar{C}_P^0$) of inorganic neutral aqueous species as a function of temperature at P_{SAT}, or in the case of $Ar_{(aq)}$ at 172 bars. The symbols represent experimental data taken from the sources shown in the figure, but the curves were generated from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

(13)–(15). The temperature dependence of $\Delta\bar{V}^0_n$ can be expressed as

$$\Delta\bar{V}^0_n = \sigma + \xi\left(\frac{1}{T-\Theta}\right) \quad (25)$$

where

$$\sigma = a_1 + a_2\left(\frac{1}{\Psi+P}\right) \quad (25a)$$

and

$$\xi = a_3 + a_4\left(\frac{1}{\Psi+P}\right) \quad (25b)$$

and that of $\Delta\bar{C}^0_{P,n}$ at $P = P_r$ as

$$\Delta\bar{C}^0_{P,n} = c_1 + c_2\left(\frac{1}{T-\Theta}\right)^2. \quad (26)$$

Equations (25) and (26) can also be used together with values of σ and ξ for $P = P_r$ to represent closely the nonsolvation standard partial molal 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_2O is only 15.537 bars (HAAR *et al.*, 1984). Complete expressions of the temperature and pressure dependence of the standard partial molal volumes and heat capacities of neutral species analogous to Eqns. (8) and (9) are given by

$$\bar{V}^0 = a_1 + a_2\left(\frac{1}{\Psi+P}\right) + \left(a_3 + a_4\left(\frac{1}{\Psi+P}\right)\right)\left(\frac{1}{T-\Theta}\right) - \omega_e Q \quad (27)$$

and

$$\bar{C}^0_P = c_1 + c_2\left(\frac{1}{T-\Theta}\right)^2 - \left[2T\left(\frac{1}{T-\Theta}\right)^3 \times \left(a_3(P-P_r) + a_4 \ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\right)\right] + \omega_e T X. \quad (28)$$

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

$$\bar{S}^0 = \bar{S}^0_{P_r,T_r} + c_1 \ln\left(\frac{T}{T_r}\right) - \frac{c_2}{\Theta}\left[\left(\frac{1}{T-\Theta}\right) - \left(\frac{1}{T_r-\Theta}\right) + \frac{1}{\Theta}\ln\left(\frac{T_r(T-\Theta)}{T(T_r-\Theta)}\right)\right] + \left(\frac{1}{T-\Theta}\right)^2 \times \left[a_3(P-P_r) + a_4 \ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\right] + \omega_e(Y - Y_{P_r,T_r}). \quad (29)$$

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

$$\Delta\bar{H}^0 \equiv \Delta\bar{H}^0_f + (\bar{H}^0_{P,T} - \bar{H}^0_{P_r,T_r})$$

$$= \Delta\bar{H}^0_f + c_1(T-T_r) - c_2\left(\left(\frac{1}{T-\Theta}\right) - \left(\frac{1}{T_r-\Theta}\right)\right) + a_1(P-P_r) + a_2 \ln\left(\frac{\Psi+P}{\Psi+P_r}\right) + \left(\frac{2T-\Theta}{(T-\Theta)^2}\right)\left(a_3(P-P_r) + a_4 \ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\right) + \omega_e\left(TY_{P,T} - T_rY_{P_r,T_r} - \left(\frac{1}{\epsilon_{P_r,T_r}} - 1\right) + \left(\frac{1}{\epsilon_{P,T}} - 1\right)\right) \quad (30)$$

and

$$\Delta\bar{G}^0 \equiv \Delta\bar{G}^0_f + (\bar{G}^0_{P,T} - \bar{G}^0_{P_r,T_r})$$

$$= \Delta\bar{G}^0_f - \bar{S}^0_{P_r,T_r}(T-T_r) - c_1\left(T\ln\left(\frac{T}{T_r}\right) - T + T_r\right) + a_1(P-P_r) + a_2\ln\left(\frac{\Psi+P}{\Psi+P_r}\right) - c_2\left[\left(\left(\frac{1}{T-\Theta}\right) - \left(\frac{1}{T_r-\Theta}\right)\right)\left(\frac{\Theta-T}{\Theta}\right) - \frac{T}{\Theta^2}\ln\left(\frac{T_r(T-\Theta)}{T(T_r-\Theta)}\right)\right] + \left(\frac{1}{T-\Theta}\right)\left(a_3(P-P_r) + a_4\ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\right) + \omega_e\left(Y_{P_r,T_r}(T-T_r) + \left(\frac{1}{\epsilon_{P,T}} - 1\right) - \left(\frac{1}{\epsilon_{P_r,T_r}} - 1\right)\right). \quad (31)$$

REGRESSION OF EXPERIMENTAL DATA

The experimentally determined isobaric standard partial molal heat capacities of aqueous argon represented by the symbols in Fig. 2 were regressed in the present study with Eqns. (23) and (26) to obtain the c_1, c_2 and ω_e parameters for $Ar_{(aq)}$ given in Table 2. The results of these regression calculations are represented by the curve shown in Fig. 2. The value of $\omega_{e,Ar}$ (-0.3073×10^5 cal mol^{-1}) is opposite in sign but similar in magnitude to that of ω_{Na^+} (0.3306×10^5 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_2O 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 ω_{Na^+}.

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

Species	c_1[a]	$c_2 \times 10^{-4}$[b]	σ[c]	ξ[d]	$\omega_e \times 10^{-5}$[e]
$H_2S_{(aq)}$	32.3	4.73	38.13	−2.37	−0.1
$NH_{3(aq)}$	20.3	−1.17	25.8	−0.98	−0.05
$Ar_{(aq)}$	35.65	7.316			−0.3073
$B(OH)_{3(aq)}$			43.8	−3.5	−0.2

a. Cal mol^{-1} K^{-1}. b. Cal K mol^{-1}. c. Cm^3 mol^{-1}. d. Cm^3 K mol^{-1}. e. Cal mol^{-1}.

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 H_2O. These data can be regressed simultaneously with experimental standard partial molal 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

$$\log K = \frac{-\Delta \bar{G}^0_r}{2.303RT} \tag{32}$$

where R stands for the gas constant (1.98719 cal mol^{-1} K^{-1}) and $\Delta \bar{G}^0_r$ denotes the standard partial molal Gibbs free energy of the rth reaction given by

$$\Delta \bar{G}^0_r \equiv \sum_r \hat{n}_{i,r} \Delta \bar{G}^0 \tag{33}$$

where $\hat{n}_{i,r}$ stands for the reaction coefficient of the ith species in the reaction, which is positive for products and negative for reactants.

Experimental equilibrium constants for reactions involving $NH_{3(aq)}$ and $H_2S_{(aq)}$ at temperatures and pressures along the vapor-liquid saturation curve for H_2O are represented by the symbols shown in Fig. 3. It can be seen in this figure that the data for these species extend to temperatures of 300 and 350°C, respectively. Because pressure changes along the vapor-liquid saturation curve for H_2O have a negligible effect on the apparent standard partial molal Gibbs free energies of formation ($\Delta \bar{G}^0$) of aqueous species at temperatures $\leq$ 350°C (HELGESON *et al.*, 1981; TANGER and HELGESON, 1988), the data for $H_2S_{(aq)}$ and $NH_{3(aq)}$ 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 ω_e given in Table 2. The values of ω_e obtained in this manner were then used to calculate the values of $\Delta \bar{V}^0_s$ and $\Delta \bar{V}^0_n$ shown in Table 3 from Eqn. (22) using experimental values of $\bar{V}^0$ taken from Table 3. The σ and ξ parameters for $H_2S_{(aq)}$ and $NH_{3(aq)}$ given in Table 2 were obtained by graphical fits of Eqn. (25) to the values of $\Delta \bar{V}^0_n$ 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 $\Delta \bar{C}^0_{P,s}$ from Eqn. (23). These values were then used to compute corresponding values of $\Delta \bar{C}^0_{P,n}$ from the first identity in Eqn. (9) using the experimental values of $\bar{C}^0_P$ listed in Table 3.

Taking account of Eqn. (26), plots of $\Delta \bar{C}^0_{P,n}$ against $1/(T-\Theta)^2$ should fall on linear curves. Plots of this type, generated using the values of $\Delta \bar{C}^0_{P,n}$ given in Table 3, are shown for $Ar_{(aq)}$, $NH_{3(aq)}$, and $H_2S_{(aq)}$ 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 calculated the curves shown. Also shown in Fig. 4 is a plot of $\Delta \bar{V}^0_n$ against $1/(T-\Theta)$ for $B(OH)_{3(aq)}$, which was generated by regression of the experimental $\bar{V}^0$ data for $B(OH)_{3(aq)}$ in Table 3 with Eqn. (25) to obtain the values of σ, ξ and ω_e 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 molal 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

$$a_1 = 1.3684 \times 10^{-2} \Delta \bar{V}^0_n + 0.1765, \tag{34}$$

$$a_2 = 17.19 \Delta \bar{\kappa}^0_n \times 10^4 + 421.1, \tag{35}$$

$$\sigma = 1.11 \Delta \bar{V}^0_n + 1.8, \tag{36}$$

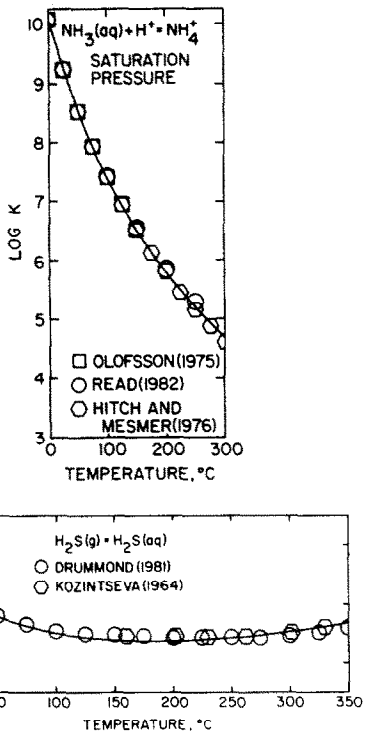

FIG. 3. Logarithms of the equilibrium constants for reactions (1) and (39) as functions of temperature at P_{SAT}. The symbols represent experimental data taken from the references shown in the figure, but the curves were generated by regression of these data and those for H_2S and NH_3 shown in Figs. 1 and 2 with Eqns. (12), (27), (28) and (31)–(33) and equation of state parameters for H^+ and NH_4^+ taken from SHOCK and HELGESON (1988) (see text).

$$a_4 = -4.134 a_2 - 27790., \tag{37}$$

and

$$c_2 \times 10^{-4} = 0.2037 \bar{C}^0_P - 3.0346 \tag{38}$$

where $\Delta \bar{\kappa}^0_n = -(\partial \Delta \bar{V}^0_n / \partial P)_T$. Equation (36) represents the linear correlation of σ with $\Delta \bar{V}^0_n$ 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 $\bar{C}^0_P$ at 25°C and 1 bar in Table 3. Values of c_2 and $\bar{C}^0_P$ for $C_2H_{4(aq)}$ (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

$$NH_{3(aq)} + H^+ = NH_4^+ \tag{39}$$

as a function of temperature at pressures of 1, 2, 3 and 4 kb.

