

Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Correlation algorithms for ionic species and equation of state predictions to 5 kb and 1000°C

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Abstract—Correlation algorithms permit prediction of species-dependent parameters in revised equations of state (TANGER and HELGESON, 1988) for aqueous ions and electrolytes which can be used together with values at 25°C and 1 bar of the standard partial molal entropies (S^0), volumes (V^0), and heat capacities (C_p^0) of the ions to calculate their standard partial molal thermodynamic properties at pressures and temperatures to 5 kb and 1000°C. Values of V^0 and C_p^0 at 25°C and 1 bar have been calculated for 128 aqueous ions from analysis of published experimental data or from correlations of these properties with S^0 . Equation of state parameters have also been generated for these ions and examples are given of predicted standard partial molal thermodynamic properties of representative cations and anions at high pressures and temperatures. Close agreement between independently predicted and experimentally determined equilibrium constants for acid anion dissociation reactions at high temperatures supports the validity and generality of the predictive algorithms.

INTRODUCTION

THE CHEMICAL INTERACTION of minerals and aqueous solutions at supercritical pressures and temperatures is a sensitive function of the thermodynamic behavior of aqueous species. Recent advances in high temperature solution chemistry permit calculation of the standard partial molal thermodynamic properties of these species to 1000°C and 5 kb using revised and extended equations of state based in part on scaling laws and solvation theory (TANGER and HELGESON, 1988; SHOCK *et al.*, 1988b). Until recently, the species-dependent parameters required to evaluate these equations of state could be obtained only by regression of experimental data over a range of temperatures, which limited the applicability of these equations to relatively few (≤ 20) aqueous ions. The purpose of the present communication is to demonstrate that correlation algorithms can be used with confidence to estimate species-dependent equation of state parameters, which permit calculation of the standard partial molal thermodynamic properties of a wide variety of aqueous ions and electrolytes at high pressures and temperatures for which few or no experimental data are available for temperatures $\geq 25^\circ\text{C}$.

Numerous correlation algorithms and corresponding states relations have been proposed for the partial molal thermodynamic properties of aqueous ions (LATIMER and KASPER, 1929; FAJANS and JOHNSON, 1942; POWELL and LATIMER, 1951; COBBLE, 1953a–c; LATIMER, 1955; LAIDLER, 1956; COUTURE and LAIDLER, 1956, 1957; HEPLER, 1957; LAIDLER and PEGIS, 1957; STOKES and ROBINSON, 1957; MUKERJEE, 1961; LITVENENKO, 1963; CRISS and COBBLE, 1964a,b; GLUECKAUF, 1964, 1965; NOYES, 1964; DESNOYERS *et al.*, 1965; HEPLER *et al.*, 1965; CONWAY *et al.*, 1965, 1966; HELGESON, 1969; PANKHURST, 1969; MILLERO, 1971, 1972; MATHIESON and CONWAY, 1974; HELGESON and KIRKHAM, 1976; CONWAY, 1978; AKITT, 1980; HELGESON *et al.*, 1981;

MILLERO, 1982; SWADDLE and MAK, 1983; NOTOYA and MATSUDA, 1985; MARCUS, 1986; ABRAHAM and MARCUS, 1986). These have been used successfully to estimate the standard partial molal entropies, volumes, compressibilities and heat capacities of many aqueous species for which experimental data are not available. Similar correlations have been observed for parameters in equations of state for both the standard and relative partial molal properties of aqueous electrolytes (HELGESON and KIRKHAM, 1976; HELGESON *et al.*, 1981; PITZER *et al.*, 1978), which is also true (see below) for those in TANGER and HELGESON'S (1988) revised HKF (HELGESON, KIRKHAM and FLOWERS, 1981) equations of state.

Standard state conventions

The standard state convention for aqueous ions and electrolytes adopted in the present study is one of unit activity of the aqueous species in a hypothetical one molal solution referenced to infinite dilution at any pressure and temperature. The standard state for H_2O calls for unit activity of the pure solvent at any pressure and temperature. Any standard partial molal property of the k th aqueous electrolyte (\bar{z}_k^0) is related to the corresponding absolute standard partial molal properties of its constituent ions by

$$\bar{z}_k^0 = \sum_j \nu_{j,k} \bar{z}_j^{\text{Obs}} \quad (1)$$

where the subscripts k and j refer to the electrolyte and ion, respectively. The conventional standard partial molal properties of the j th ion are defined by

$$\bar{z}_j^0 = \bar{z}_j^{\text{Obs}} - Z_j \bar{z}_{\text{H}^+}^{\text{Obs}} \quad (2)$$

where $\bar{z}_{\text{H}^+}^{\text{Obs}}$ refers to the absolute standard partial molal property of the hydrogen ion. It follows from Eqns. (1) and (2) and the requirement for electrical neutrality of an aqueous electrolyte that

$$\bar{z}_k^0 = \sum_j \nu_{j,k} \bar{z}_j^0 \quad (3)$$

REVIEW OF THE REVISED HKF EQUATIONS OF STATE

Any standard partial molal thermodynamic property of an aqueous electrolyte or ionic species can be considered to be a combination of intrinsic properties and electrostriction

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contributions (COUTURE and LAIDLER, 1956; HEPLER, 1957; STOKES and ROBINSON, 1957; MUKERJEE, 1961; BENSON and COPELAND, 1963; GLUECKAUF, 1965; DESNOYERS *et al.*, 1965; HELGESON and KIRKHAM, 1976; AKITT, 1980; IMPEY *et al.*, 1983; TANGER and HELGESON, 1988). The intrinsic properties are attributed to the ion itself, but the electrostriction contributions arise from ion-solvent interactions. These interactions include those arising from collapse of the local solvent structure and solvation of the ion. The nonsolvation intrinsic and collapse contributions to the standard partial molal thermodynamic properties of an aqueous ion are regarded as nonelectrostatic. In contrast, the solvation contribution is represented in the revised HKF model by a modified Born transfer equation in which the effective electrostatic radius of the aqueous ion is regarded as a function of pressure and temperature. Application of the revised HKF equations of state to a wide variety of electrolytes indicates that the equations yield highly accurate descriptions of the standard partial molal thermodynamic properties of aqueous electrolytes at high pressures and temperatures (TANGER and HELGESON, 1988; SHOCK *et al.*, 1988b).

Standard partial molal volume, compressibility, and expansibility

The standard partial molal volume (\bar{V}^0) of an aqueous ion or electrolyte can be expressed as

$$\bar{V}^0 = \Delta\bar{V}_n^0 + \Delta\bar{V}_s^0 \quad (4)$$

where $\Delta\bar{V}_n^0$ and $\Delta\bar{V}_s^0$ represent the nonsolvation and solvation contributions to \bar{V}^0 , respectively. The solvation term in Eqn. (4) is given by

$$\Delta\bar{V}_s^0 = -\omega Q + \left(\frac{1}{\epsilon} - 1\right) \left(\frac{\partial\omega}{\partial P}\right)_T \quad (5)$$

where P stands for pressure, T refers to temperature, ϵ denotes the dielectric constant of water, ω designates a temperature- and pressure-dependent Born coefficient, and the Born function Q is given by

$$Q = \frac{1}{\epsilon} \left(\frac{\partial \ln \epsilon}{\partial P}\right)_T \quad (6)$$

Taking account of the singular temperature of supercooled water (ANGELL, 1983), TANGER and HELGESON (1988) demonstrated that the nonsolvation contribution to the standard partial molal volume can be represented by

$$\Delta\bar{V}_n^0 = \sigma + \xi \left(\frac{1}{T - \theta}\right) \quad (7)$$

where σ and ξ correspond to temperature-independent coefficients characteristic of an aqueous ion or electrolyte at a given pressure, respectively, and θ represents a solvent parameter equal to 228 K. The pressure dependence of σ and ξ can be expressed as

$$\sigma = a_1 + a_2 \left(\frac{1}{\Psi + P}\right) \quad (8)$$

and

$$\xi = a_3 + a_4 \left(\frac{1}{\Psi + P}\right) \quad (9)$$

where Ψ refers to a solvent parameter equal to 2600 bars (TANGER and HELGESON, 1988), and a_1 , a_2 , a_3 , and a_4 , stand for temperature- and pressure-independent parameters characteristic of the aqueous ion or electrolyte. Combining Eqns. (7), (8), and (9) yields