Table 3. Summary of experimental standard partial molal volumes ($\bar{V}°$) and heat capacities ($\bar{C}°_P$), together with the solvation and nonsolvation contributions to the standard partial molal volumes ($\Delta\bar{V}°_s$ and $\Delta\bar{V}°_n$) and heat capacities ($\Delta\bar{C}°_{P,s}$ and $\Delta\bar{C}°_{P,n}$) as a function of temperature for $Ar_{(aq)}$ at 172 bars and $H_2S_{(aq)}$, $NH_{3(aq)}$, and $B(OH)_{3(aq)}$ at P_{SAT}.

$H_2S^a_{(aq)}$						
T	$\bar{V}°$	$\Delta\bar{V}°_s$	$\Delta\bar{V}°_n$	$\bar{C}°_P$	$\Delta\bar{C}°_{P,s}$	$\Delta\bar{C}°_{P,n}$
10	34.04	0.23	33.81	44.8	0.90	43.9
25	34.92	0.25	34.67	42.7	0.92	41.8
40	35.60	0.27	35.33	39.9	0.99	38.9

$NH^b_{3(aq)}$						
T	$\bar{V}°$	$\Delta\bar{V}°_s$	$\Delta\bar{V}°_n$	$\bar{C}°_P$	$\Delta\bar{C}°_{P,s}$	$\Delta\bar{C}°_{P,n}$
10	24.10	0.07	24.03	17.1	0.27	16.8
25	24.43	0.07	24.36	17.9	0.28	17.6
40	24.77	0.08	24.69	19.2	0.30	18.9

$Ar^c_{(aq)}$				$B(OH)^d_{3(aq)}$			
T	$\bar{C}°_P$	$\Delta\bar{C}°_{P,s}$	$\Delta\bar{C}°_{P,n}$	T	$\bar{V}°$	$\Delta\bar{V}°_s$	$\Delta\bar{V}°_n$
32.85	48.7	2.8	45.9	0	36.56	0.45	36.11
51.25	48.7	3.1	45.6	15	38.44	0.47	37.97
75.95	45.7	3.6	42.1	25	39.22	0.49	38.73
130.25	43.2	5.3	37.9	50	41.04	0.59	40.45
175.75	43.9	8.2	35.7	25	40.1	0.49	39.6
227.05	51.6	15.6	36.0	50	41.3	0.59	40.7
278.75	76.6	39.9	36.7	75	42.5	0.74	41.8
				100	43.1	0.95	41.2
				125	43.5	1.25	42.3
				150	44.0	1.69	42.3
				175	44.2	2.34	41.9
				200	44.5	3.33	41.2

a. Barbero et al. (1982). b. Allred and Woolley (1981). c. Biggerstaff et al. (1985) at 172 bars. d. Ward and Millero (1974) and Ellis and McFadden (1972).

The curves were generated from Eqns. (12) and (31)–(33) using parameters for NH_4^+ 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 σ 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 $He_{(aq)}$, $H_3PO_{4(aq)}$, and $N_{2(aq)}$ (see below) provides 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 ≥ 250°C to obtain values of ω_e 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 $\bar{S}^0_j$ and $\bar{C}^0_{P,j}$ 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 $H_3PO_{4(aq)}$. 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 ω_e given in Table 4. In the case of the reaction involving $B(OH)_{3(aq)}$, the value of $\bar{S}^0$ 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 the equation of state parameters except ω_e 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 (1891a), CADY *et al.* (1922), 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 MATHER (1977), GORDON *et al.* (1977), BERG and VANDERZEE (1978), HEPLER and HOPKINS (1979), YASUNISHI and YOSHIDA (1979), GILL and WADSÖ (1982), MOORE *et al.* (1982), PERRIN (1982), PLUMMER and BUSENBERG (1982), BIGNELL (1984), KUTSCHE *et al.* (1984), DEC and GILL (1985), POSTIGO and KATZ (1987), and VERSTEEG and VAN SWAAIJ (1988).

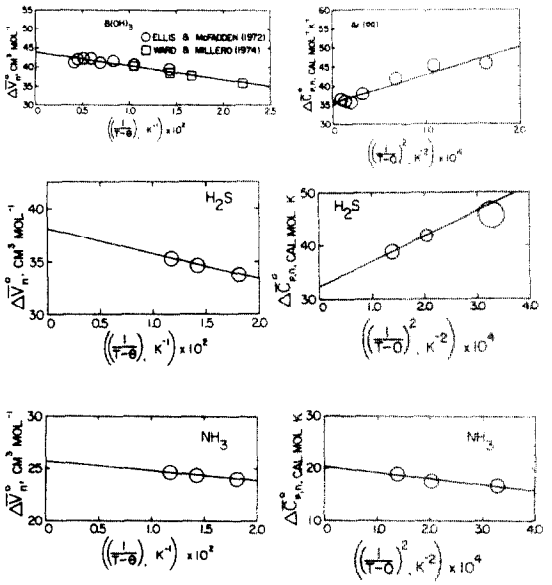

FIG. 4. Graphic representation of Eqns. (25) and (26) for the nonsolvation contributions to the standard partial molal volume ($\Delta\bar{V}^0_n$) and heat capacity ($\Delta\bar{C}^0_{P,n}$) of neutral aqueous species at various temperatures and P_{SAT}. The symbols represent experimental data taken from the references given in Figs. 1 and 2, but the curves correspond to regression values (see text).

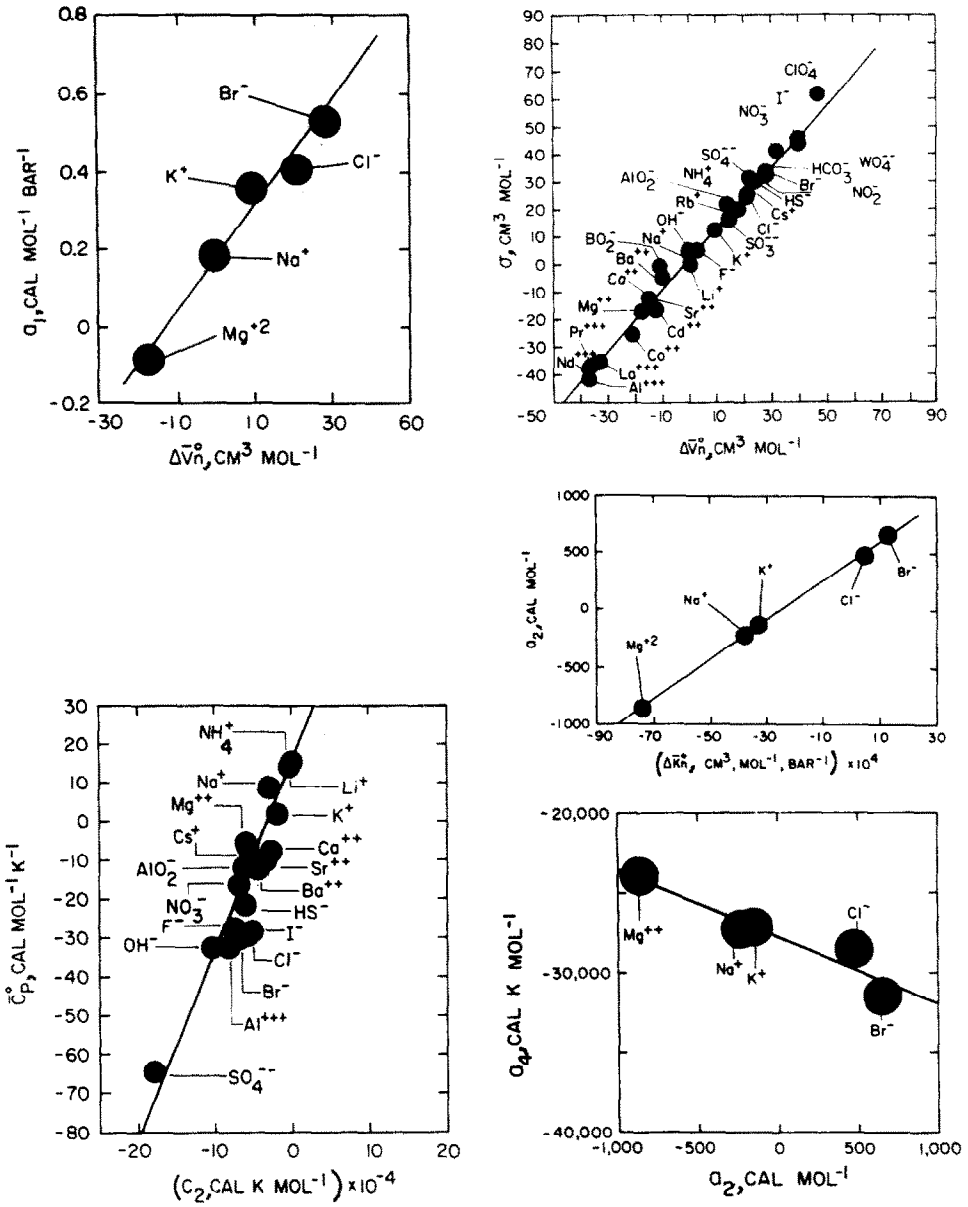

FIG. 5. Summary of correlations observed among equation of state parameters and various standard partial molal properties of inorgnic aqueous ions at 25°C and 1 bar (SHOCK and HELGESON, 1988).

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 $\bar{V}^0_j$ and/or $\bar{C}^0_{P,j}$ at 25°C and 1 bar are available in the literature. Given an independent means of estimating ω_e, Eqns. (12) and (31)–(33) can be used together with the correlation algorithms represented by Eqns. (34)–(38) to regress equilibrium constant data for values of $\bar{V}^0_j$ and/or $\bar{C}^0_{P,j}$ at 25°C and 1 bar. The requisite estimates of $\omega_{e,j}$ for neutral aqueous species can be made by first considering the relation between ω_j and $\bar{S}^0_j$ for aqueous ions.

Correlation of ω_j and $\bar{S}^0_j$

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 $\Gamma_\pm$ is unknown for $Z_j = 0$. As emphasized elsewhere (HELGESON and KIRKHAM, 1976; SHOCK and HELGESON, 1988), $r_{x,j}$ is also ambiguous for polyatomic ionic species. However, estimates of $r_{e,j}$ at 25°C and 1 bar for polyatomic ionic species can be made from their standard partial molal entropies using the relation (SHOCK and HELGESON, 1988)

$$r_{e,j} = \frac{Z_j^2(\eta Y - 100)}{\bar{S}^0_j - \alpha_Z}, \qquad (40)$$

where α_Z represents a charge-dependent constant. Values of $r_{e,j}$ computed from Eqn. (40) permit calculation of ω_j^{abs} from Eqn. (17), which can in turn be used to compute values of ω_j from Eqn. (16) and the standard partial molal solvation

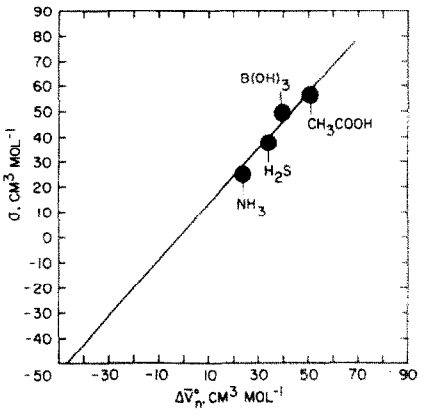

FIG. 6. Correlation of the σ equation of state parameters for neutral aqueous species at 1 bar with their nonsolvation standard partial molal volumes ($\Delta\bar{V}^0_n$) at 25°C and 1 bar. The symbols represent data taken from Table 2 and SHOCK and HELGESON (1989), but the curve was generated from Eqn. (36) and the corresponding correlation for aqueous ions depicted in Fig. 5.

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

$$\bar{S}^0_j - \alpha_Z = \omega_j^{abs}\left(Y - \frac{100}{\eta}\right) \tag{41}$$

which can be combined with Eqn. (16) to yield

$$\omega_j = -1514.4\bar{S}^0_j + \beta_Z \tag{42}$$

where

$$\beta_Z = \frac{-\alpha_Z\eta}{Y\eta - 100} - Z_j\omega^{abs}_{H^+}. \tag{43}$$

Values of β_Z for charged species computed from Eqn. (43) using values of α_Z 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 $\bar{S}^0_j$ and ω_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 $\alpha_z = 0$, β_Z will also equal 0, and therefore Eqn. (42) reduces to

$$\omega_j = \omega_{e,j} = -1514.4\bar{S}^0_j, \tag{44}$$

which was used to generate the lower curve in Fig. 11. The solid symbols shown in this figure represent values of $\bar{S}^0_j$ and $\omega_{e,j}$ 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 $SiO_{2(aq)}$, the open symbols in Fig. 11 represent species in Table 4 for which $\omega_{e,j}$ was obtained in the present study by regression of high-temperature equilibrium constant data. The open symbol for $SiO_{2(aq)}$ denotes the value of $\omega_{e,j}$ given by WALTHER and HELGESON (1977) and the value of $\bar{S}^0_j$ obtained in the present study (see below).

It can be seen in Fig. 11 that the points representing $Ar_{(aq)}$, $He_{(aq)}$, $Xe_{(aq)}$, $H_{2(aq)}$ and $O_{2(aq)}$ fall along the curve predicted independently from Eqn. (44). The symbols representing $SiO_{2(aq)}$, $H_2S_{(aq)}$, $NH_{3(aq)}$, $CO_{2(aq)}$, $HNO_{3(aq)}$, $B(OH)_{3(aq)}$, and $H_3PO_{4(aq)}$ lie at more positive values of $\omega_{e,j}$, 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

$$\omega_{e,j} = -1514.4\bar{S}^0_j + 0.34 \times 10^5. \tag{45}$$

Note that the upper curve in Fig. 11 crosses $\omega_{e,j} = 0$ at $\bar{S}^0_j = 22.45$, which leads to positive values of $\omega_{e,j}$ for this group of neutral aqueous species at lower values of $\bar{S}^0_j$. 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 $\omega_{e,j}$ 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 $\omega_{e,j}$ for 32 neutral inorganic aqueous species generated from Eqns. (44) and (45) using these criteria (see below) and values of $\bar{S}^0_j$ taken from the literature are listed in Table 6.

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

$$\beta_Z = 0.54 \times 10^5|Z_j| \tag{46}$$

for cations and

$$\beta_Z = 1.62 \times 10^5|Z_j| \tag{47}$$

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

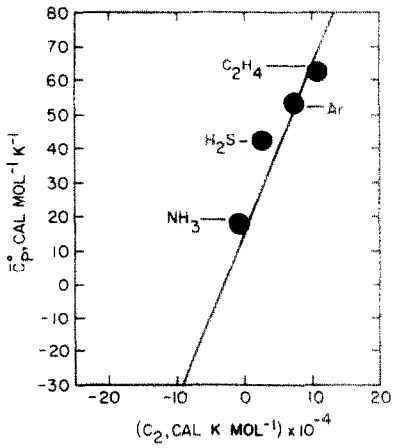

FIG. 7. Correlation of the c_2 equation of state parameters for neutral aqueous species with their standard partial molal heat capacities ($\bar{C}^0_P$) at 25°C and 1 bar. The symbols represent data taken from Table 2 and SHOCK and HELGESON (1989), but the curve was generated from Eqn. (38) and the corresponding correlation for aqueous ions depicted in Fig. 5.

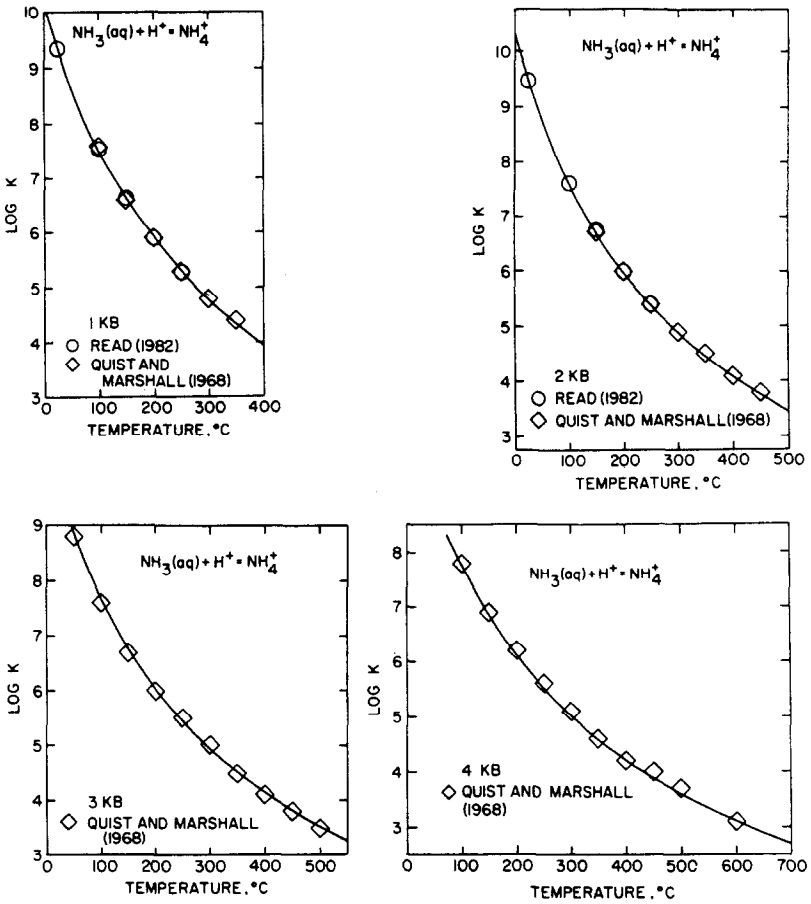

FIG. 8. Logarithm of the equilibrium constant for reaction (39) as a function of temperature at pressures of 1, 2, 3, and 4 kilobars. The symbols represent experimental data, but the curves were generated from Eqns. (12) and (31)–(33) using parameters and thermodynamic data for $NH_{3(aq)}$ taken from Table 4 and those for H^+ and NH_4^+ 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 $\omega_{e,j}$ 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 $\omega_{e,j}$ 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_{SAT} for solubility reactions involving the liquid phase in the system H_2O 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, $(\partial^2 \log K/\partial T^2)_{P_{SAT}}$ for reactions involving the liquid phase is negative and log K at P_{SAT} maximizes with increasing temperature. Under these circumstances, $(\partial \log K/\partial T)_{P_{SAT}}$ in the liquid phase region approaches $-\infty$ at the critical point of H_2O. In contrast, if the solubility of the dissolving phase is greater in H_2O vapor than in the coexisting liquid phase, which is generally true of gas solubilities, then $(\partial^2 \log K/\partial T^2)_{P_{SAT}}$ for the liquid phase is positive and log K minimizes with increasing temperature at P_{SAT}. As a consequence, $(\partial \log K/\partial T)_{P_{SAT}}$ for the liquid phase approaches ∞ at the critical point of H_2O. For intermediate cases in which the solubility of the dissolving phase is higher in liquid H_2O 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 sigmoid or sigmoid configuration with increasing temperature at P_{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 Eqns. (31)–(33) using values of $\Delta\bar{G}^0$ 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 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 Eqns. (27) through (31). The values of ω_e shown below were obtained by regression of experimental data, but those for a_1, a_2, a_3, a_4, c_1, and c_2 were estimated with the aid of Eqns. (22), (23), (25)–(28), (34), and (36)–(38)—see text.