$$\Delta\bar{V}_n^0 = a_1 + a_2 \left(\frac{1}{\Psi + P}\right) + \left(a_3 + a_4 \left(\frac{1}{\Psi + P}\right)\right) \left(\frac{1}{T - \theta}\right) \quad (10)$$

which can in turn be combined with Eqns. (4) and (5) to yield the expression for the temperature and pressure dependence of the standard partial molal volume of an ion or electrolyte given by

$$\bar{V}^0 = a_1 + a_2 \left(\frac{1}{\Psi + P}\right) + \left(a_3 + a_4 \left(\frac{1}{\Psi + P}\right)\right) \left(\frac{1}{T - \theta}\right) - \omega Q + \left(\frac{1}{\epsilon} - 1\right) \left(\frac{\partial\omega}{\partial P}\right)_T \quad (11)$$

By definition, the standard partial molal compressibility of an aqueous ion or electrolyte is given by

$$-\bar{\kappa}^0 = \left(\frac{\partial\bar{V}^0}{\partial P}\right)_T \quad (12)$$

Taking account of this definition and the derivative of Eqn. (4) with respect to pressure at constant temperature leads to

$$-\bar{\kappa}^0 = \left(\frac{\partial\Delta\bar{V}_n^0}{\partial P}\right)_T + \left(\frac{\partial\Delta\bar{V}_s^0}{\partial P}\right)_T \quad (13)$$

The two terms on the right hand side of Eqn. (13) correspond to the standard partial molal nonsolvation compressibility ($-\Delta\bar{\kappa}_n^0$) and the standard partial molal compressibility of solvation ($-\Delta\bar{\kappa}_s^0$), respectively. Equation (13) can thus be expressed as

$$\bar{\kappa} = \Delta\bar{\kappa}_n^0 + \Delta\bar{\kappa}_s^0 \quad (14)$$

Differentiation of Eqn. (5) with respect to pressure at constant temperature results in

$$-\left(\frac{\partial\Delta\bar{V}_s^0}{\partial P}\right)_T = \Delta\bar{\kappa}_s^0 = \omega N + 2Q \left(\frac{\partial\omega}{\partial P}\right)_T - \left(\frac{1}{\epsilon} - 1\right) \left(\frac{\partial^2\omega}{\partial P^2}\right)_T \quad (15)$$

where

$$N = \left(\frac{\partial Q}{\partial P}\right)_T \quad (16)$$

Similarly, differentiating Eqns. (7) through (9) with respect to pressure at constant temperature leads to

$$-\left(\frac{\partial\Delta\bar{V}_n^0}{\partial P}\right)_T = \Delta\bar{\kappa}_n^0 = \left(\frac{\partial\sigma}{\partial P}\right)_T + \left(\frac{\partial\xi}{\partial P}\right)_T \left[\frac{1}{T - \theta}\right] = \left[a_2 + a_4 \left(\frac{1}{T - \theta}\right)\right] \left(\frac{1}{\Psi + P}\right)^2 \quad (17)$$

Combining Eqns. (13), (15) and (17) yields the complete expression for the temperature and pressure dependence of the standard partial molal compressibility of an aqueous ion or electrolyte, which can be written as

$$\bar{\kappa}^0 = \left[a_2 + a_4 \left(\frac{1}{T - \theta}\right)\right] \left(\frac{1}{\Psi + P}\right)^2 + \omega N + 2Q \left(\frac{\partial\omega}{\partial P}\right)_T - \left(\frac{1}{\epsilon} - 1\right) \left(\frac{\partial^2\omega}{\partial P^2}\right)_T \quad (18)$$

Taking account of Eqns. (8) and (9) together with their partial derivatives with respect to pressure at constant temperature permits us to express a_1 , a_2 , a_3 , and a_4 as

$$a_1 = \sigma + \left(\frac{\partial\sigma}{\partial P}\right)_T (\Psi + 1), \quad (19)$$

$$a_2 = -\left(\frac{\partial\sigma}{\partial P}\right)_T (\Psi + 1)^2, \quad (20)$$

$$a_3 = \xi + \left(\frac{\partial\xi}{\partial P}\right)_T (\Psi + 1), \quad (21)$$

and

$$a_4 = -\left(\frac{\partial \xi}{\partial P}\right)_T (\Psi + 1)^2. \quad (22)$$

The standard partial molal expansibility of an aqueous ion or electrolyte (\bar{E}_x^0) can be expressed in terms of its nonsolvation ($\Delta\bar{E}_{x,n}^0$) and solvation ($\Delta\bar{E}_{x,s}^0$) counterparts by differentiating Eqn. (4) with respect to temperature at constant pressure to give

$$\bar{E}_x = \left(\frac{\partial \bar{V}^0}{\partial T}\right)_P = \Delta\bar{E}_{x,n}^0 + \Delta\bar{E}_{x,s}^0 = \left(\frac{\partial \Delta\bar{V}_n^0}{\partial T}\right)_P + \left(\frac{\partial \Delta\bar{V}_s^0}{\partial T}\right)_P \quad (23)$$

where

$$\begin{aligned} \left(\frac{\partial \Delta\bar{V}_n^0}{\partial T}\right)_P &= \Delta\bar{E}_{x,n}^0 = -\xi \left(\frac{1}{T-\Theta}\right)^2 \\ &= -\left[a_3 + a_4 \left(\frac{1}{\Psi+P}\right)\right] \left(\frac{1}{T-\Theta}\right)^2 \end{aligned} \quad (24)$$

and

$$\begin{aligned} \left(\frac{\partial \Delta\bar{V}_s^0}{\partial T}\right)_P &= \Delta\bar{E}_{x,s}^0 = -\omega U - Q \left(\frac{\partial \omega}{\partial T}\right)_P \\ &\quad - Y \left(\frac{\partial \omega}{\partial P}\right)_T + \left(\frac{1}{\epsilon} - 1\right) \left(\frac{\partial \left(\frac{\partial \omega}{\partial P}\right)_T}{\partial T}\right)_P \end{aligned} \quad (25)$$

which follow from the partial derivatives of Eqns. (5) and (7) through (9) with respect to temperature at constant pressure.

Equations (23) through (25) can be combined to give the equation of state for the standard partial molal expansibility of an aqueous ion or electrolyte, which can be expressed as

$$\begin{aligned} \bar{E}_x^0 &= -\left[a_3 + a_4 \left(\frac{1}{\Psi+P}\right)\right] \left(\frac{1}{T-\Theta}\right)^2 - \omega U \\ &\quad - Q \left(\frac{\partial \omega}{\partial T}\right)_P - Y \left(\frac{\partial \omega}{\partial P}\right)_T + \left(\frac{1}{\epsilon} - 1\right) \left(\frac{\partial \left(\frac{\partial \omega}{\partial P}\right)_T}{\partial T}\right)_P \end{aligned} \quad (26)$$

where

$$U = \left(\frac{\partial Q}{\partial T}\right)_P \quad (27)$$

and

$$Y = \frac{1}{\epsilon} \left(\frac{\partial \ln \epsilon}{\partial T}\right)_P. \quad (28)$$

Standard partial molal heat capacity and entropy

As in the case of the standard partial molal volume of an aqueous ion or electrolyte, the standard partial molal heat capacity (\bar{C}_P^0) can be expressed as

$$\bar{C}_P^0 = \Delta\bar{C}_{P,n}^0 + \Delta\bar{C}_{P,s}^0, \quad (29)$$

where $\Delta\bar{C}_{P,n}^0$ and $\Delta\bar{C}_{P,s}^0$ correspond to the heat capacity analogs of $\Delta\bar{V}_n^0$ and $\Delta\bar{V}_s^0$. Consideration of the temperature dependence of the standard partial molal heat capacity Born function (X) defined by (HELGESON and KIRKHAM, 1974a)

$$X = \frac{1}{\epsilon} \left[\left(\frac{\partial^2 \ln \epsilon}{\partial T^2}\right)_P - \left(\frac{\partial \ln \epsilon}{\partial T}\right)_P^2 \right], \quad (30)$$

together with scaling laws and the standard partial molal heat capacities of aqueous electrolytes at elevated temperatures indicates that the temperature dependence of $\Delta\bar{C}_{P,n}^0$ can be represented by a positive asymptotic function of temperature of the form (TANGER and HELGESON, 1988)

$$\Delta\bar{C}_{P,n}^0 = c_1 + c_2 \left(\frac{1}{T-\Theta}\right)^2, \quad (31)$$