Species	$\Delta\bar{G}^\circ_f$ [a]	$\Delta\bar{H}^\circ_f$ [a]	$\bar{S}^\circ$ [b]	$\bar{C}^\circ_P$ [b]	$\bar{V}^\circ$ [c]
$He_{(aq)}$	4658.[g]	−150.[h]	14.02[i]	37.3[h]	13.0[j]
$Ar_{(aq)}$	3900.[g]	−2870.[h]	14.30[i]	52.8[h]	31.71[k]
$Xe_{(aq)}$	3225.[g]	−4510.[h]	14.62[i]	64.8[h]	42.6[l]
$H_{2(aq)}$	4236.[m]	−1000.[m]	13.8[m]	39.9[n]	25.2[k]
$O_{2(aq)}$	3954.[g]	−2900.[h]	26.04[i]	56.0[h]	30.38[k]
$NH_{3(aq)}$	−6383.[p]	−19440.[p]	25.77[p]	17.9[q]	24.43[q]
$CO_{2(aq)}$	−92250.[m]	−98900.[m]	28.1[m]	58.1[r]	32.8[r]
$H_2S_{(aq)}$	−6673.[g]	−9001.[t]	30.0[s]	42.7[u]	34.92[u]
$B(OH)_{3(aq)}$	−231540.[m]	−256820[t]	37.0[s]	12.0[w]	39.22[v]
$HNO_{3(aq)}$	−24730.[g]	−45410[t]	42.7[s]	18.0[w]	
$SiO_{2(aq)}$	−199190.[z]	−209775.[t]	18.0[s]	−76.1[w]	16.1[y]
$H_3PO_{4(aq)}$	−273100.[m]	−307920.[t]	38.0[s]	23.6[w]	48.1[aa]

Species	$a^a_1\times 10$	$a^a_2\times 10^{-2}$	a^a_3	$a^a_4\times 10^{-4}$	c^b_1	$c^c_2\times 10^{-4}$	$\omega^a_e\times 10^{-5}$
$He_{(aq)}$	3.4722	0.6967	5.4762	−2.8078	26.0707	4.5634	−0.2123
$Ar_{(aq)}$	6.0003	6.8698	3.0499	−3.0630	35.6471[x]	7.3160[x]	−0.3073[x]
$Xe_{(aq)}$	7.5196	10.5793	1.5919	−3.2163	42.1036	10.1652	−0.2214
$H_{2(aq)}$	5.1427	4.7758	3.8729	−2.9764	27.6251	5.0930	−0.2090
$O_{2(aq)}$	5.7889	6.3536	3.2528	−3.0417	35.3530	8.3726	−0.3943
$NH_{3(aq)}$	5.0911	2.7970	8.6248	−2.8946	20.3[x]	−1.17[x]	−0.05[x]
$CO_{2(aq)}$	6.2466	7.4711	2.8136	−3.0879	40.0325	8.8004	−0.02
$H_2S_{(aq)}$	6.5097	6.7724	5.9646	−3.0590	32.3[x]	4.73[x]	−0.10[x]
$B(OH)_{3(aq)}$	7.0643	8.8547	3.5844	−3.1451	11.3568	−0.5902	−0.2[x]
$HNO_{3(aq)}$					15.2159	1.2635	−0.36
$SiO_{2(aq)}$	1.9[y]	1.7[y]	20.0[y]	−2.7[y]	29.1[y]	−51.2[y]	0.1291[z]
$H_3PO_{4(aq)}$	8.2727	12.4182	0.8691	−3.2924	17.9708	1.7727	−0.22

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 K mol^{-1}. g. Calculated from values of log K at 25 °C and 1 bar for solubility and/or dissociation reactions using values of ΔG°_f of the gas species taken from Wagman et al. (1982) and those of $\Delta\bar{G}^\circ_f$ for aqueous ions from Shock and Helgeson (1988). h. Olofsson et al. (1985). i. Calculated from values of $\Delta\bar{G}^\circ_f$ and $\Delta\bar{H}^\circ_f$ using S° of the elements taken from Wagman et al. (1982). j. Calculated from a fit of high-pressure solubility data (see text and Fig. 9). k. Tiepel and Gubbins (1972). l. Biggerstaff (1986). m. Wagman et al. (1982). n. Calculated from the value of $\Delta\bar{C}^\circ_{P,r}$ given by Clever and Han (1980) and that of $C^\circ_{P_r}$ of the gas taken from Wagman et al. (1982). p. Vanderzee and King (1972). q. Allred and Woolley (1981). r. Barbero et al. (1983). s. Calculated from the temperature dependence of log K for solubility and/or dissociational reactions using S° of the elements taken from Wagman et al. (1982). t. Calculated from values of $\Delta\bar{G}^\circ_f$ and $\Delta\bar{S}^\circ_f$ using S° of the elements taken from Wagman et al. (1982). u. Barbero et al. (1982). v. Ward and Millero (1974). w. Calculated from fits of high-temperature log K data for solubility or dissociational reactions. x. Taken from table 2. y. Generated by regression (see text). z. Walther and Helgeson (1977). aa. Larson et al. (1982).

1941a; MORRISON and BILLET, 1952; PRAY *et al.*, 1952; MORRISON and JOHNSTONE, 1954; STEPHAN *et al.*, 1956; KLOTS and BENSON, 1963; RABE and HARRIS, 1963; ELLIS and GOLDING, 1963; KOSINTSEVA, 1964; DOUGLAS, 1964, 1965; ENNS *et al.*, 1965; BEN-NAIM, 1965a; BEN-NAIM and EGEL-THAL, 1965; CLEVER and HOLLAND, 1968; SHOOR *et al.*, 1969; MURRAY *et al.*, 1969; MURRAY and RILEY, 1969, 1970, 1971; O'SULLIVAN and SMITH, 1970; WEISS, 1970, 1971; CLARKE and GLEW, 1971; GARDINER and SMITH, 1972; BEN-NAIM *et al.*, 1973; CROZIER and YAMAMOTO, 1974; TOKUNAGA, 1974; BENSON and KRAUSE, 1976; LAVROVA and TUDOROVSKAYA, 1977; POTTER and CLYNNE, 1978; BLANCO and SMITH, 1978; BENSON *et al.*, 1979; DRUMMOND, 1981; ZAWISZA and MALESINSKA, 1981; CROVETTO *et al.*, 1982a; GERTH, 1983; SMITH and KENNEDY, 1983; RETTICH *et al.*, 1984; KUTSCHE *et al.*, 1984; DACEY *et al.*, 1984; DAKE and CHAUDHARI, 1985; ALETA and ROBERTS, 1986; POSTIGO and KATZ, 1987; VERSTEEG and VAN SWAAIJ, 1988; ALVAREZ *et al.*, 1988; KHAN and HALLIGUDI, 1988; among others), and many comprehensive compilations have appeared (including, MARKHAM and KOBE, 1941b; WILHELM *et al.*, 1977; ABRAHAM, 1979; CLEVER, 1979a,b, 1980; CLEVER and HAN, 1980; BATTINO, 1981, 1982; YOUNG, 1981a,b, 1983; GOLDBERG and PARKER, 1985). Plots of log K against temperature for various gas solubility reactions are shown in Fig. 13. The curves for the reactions involving $Ar_{(aq)}$, $Ne_{(aq)}$, $Kr_{(aq)}$ and $SO_{2(aq)}$ shown in this figure represent predicted equilibrium constants at high temperatures using equation of state parameters that were estimated from the correlation algorithms summarized above and thermodynamic data at 25°C and 1 bar taken from the literature. The curves for these reactions in Fig. 13 are thus independent of the experimental data represented by the symbols at temperatures > 25°C. The experimental solubility data reported by WINKLER (1891b), LANNUNG (1930), BEN-NAIM and BAER (1963), KLOTS and BENSON (1963), KÖNIG (1963), DE WET (1964), DOUGLAS (1964), BEN-NAIM (1965b), KRESTOV and NEDELKO (1969), KRESTOV and PATSATSIYA (1969), MASTERTON *et al.* (1973), BORINA and SAMOILOV (1974), BORINA (1977a,b), WEISS and KYSER (1978), KUTSCHE *et al.* (1984), and DOUABAL and RILEY (1979) are not shown in Fig. 13, but they are generally consistent

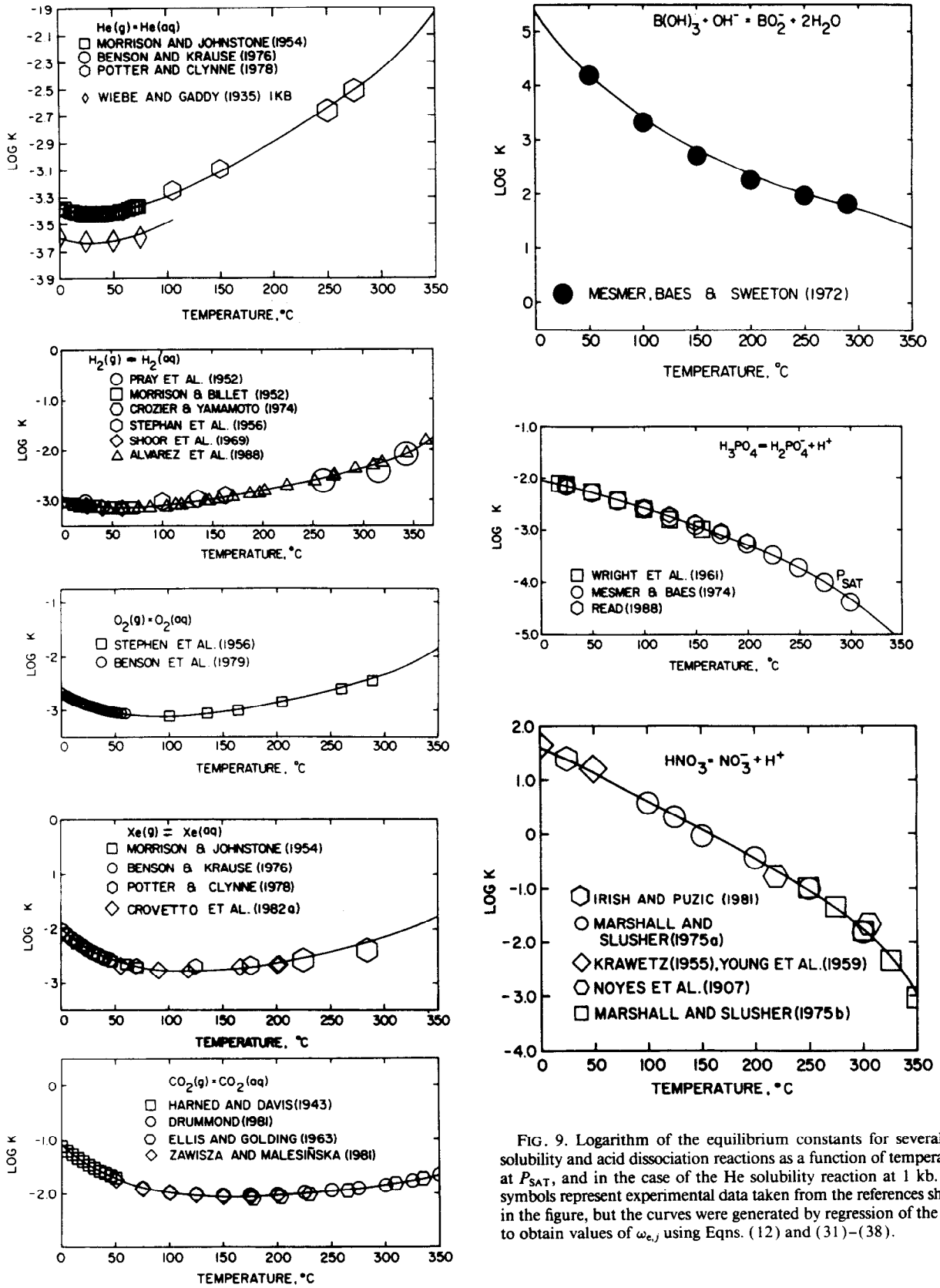

FIG. 9. Logarithm of the equilibrium constants for several gas solubility and acid dissociation reactions as a function of temperature at P_{SAT}, and in the case of the He solubility reaction at 1 kb. The symbols represent experimental data taken from the references shown in the figure, but the curves were generated by regression of the data to obtain values of $\omega_{e,j}$ using Eqns. (12) and (31)–(38).