where $\Delta\bar{C}_{P,n}^0$ represents the nonsolvation contributions to the standard partial molal heat capacity at a reference pressure designated by P_r , c_1 and c_2 stand for temperature- and pressure-independent parameters characteristic of the aqueous ion or electrolyte, and Θ again refers to the solvent parameter equal to 228 K. Taking account of the nonsolvation analog of

$$\left(\frac{\partial^2 \bar{V}^0}{\partial T^2}\right)_P = -\frac{1}{T} \left(\frac{\partial \bar{C}_P^0}{\partial P}\right)_T \quad (32)$$

and combining Eqn. (31) with the isothermal pressure integral of the isobaric temperature derivative of Eqn. (24) leads to

$$\begin{aligned} \Delta\bar{C}_{P,n}^0 &= c_1 + c_2 \left(\frac{1}{T-\Theta}\right)^2 \\ &\quad - 2T \left(\frac{1}{T-\Theta}\right)^3 \left[a_3(P - P_r) + a_4 \ln \left(\frac{\Psi+P}{\Psi+P_r}\right) \right]. \end{aligned} \quad (33)$$

The analog of Eqn. (5) for the standard partial molal entropy of solvation ($\Delta\bar{S}_s^0$) can be written as

$$\Delta\bar{S}_s^0 = \omega Y - \left(\frac{1}{\epsilon} - 1\right) \left(\frac{\partial \omega}{\partial T}\right)_P. \quad (34)$$

Differentiating this expression with respect to temperature leads to

$$\Delta\bar{C}_{P,s}^0 = \omega TX + 2TY \left(\frac{\partial \omega}{\partial T}\right)_P - T \left(\frac{1}{\epsilon} - 1\right) \left(\frac{\partial^2 \omega}{\partial T^2}\right)_P \quad (35)$$

which can be combined with Eqns. (29) and (33) to give the following equation for the standard partial molal heat capacity of an ion or electrolyte as a function of temperature and pressure:

$$\begin{aligned} \bar{C}_P^0 &= c_1 + \frac{c_2}{(T-\Theta)^2} - \left(\frac{2T}{(T-\Theta)^3}\right) \\ &\quad \times \left[a_3(P - P_r) + a_4 \ln \left(\frac{\Psi+P}{\Psi+P_r}\right) \right] \\ &\quad + \omega TX + 2TY \left(\frac{\partial \omega}{\partial T}\right)_P - T \left(\frac{1}{\epsilon} - 1\right) \left(\frac{\partial^2 \omega}{\partial T^2}\right)_P. \end{aligned} \quad (36)$$

Integration of Eqn. (33) with respect to temperature results in the equation of state for the nonsolvation standard partial molal entropy, which can be written as

$$\begin{aligned} \Delta\bar{S}_n^0 &= c_1 \ln \left(\frac{T}{T_r}\right) - \frac{c_2}{\Theta} \left[\left(\frac{1}{T-\Theta}\right) - \left(\frac{1}{T_r-\Theta}\right) \right] \\ &\quad + \frac{1}{\Theta} \ln \left(\frac{T_r(T-\Theta)}{T(T_r-\Theta)}\right) \\ &\quad + \left(\frac{1}{T-\Theta}\right)^2 \left[a_3(P - P_r) + a_4 \ln \left(\frac{\Psi+P}{\Psi+P_r}\right) \right]. \end{aligned} \quad (37)$$

Combining Eqn. (37) with Eqn. (34) and the entropy analog of Eqn. (4) leads to

$$\begin{aligned} \bar{S}^0 &= \bar{S}_{P_r,T_r}^0 + c_1 \ln \left(\frac{T}{T_r}\right) \\ &\quad - \frac{c_2}{\Theta} \left[\left(\frac{1}{T-\Theta}\right) - \left(\frac{1}{T_r-\Theta}\right) + \frac{1}{\Theta} \ln \left(\frac{T_r(T-\Theta)}{T(T_r-\Theta)}\right) \right] \\ &\quad + \left(\frac{1}{T-\Theta}\right)^2 \left[a_3(P - P_r) + a_4 \ln \left(\frac{\Psi+P}{\Psi+P_r}\right) \right] \\ &\quad + \omega Y - \left(\frac{1}{\epsilon} - 1\right) \left(\frac{\partial \omega}{\partial T}\right)_P - \omega_{P_r,T_r} Y_{P_r,T_r} \end{aligned} \quad (38)$$

which corresponds to the equation of state for the standard partial molal entropy of an aqueous ion or electrolyte.