Table 5. Values of β_Z calculated from Eqn. (43) for aqueous ions of various charges.

Z_j	$\beta_Z \times 10^{-5}$
+1	0.5517
+2	1.0579
+3	1.5793
+4	2.1764
−1	1.6291
−2	3.2127
−3	4.8115
−4	6.4860

with the other data represented by the symbols in the figure. In the case of $Rn_{(aq)}$ and $N_{2(aq)}$, for which no $\bar{C}^0_P$ 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 $\bar{C}^0_P$ 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 $\Delta\bar{G}^0_f$, $\Delta\bar{H}^0_f$, $\bar{S}^0$, ω_e, 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 CROVETTO *et al.* (1982a), POTTER and

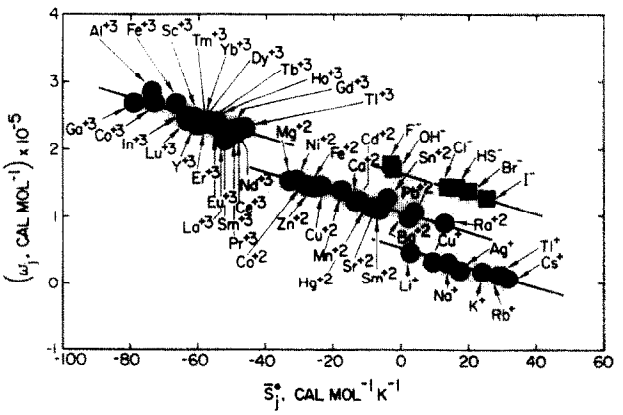

FIG. 10. Correlation of the Born coefficients (ω_j) of aqueous ions with their standard partial molal entropies ($\bar{S}^0_j$) at 25°C and 1 bar. The symbols represent data taken from SHOCK and HELGESON (1988), but the curves were generated from Eqn. (42) using values of β_Z taken from Table 5.

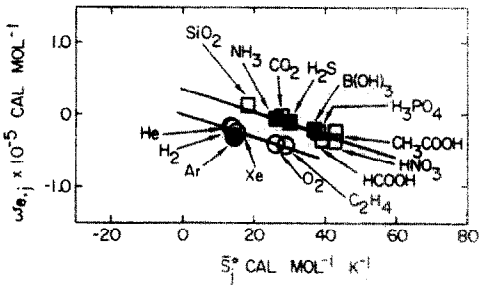

FIG. 11. Correlation of the effective Born coefficients ($\omega_{e,j}$) of neutral aqueous species with their standard partial molal entropies ($\bar{S}^0_j$) at 25°C and 1 bar. The solid symbols represent regression values of $\omega_{e,j}$ derived from standard partial molal properties, but the open symbols for species other than SiO_2 correspond to values of $\omega_{e,j}$ obtained in the present study by regression of log K data (see text). The value of $\omega_{e,j}$ for SiO_2 was taken from WALTHER and HELGESON (1977). The lower curve shown above was generated from Eqn. (44), but the upper curve was simply drawn through the symbols (see text).

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 CROVETTO *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

Table 6. Experimental standard partial molal entropies ($\bar{S}^\circ$) and effective Born coefficients (ω_e) for neutral aqueous species calculated from Eqns. (44) and (45).

Aqueous Species	$\bar{S}^{\circ a}$	$\omega_e^b \times 10^{-5}$	Aqueous Species	$\bar{S}^{\circ a}$	$\omega_e^b \times 10^{-5}$
Ne	16.74[d]	−0.2545[f]	O_3	34.9[e]	−0.1885
Kr	15.06[d]	−0.2281[f]	H_2O_2	34.4[e]	−0.1810
Rn	16.0[d]	−0.2423[f]	HF	22.5[d]	−0.0007
Cl_2	28.9[e]	−0.4377[f]	HClO	34.0[e]	−0.1749
ClO_2	39.13[e]	−0.2526	$HClO_2$	45.0[e]	−0.3415
Br_2	31.2[e]	−0.4725[f]	HBrO	33.9[e]	−0.1734
I_2	32.8[e]	−0.4967[f]	HIO	22.8[e]	0.0053
N_2	22.87[e]	−0.3463[f]	HIO_3	39.9[e]	−0.2642
NO	28.43[e]	−0.0905	HCN	29.8[e]	−0.1113
N_2O	28.04[e]	−0.0846	HN_3	34.9[e]	−0.1885
N_2H_4	33.0[e]	−0.1598	HNO_2	32.4[e]	−0.1507
NF_3	35.72[e]	−0.2009	$H_4P_2O_7$	64.1[e]	−0.6307
PH_3	26.4[e]	−0.0598	H_3AsO_4	44.0[e]	−0.3263
CO	24.53[e]	−0.0315	$HAsO_2$	30.1[e]	−0.1158
SF_6	37.22[e]	−0.2237	$HSbO_2$	11.1[e]	0.1719
SO_2	38.7[e]	−0.2461	H_2Se	39.1[e]	−0.2521
AsH_3	30.21[e]	−0.1175	H_2SeO_3	49.7[e]	−0.4127

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).

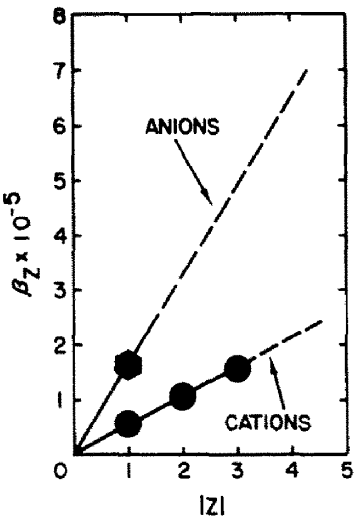

FIG. 12. Values of β_Z corresponding to the intercepts of the curves shown in Fig. 10 (symbols) and those computed from Eqns. (46) and (47) (linear curves) as a function of absolute charge.

H_2 occur at temperatures < 75°C, which is consistent with their high volatility and the relatively large negative values of $\omega_{e,j}$ for the aqueous species involved in these reactions. In other cases for which $\omega_{e,j}$ 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°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°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 $\bar{C}_P^0$ 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 $Ar_{(aq)}$, $Xe_{(aq)}$, 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 (BEUTIER 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 ($\Delta\bar{H}_r^0$, $\Delta\bar{C}_{P,r}^0$, $\Delta\bar{S}_r^0$, $\Delta\bar{V}_r^0$, $(\partial\Delta\bar{V}_r^0/\partial T)_P$, and $(\partial\Delta\bar{V}_r^0/\partial P)_T$) increase with increasing temperature at P_{SAT} and approach ∞ at the critical point of H_2O. In contrast, the standard partial molal heat capacities, compressibilities, and expansibilities of dissolved gases in steam approach −∞ 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°C and 9 kb (KENNEDY, 1950; MOREY and HESSELGESSER, 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

$$SiO_{2(quartz)} = SiO_{2(aq)} \qquad (48)$$

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°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°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 −∞ 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 ∞ 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 $Si(OH)_4 \cdot 2H_2O$ (WALTHER and ORVILLE, 1983). Hence, hydrogen bonds may be in part responsible for the positive value of $\omega_{e,j}$ and the relatively low standard partial molal entropy of aqueous silica at 25°C and 1 bar. As indicated above, the value of $\omega_{e,SiO_{2(aq)}}$ 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 HKF model. These same data were regressed with the revised HKF equations of state in the pres-