Apparent standard partial molal enthalpy and Gibbs free energy of formation

By definition, the apparent standard partial molal enthalpy and Gibbs free energy of formation of an aqueous species are given by (BENSON, 1968, 1976; HELGESON, 1969; HELGESON and KIRKHAM, 1976; HELGESON *et al.*, 1981; TANGER and HELGESON, 1988)

$$\Delta\bar{H}^0 = \Delta\bar{H}_f^0 + (\bar{H}_{P,T}^0 - \bar{H}_{P_r,T_r}^0) \quad (39)$$

and

$$\Delta\bar{G}^0 = \Delta\bar{G}_f^0 + (\bar{G}_{P,T}^0 - \bar{G}_{P_r,T_r}^0) \quad (40)$$

where $\Delta\bar{H}^0$ and $\Delta\bar{G}^0$ stand for the conventional apparent standard partial molal enthalpy and Gibbs free energy of formation of an aqueous species at a given pressure and temperature, $\Delta\bar{H}_f^0$ and $\Delta\bar{G}_f^0$ denote the conventional standard partial molal enthalpy and Gibbs free energy of formation of the species from the elements at a reference pressure (P_r) and temperature (T_r) of 1 bar and 298.15 K, and the parenthetical terms correspond to the difference in the conventional standard partial molal enthalpy and Gibbs free energy of formation of an aqueous species at the temperature and pressure of interest and those at the reference conditions. It thus follows from Eqns. (11), (26), (36), (39), and (40), together with

$$\bar{H}_{P,T}^0 - \bar{H}_{P_r,T_r}^0 = \int_{T_r}^T \bar{C}_{P_r,T_r}^0 dT + \int_{P_r}^P (\bar{V}^0 - T\bar{E}_T^0)_T dP \quad (41)$$

and

$$\begin{aligned} \bar{G}_{P,T}^0 - \bar{G}_{P_r,T_r}^0 = & -\bar{S}_{P_r,T_r}^0(T - T_r) + \int_{T_r}^T \bar{C}_{P_r,T_r}^0 dT \\ & - T \int_{T_r}^T \bar{C}_{P_r,T_r}^0 d \ln T + \int_{P_r}^P \bar{V}_T^0 dP \end{aligned} \quad (42)$$

that we can write

$$\begin{aligned} \Delta\bar{H}^0 = & \Delta\bar{H}_f^0 + c_1(T - T_r) - c_2 \left(\left(\frac{1}{T - \theta} \right) - \left(\frac{1}{T_r - \theta} \right) \right) \\ & + a_1(P - P_r) + a_2 \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) \\ & + \left(\frac{2T - \theta}{(T - \theta)^2} \right) \left(a_3(P - P_r) + a_4 \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) \right) \\ & + \omega \left(\frac{1}{\epsilon} - 1 \right) + \omega TY - T \left(\frac{1}{\epsilon} - 1 \right) \left(\frac{\partial \omega}{\partial T} \right)_P \\ & - \omega_{P_r,T_r} \left(\frac{1}{\epsilon_{P_r,T_r}} - 1 \right) - \omega_{P_r,T_r} T_r Y_{P_r,T_r} \end{aligned} \quad (43)$$

and

$$\begin{aligned} \Delta\bar{G}^0 = & \Delta\bar{G}_f^0 - \bar{S}_{P_r,T_r}^0(T - T_r) - c_1 \left(T \ln \left(\frac{T}{T_r} \right) - T + T_r \right) \\ & + a_1(P - P_r) + a_2 \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) \\ & - c_2 \left(\left(\left(\frac{1}{T - \theta} \right) - \left(\frac{1}{T_r - \theta} \right) \right) \left(\frac{\theta - T}{\theta} \right) - \frac{T}{\theta^2} \ln \left(\frac{T_r(T - \theta)}{T(T_r - \theta)} \right) \right) \\ & + \left(\frac{1}{T - \theta} \right) \left(a_3(P - P_r) + a_4 \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) \right) + \omega \left(\frac{1}{\epsilon} - 1 \right) \\ & - \omega_{P_r,T_r} \left(\frac{1}{\epsilon_{P_r,T_r}} - 1 \right) + \omega_{P_r,T_r} Y_{P_r,T_r}(T - T_r). \end{aligned} \quad (44)$$

BORN COEFFICIENTS AND THE EFFECTIVE ELECTROSTATIC RADII OF AQUEOUS IONIC SPECIES

The absolute Born coefficient of the j th aqueous ionic species (ω_j^{abs}) is defined in terms of the charge and effective electrostatic radius of the ion as

$$\omega_j^{\text{abs}} = \frac{N^0 e^2 Z_j^2}{2r_{e,j}} = \frac{\eta Z_j^2}{r_{e,j}} \quad (45)$$

where Z_j refers to the charge of the subscripted ion, $r_{e,j}$ denotes the effective electrostatic radius of the j th ion (HELGESON and KIRKHAM, 1976; HELGESON *et al.*, 1981), which is taken in the revised HKF model to be a function of temperature and pressure (TANGER and HELGESON, 1988; SHOCK *et al.*, 1988b), and

$$\eta = \frac{N^0 e^2}{2} = 1.66027 \times 10^5 \text{ \AA cal mol}^{-1}, \quad (46)$$

where N^0 represents Avogadro's number ($6.02252 \times 10^{23} \text{ mol}^{-1}$) and e stands for the absolute electronic charge ($4.80298 \times 10^{-10} \text{ esu}$). By analogy to Eqn. (2), the conventional Born coefficient (ω_j) is given by

$$\omega_j = \omega_j^{\text{abs}} - Z_j \omega_{\text{H}^+}^{\text{abs}} \quad (47)$$

where $\omega_{\text{H}^+}^{\text{abs}}$ stands for the absolute Born coefficient of the hydrogen ion at the temperature and pressure of interest, which is taken as $0.5387 \times 10^5 \text{ cal mol}^{-1}$ at 25°C and 1 bar (HELGESON and KIRKHAM, 1976). The effective electrostatic radius of an ion can be expressed in terms of its corresponding crystallographic radius ($r_{x,j}$) by writing

$$r_{e,j} = r_{x,j} + |Z_j| \Gamma_{\pm} \quad (48)$$

where Γ_{\pm} in the revised HKF model is given by (TANGER and HELGESON, 1988)

$$\Gamma_{\pm} = k_{\pm} + g \quad (49)$$

where k_{\pm} represents a charge-dependent constant equal to 0.0 Å for anions and 0.94 Å for cations, and g denotes a solvent function of temperature and density. The g function has been characterized by fitting orthogonal temperature-density polynomials to values of the Born coefficient for the electrolyte (ω_k) generated from fits of Eqns. (11) and (36) to experimentally determined partial molal properties of NaCl (TANGER and HELGESON, 1988), or by regression of values of g calculated from Eqn. (44) and apparent standard partial molal Gibbs free energies of formation of NaCl⁰ derived from supercritical dissociation constants (SHOCK *et al.*, 1988b). These explicit functions for ω_k or g in different pressure-temperature regions permit evaluation of the partial derivatives of ω in Eqns. (5), (11), (15), (18), (25), (26), (34), (35), (36), (38), (43), and (44). At low temperatures and pressures, the g function and its derivatives approach 0. As a consequence, Γ_{\pm} , and therefore $r_{e,j}$ are essentially constant at temperatures below ~170°C and pressures corresponding to the vapor-liquid saturation curve for H₂O or 1 bar at temperatures $\leq 100^\circ\text{C}$ (P_{SAT}). Γ_{\pm} and $r_{e,j}$ are also essentially constant at (SHOCK *et al.*, 1988b)

$$T \leq \frac{P - P_{\text{SAT}}}{10} + 170, \quad (50)$$

where P and P_{SAT} are expressed in bars and T in °C.