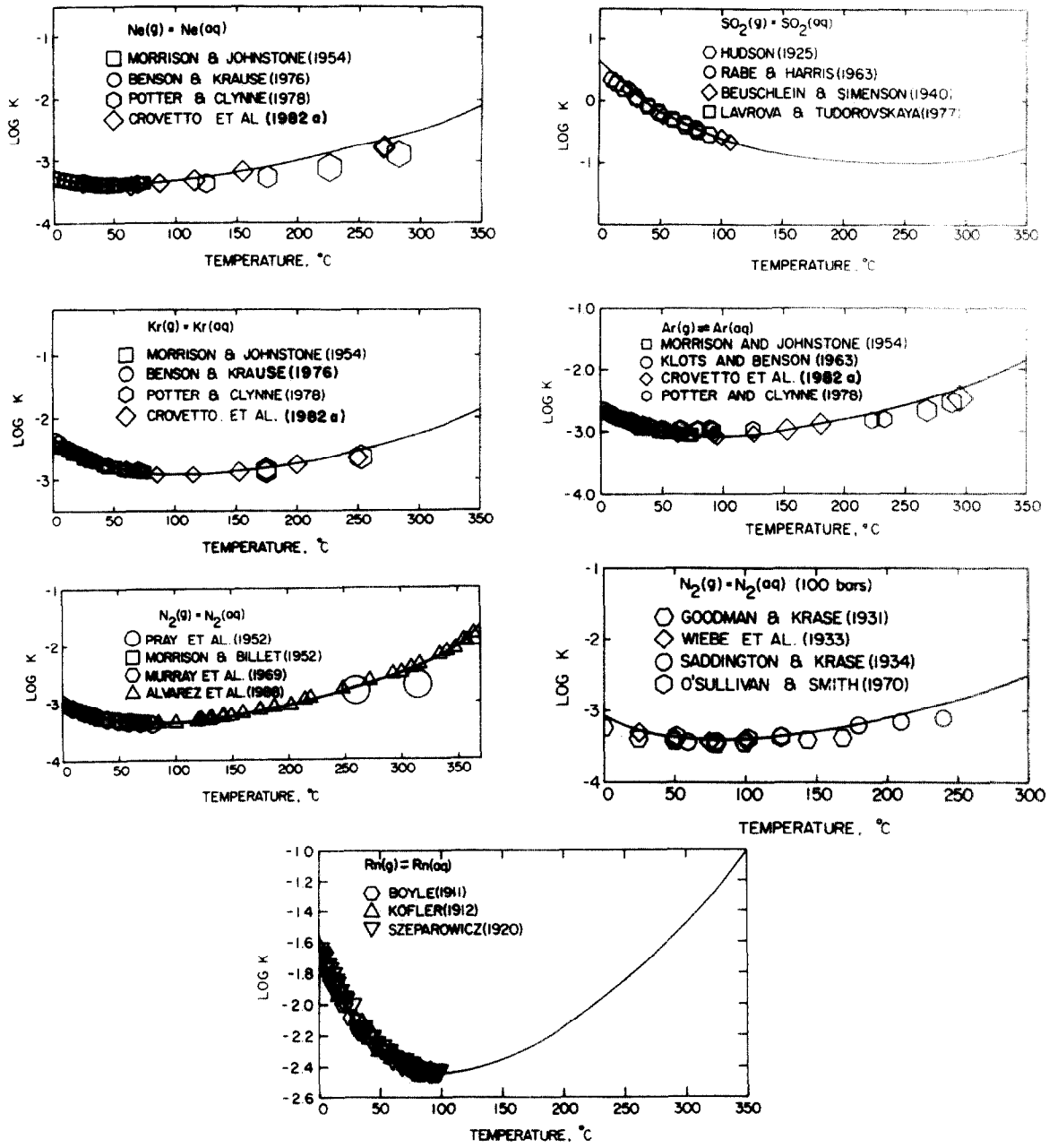

FIG. 13. Logarithms of the equilibrium constants for gas solubility reactions as functions of temperature at P_{SAT}, and in the case of $N_{2(g)} \rightleftarrows N_{2(aq)}$ at 100 bars. The symbols represent experimental data, but the curves were generated from Eqns. (31)–(33) using parameters and thermodynamic data taken from Table 7. The curves for the reaction involving $Ne_{(aq)}$, $Kr_{(aq)}$, $Ar_{(aq)}$, and $SO_{2(aq)}$ correspond to independent predictions at temperatures > 25°C, but those for N_2 and Rn were produced by regression of the data with Eqns. (31)–(38) to obtain values of the standard partial molal heat capacities ($\bar{C}^0_P$) of the neutral aqueous species at 25°C and 1 bar.

ent study to obtain equation of state parameters and revised values of $\bar{S}^0_{SiO_{2(aq)}}$, $\bar{V}^0_{SiO_{2(aq)}}$, and $\bar{C}^0_{P,SiO_{2(aq)}}$ at 25°C and 1 bar. Values of the standard partial molal properties and the revised HKF equation of state parameters for $SiO_{2(aq)}$ are given in Table 4. These properties and parameters were used to generate the curves shown in Fig. 14, where it can be seen that the curves represent closely the experimental data.

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 Eqns. (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 Eqns. (27) through (31). The values of ω_c shown below are estimates taken from Table 6 but those given for a_1, a_2, a_3, a_4, c_1, and c_2 were estimated from Eqns. (22), (23), (25)–(28), (34), and (36)–(38)—see text.

Species	$\Delta\bar{G}^{\circ}_f$	$\Delta\bar{H}^{\circ}_f$	$\bar{S}^{\circ}$	$\bar{C}^{\circ}_P$	$\bar{V}^{\circ}$
$Ne_{(aq)}$	4565.[g]	−870.[h]	16.74[i]	39.7[h]	20.4[j]
$Kr_{(aq)}$	3554.[g]	−3650.[h]	15.06[i]	57.6[h]	33.5[j]
$Rn_{(aq)}$	2790.[g]	−5000.[k]	16.0[l]	83.0[l]	54.1[l]
$N_{2(aq)}$	4347.[m]	−2495.[m]	22.9[m]	56.0[n]	33.3[p]
$SO_{2(aq)}$	−71980.[g]	−77194.[q]	38.7[q]	46.6[r]	38.5[r]
$HF_{(aq)}$	−71662.[t]	−76835.[k]	22.5[l]	14.0[l]	12.5[s]

Species	$a^a_1\times 10$	$a^a_2\times 10^{-2}$	a^a_3	$a^a_4\times 10^{-4}$	c^b_1	$c^b_2\times 10^{-4}$	$\omega^a_c\times 10^{-5}$
$Ne_{(aq)}$	4.4709	3.1352	4.5177	−2.9086	27.0977	5.0523	−0.2535
$Kr_{(aq)}$	6.2721	7.5333	2.7891	−3.0904	37.8226	8.6985	−0.2281
$Rn_{(aq)}$	9.0862	14.4045	0.0884	−3.3745	52.5774	13.8725	−0.2423
$N_{2(aq)}$	6.2046	7.3685	2.8539	−3.0836	35.7911	8.3726	−0.3468
$SO_{2(aq)}$	6.9502	9.1890	2.1383	−3.1589	31.2101	6.4578	−0.2461
$HF_{(aq)}$	3.4753	0.7042	5.4732	−2.8081	14.3647	−0.1828	−0.0007

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 K mol^{-1}. g. Calculated from values of log K at 25 °C and 1 bar for solubility reactions using values of ΔG°_f for the gas given by Wagman et al. (1982). h. Olofsson et al. (1985). i. Calculated from values of $\Delta\bar{G}^{\circ}_f$ and $\Delta\bar{H}^{\circ}_f$ using values of S° for the elements given by Wagman et al. (1982). j. Calculated from the temperature dependence of log K data shown in Fig. 13 (see text). k. Calculated from $\Delta\bar{G}^{\circ}_f$ and $\Delta\bar{S}^{\circ}_f$ using S° of the elements taken from Wagman et al. (1982). l. Picrotti (1965). m. Wilhelm et al. (1977). n. Calculated from a fit of log K data at P_{SAT} and 100 bars (see text and Fig. 13). p. Enns et al. (1965). q. Wagman et al. (1982). r. Barbero et al. (1983). s. Calculated from the value of $\Delta\bar{V}^{\circ}_f$ at 25° and 1 bar given by Hamann (1974). t. Calculated from log K at 25 °C and 1 bar.

in Figs. 15 and 16, where they can be compared with the experimental values represented by the symbols. In the case of $HF_{(aq)}$, for which no reliable value of $\bar{C}^0_P$ at 25°C and 1 bar is available in the literature, the experimental equilibrium constants were regressed to retrieve a value of this heat capacity. However, all of the other curves were generated independently of the data represented by the symbols at temperatures > 25°C. It can be seen that the predicted curves are in close agreement with all of the experimental data represented by the symbols, except in the case of the high-temperature dissociation constants for $H_2S_{(aq)}$ reported by ELLIS and GIGGENBACH (1971), and those for carbonic acid given by READ (1975) at 1 and 2 kb and temperatures > 150°C. It should be noted in this regard that the predicted values of log K for the dissociation of $H_2S_{(aq)}$ are nevertheless consistent with the high-temperature measurements reported by TSONOPOULOS *et al.* (1976), which are considerably more positive than those given by ELLIS and GIGGENBACH (1971). As noted by BARBERO *et al.* (1982), this latter set of experimental data appears to be inconsistent with all of the other high-temperature measurements of log K, as well as with the experimental standard partial molal volumes and heat capacities of $H_2S_{(aq)}$ listed in Table 3 and those for NaHS summarized by SHOCK and HELGESON (1988). The predicted equilibrium constants for the reaction

$$CO_{2(aq)} + H_2O = HCO_3^- + H^+ \qquad (49)$$

generated in the present study are consistent with all of the sets of experimental data at P_{SAT}. Other experimental data for this reaction that are not shown in Fig. 15 are also consistent with the predicted values of log K at P_{SAT}, including those reported by SHEDLOVSKY and MACINNES (1935), TARTAR and GARRETSON (1941), HARNED and BONNER (1945), BROENE and DEVRIES (1947), NÄSÄNEN (1947), ELLIS and ANDERSON (1961a,b), RYZHENKO (1963), VANDERBORGH (1968), and PATEL *et al.* (1971). However, the predicted values at 1 and 2 kilobars are more negative than the corresponding values reported by READ (1975) at temperatures > 150°C. These are the only high-pressure/temperature experimental equilibrium constant data that differ by more than ±0.2 units of log K from the various independent predictions made in the present study. It can be seen in Fig. 16 that the curves representing the independently predicted values of the first dissociation constant of $H_3PO_{4(aq)}$ agree closely with the experimental values of log K at both 1 and 2 kb. The curves in Fig. 16 are consistent with the regression curve for the dissociation of $H_3PO_{4(aq)}$ at P_{SAT} 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 $H_2S_{(aq)}$ at high temperatures and pressures can be used to generate curves representing equal activities of HS^- and $H_2S_{(aq)}$ as a function of pH and temperature at constant pressure. Curves of this kind are shown in Fig. 17, together with analogous curves generated for equal activities of $H_3PO_{4(aq)}$ and $H_2PO_4^-$, and $H_2PO_4^-$ and HPO_4^{--} using data and parameters taken from Table 4 and those for the ionic species from SHOCK and 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 $H_2S_{(aq)}$ and HS^-, as well as those for $H_2PO_4^-$ and HPO_4^{--}, exhibit pH minima in the vicinity of 100°C. In contrast, those representing equal activities of $H_3PO_{4(aq)}$ and $H_2PO_4^-$ do not. The latter behavior is typical of reactions for which the dissociation constant is $\gtrsim -2$ at 25°C and 1 bar. Otherwise, $\Delta\bar{H}^0_r$ is commonly positive at low temperatures and a minimum 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 13–15 lends considerable support to the validity and generality of the equations, correlations, and parameters summarized above. Eqns. (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 Gibbs free energies of formation of $CO_{2(aq)}$, $O_{2(aq)}$, $H_2S_{(aq)}$, and $SiO_{2(aq)}$ 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 O_2 increases by ~350 cm^3 mol^{-1} over the tem-

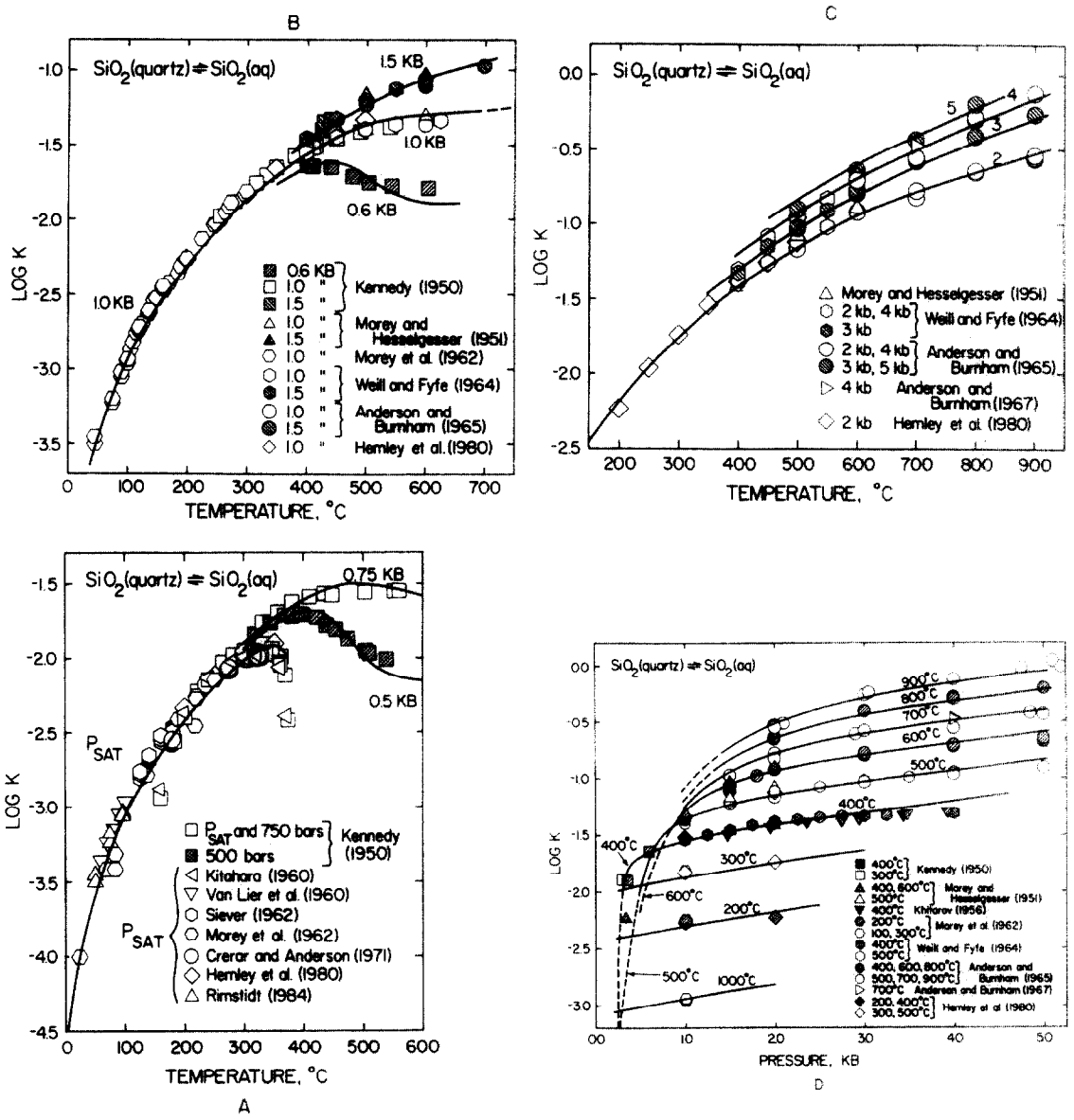

FIG. 14. Logarithm of the equilibrium constant for reaction (48) as a function of temperature at P_{SAT} and constant pressure (diagrams A, B, and C) and pressure at constant temperature (diagram D). The symbols represent experimental data, but the curves were generated by regression of the experimental 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 $\bar{S}^0$, $\bar{V}^0$, and $\bar{C}_P^0$ of $SiO_{2(aq)}$ at 25°C and 1 bar. The value of $\omega_{e,j}$ 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).

perature range 0 to 350°C at P_{SAT}, but those of $H_2S_{(aq)}$ and $CO_{2(aq)}$ increase by only ~90 and ~25 cm^3 mol^{-1}, respectively, at P_{SAT} over the same range of temperature increase. Similar differences in magnitude for changes of $\bar{C}_P^0$, $\bar{S}^0$ and $\Delta\bar{H}^0$ 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 nonsolvation 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 $\omega_{e,j}$ obtained either by regression of experimental

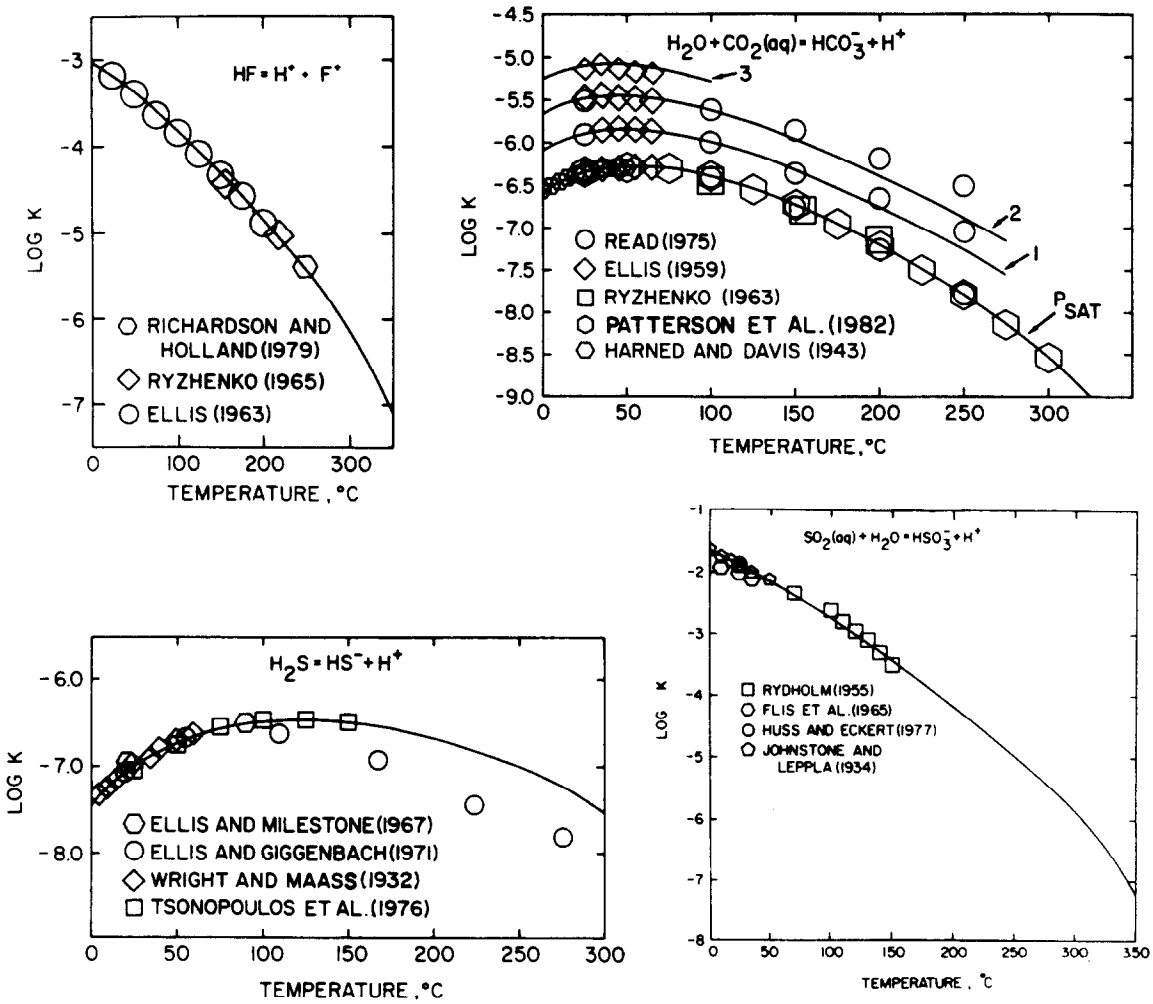

FIG. 15. Logarithms of the equilibrium constants for acid dissociation reactions as functions of temperature at P_{SAT}, and in the case of carbonic acid at higher pressures (labeled in kb). The symbols represent experimental data, but the curves for all of the reactions except the dissociation of HF correspond to independent predictions at temperatures > 25°C, which were generated from Eqns. (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 SHOCK and HELGESON (1988). The curve shown in the plot for HF dissociation was generated by regression of the data with Eqns. (31)–(38) to obtain a value of $\bar{C}_P^0$ for the aqueous HF ion pair at 25°C and 1 bar.

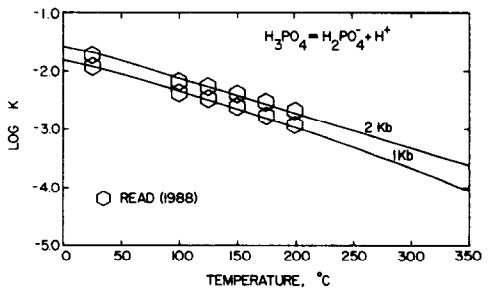

FIG. 16. Logarithm of the equilibrium constant for the first dissociation of $H_3PO_{4(aq)}$ as a function of temperature at 1 and 2 kb. The symbols represent experimental data, but the curves correspond to independent predictions generated from Eqns. (12) and (31)–(33) using parameters and thermodynamic data taken from Table 4 and SHOCK and HELGESON (1988).

data or estimated from the correlations represented by Eqns. (44) and (45). The latter uncertainties do not affect ω_j values for simple ions, which can be calculated from Eqns. (17) and (18). Values of $\omega_{e,j}$ 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 $\omega_{e,j}$ are generally less than $\sim \pm 10^4$ cal mol^{-1}.

Assuming a "typical" uncertainty in $\omega_{e,j}$ of ± 5000 cal mol^{-1} leads to a corresponding uncertainty in $\Delta\bar{G}^0$ of ± 2.6 cal mol^{-1} at 25°C and 1 kb. At 500°C and 1 kb, the corresponding uncertainty in $\Delta\bar{G}^0$ is ± 328 cal mol^{-1}. With increasing pressure to 5 kb, the uncertainty in $\Delta\bar{G}^0$ at 500°C decreases to ± 61 cal mol^{-1}, but increases with increasing temperature at 5 kb to ± 337 cal mol^{-1} at 1000°C. It should be noted in this

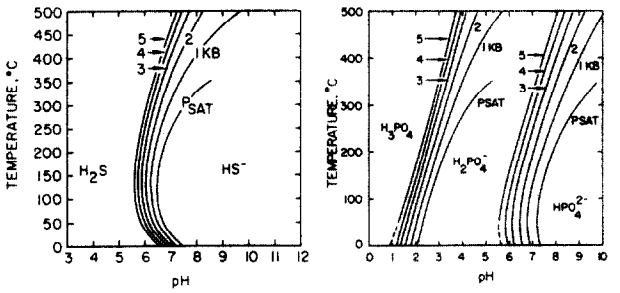

FIG. 17. pH as a function of temperature and pressure from 0 to 500°C and P_{SAT} to 5 kb for equal activities of aqueous H_2S and HS^-, H_3PO_4 and $H_2PO_4^-$, and $H_2PO_4^-$ and HPO_4^{--}. The curves were generated with the aid of Eqns. (12) and (31)–(33) using parameters and thermodynamic data taken from Table 4 and SHOCK and HELGESON (1988).

regard that uncertainties in calculated high-temperature/pressure standard partial molal properties of aqueous species arising from uncertainties in $\omega_{e,j}$ 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 ∞ or $-\infty$ at the critical point of H_2O, 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 $\bar{C}^0_P$ resulting from uncertainties in the nonsolvation equation of state parameters adduced above, a typical uncertainty of ±5000 cal mol^{-1} in $\omega_{e,j}$ leads to an uncertainty in $\bar{C}^0_P$ ($\delta\bar{C}^0_P$) of ±0.5 cal mol^{-1} K^{-1} at 25°C and 1 bar, which decreases with increasing pressure to ±0.36 cal mol^{-1} K^{-1} at 25°C and 1 kb. However, $\delta\bar{C}^0_P$ then increases with increasing temperature, reaching ±18.2 cal mol^{-1} K^{-1} in the supercritical region at 500°C and 1 kb. From there the uncertainty in $\bar{C}^0_P$ decreases with increasing temperature and pressure to ±0.92 cal mol^{-1} K^{-1}

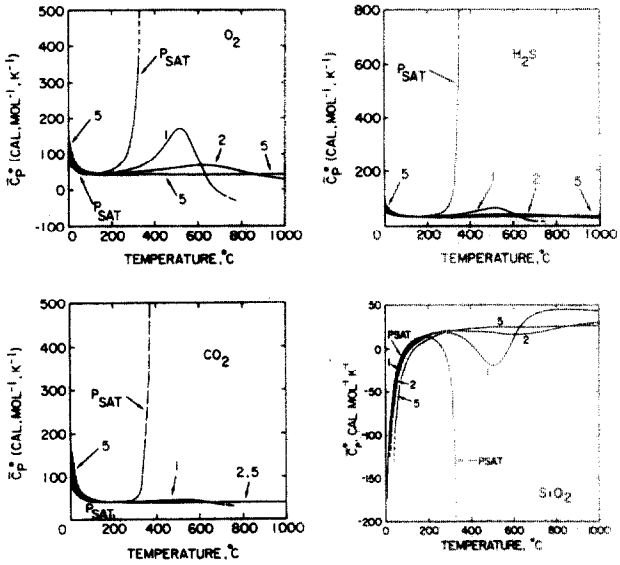

FIG. 19. Standard partial molal heat capacities ($\bar{C}^0_P$) of aqueous O_2, CO_2, H_2S and SiO_2 as a function of temperature at P_{SAT} and constant higher pressures (labeled in kb) calculated from Eqn. (28) using equation of state parameters and thermodynamic data taken from Tables 4 and 7.

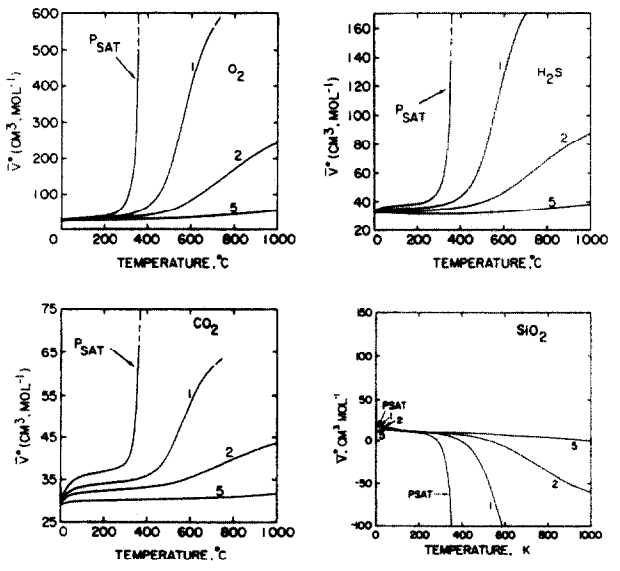

FIG. 18. Standard partial molal volumes ($\bar{V}^0$) of aqueous O_2, CO_2, H_2S and SiO_2 as a function of temperature at P_{SAT} and constant higher pressures (labeled in kb) calculated from Eqn. (27) using parameters and thermodynamic data taken from Tables 4 and 7.

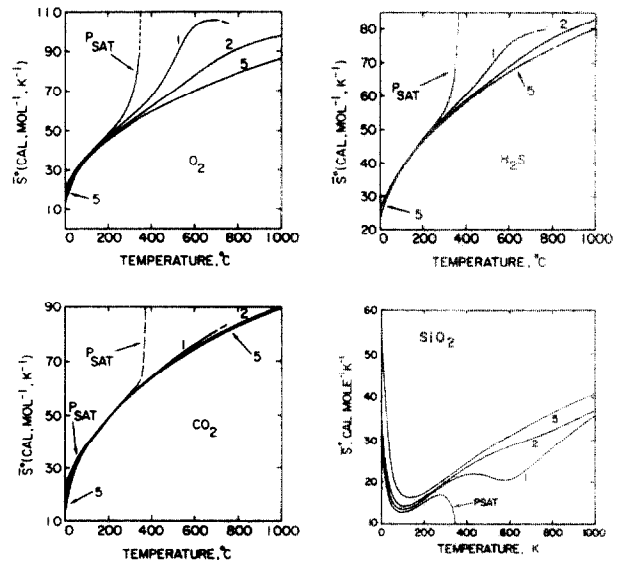

FIG. 20. Standard partial molal entropies ($\bar{S}^0$) of aqueous O_2, CO_2, H_2S and SiO_2 as a function of temperature at P_{SAT} and constant higher pressures (labeled in kb) calculated from Eqn. (29) using equation of state parameters and thermodynamic data taken from Tables 4 and 7.

at 1000°C and 5 kb. Similar trends are observed for the other standard partial molal properties. For example, the uncertainty in $\bar{V}^0$ arising from an uncertainty in $\omega_{e,j}$ of ±5000 cal mol^{-1} is ±0.12 cm^3 mol^{-1} at 25°C and 1 bar, ±9.4 × 10^{-2} cm^3 mol^{-1} at 25°C and 1 kb, ±17.2 cm^3 mol^{-1} at 500°C and 1 kb, and ±3.4 cm^3 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 $\bar{V}^0$, $\bar{C}_P^0$, $\bar{S}^0$, $\Delta\bar{H}^0$ and $\Delta\bar{G}^0$ 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 H_2O 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.

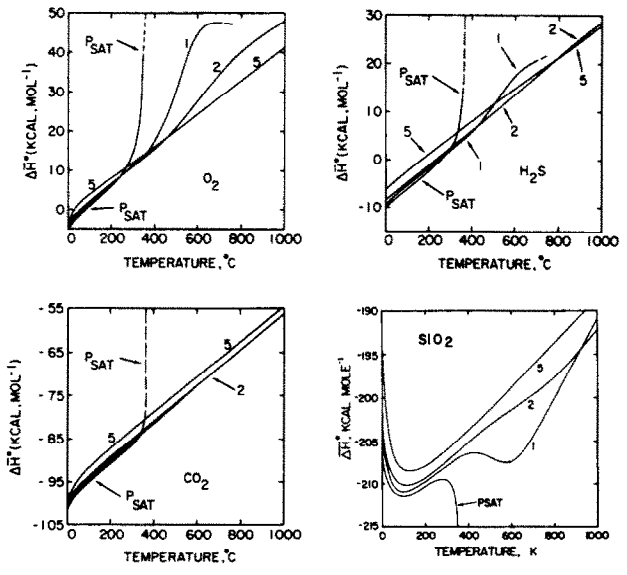

FIG. 21. Apparent standard partial molal enthalpies of formation ($\Delta\bar{H}^0$) of aqueous O_2, CO_2, H_2S and SiO_2 as a function of temperature at P_{SAT} and constant higher pressures (labeled in kb) calculated from Eqn. (30) using equation of state parameters and thermodynamic data taken from Tables 4 and 7.

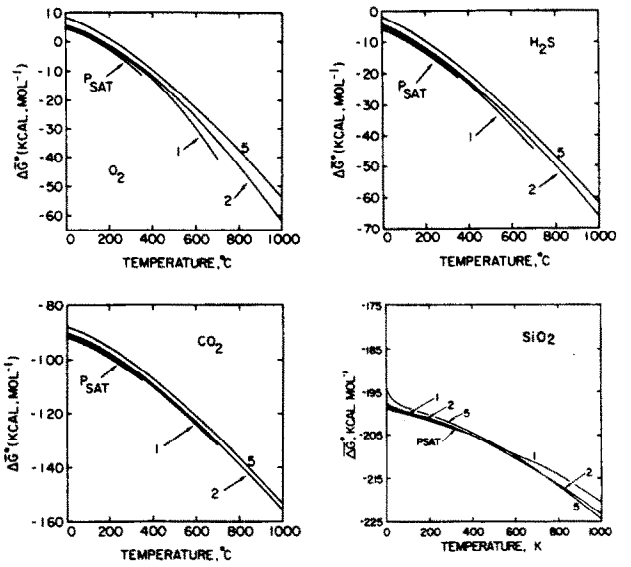

FIG. 22. Apparent standard partial molal Gibbs free energies of formation ($\Delta\bar{G}^0$) of aqueous O_2, CO_2, H_2S and SiO_2 as a function of temperature at P_{SAT} and constant higher pressures (labeled in kb) calculated from Eqn. (31) using equation of state parameters and thermodynamic data taken from Tables 4 and 7.

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