The effective electrostatic radius of an ion at 25°C and 1 bar in Eqn. (45) can be computed from its standard partial molal entropy at 25°C and 1 bar by first taking account of the standard partial molal entropy analog of Eqn. (4), which can be expressed as

$$\bar{S}_j^0 = \Delta\bar{S}_{s,j}^0 + \Delta\bar{S}_{s,j}^{\text{obs}} \quad (51)$$

This equation, combined with the solvation entropy analog of Eqn. (2) given by

$$\Delta\bar{S}_{s,j}^0 = \Delta\bar{S}_{s,j}^{\text{obs}} - Z_j \Delta\bar{S}_{s,\text{H}^+}^{\text{obs}} \quad (52)$$

leads to

$$\bar{S}_j^0 - \Delta\bar{S}_{s,j}^{\text{obs}} = \Delta\bar{S}_{s,j}^0 - Z_j \Delta\bar{S}_{s,\text{H}^+}^{\text{obs}} \quad (53)$$

which corresponds to a corrected statement of the first identity in Eqn. (67) of HELGESON and KIRKHAM (1976). Because $(\partial\omega/\partial T)_P \approx 0$ at low temperatures, the second term on the left side of Eqn. (53) can be expressed as an absolute analog of Eqn. (34) for the j th ion at 25°C and 1 bar by writing

$$\Delta S_{a,j}^{\text{obs}} = \omega_j^{\text{abs}} Y. \quad (54)$$

Values of the right side of Eqn. (53) at 25°C and 1 bar are shown in Table 1 for 53 ionic species for which crystallographic radii are available. These values were generated from Eqns. (53) and (54) using the experimental standard partial molal entropies of the ions given in Table 1, together with values of ω_j^{abs} at 25°C and 1 bar calculated from the crystallographic radii shown in the table using Eqns. (45) and (48). The right side of Eqn. (53) is also plotted in Fig. 1 as a function of $Z_j^2/r_{e,j}$, where it can be deduced that all of the values are consistent with

$$\Delta S_{a,j}^{\text{obs}} - Z_j \Delta S_{a,H^+}^{\text{obs}} = \alpha_Z - \frac{100Z_j^2}{r_{e,j}} \quad (55)$$

where α_Z represents the charge-dependent intercepts of the curves shown in the figure. These intercepts (which are equal to 72, 141, and 211 cal mol⁻¹ K⁻¹ for monovalent, divalent, and trivalent ions, respectively) are plotted in Fig. 2, where it can be seen that they are essentially a linear function of $|Z_j|$ consistent with

$$\alpha_Z = 71.5|Z_j|, \quad (56)$$

which yields a predicted intercept value for tetravalent ions of 286 cal mol⁻¹ K⁻¹.

The effective electrostatic radii at 25°C and 1 bar of aqueous ions for which there are no crystallographic radii available can be computed by first combining Eqns. (45) and (53) through (55) to give

$$r_{e,j} = \frac{Z_j^2(\eta Y - 100)}{S_j^0 - \alpha_Z}. \quad (57)$$

Values of $r_{e,j}$ at 25°C and 1 bar generated from Eqn. (57) using standard partial molal entropies of aqueous ions and the Born function Y (Eqn. 28) at 25°C and 1 bar (-5.81×10^{-5} K⁻¹ taken from HELGESON and KIRKHAM, 1974a) are given in Table 2 for 80 aqueous ions, together with the values of S_j^0 used in the calculations and the values of the corresponding absolute and conventional Born coefficients.¹ Note that Eqn. (57) can be combined with Eqn. (48) to give

$$S_j^0 = \frac{Z_j^2(\eta Y - 100)}{r_{e,j} + Z_j \Gamma_{\pm}} + \alpha_Z, \quad (58)$$

which permits prediction of the standard partial molal entropies of aqueous ions at 25°C and 1 bar for which calorimetric data are either unavailable or of questionable accuracy. Calculations of this kind for 52 such ions resulted in the values of S_j^0 given in Table 3, which also includes corresponding values of $r_{e,j}$, ω_j^{abs} , and ω_j at 25°C and 1 bar calculated from Eqns. (48), (45) and (47).

Contradictory experimental values of S_j^0 at 25°C and 1 bar have been reported in the literature for a number of the ions shown in Table 3. The predicted values in the table can be used to support one or another of these choices. For instance, the estimated value of $S_{Cr^{3+}}^0$ given in Table 3 (-75.0 cal mol⁻¹ K⁻¹) is much closer to the value given by NAUMOV *et al.* (1974) (-75.6 cal mol⁻¹ K⁻¹) than that adopted by BABUSHKIN *et al.* (1985) (-51.1 cal mol⁻¹ K⁻¹).

RETRIEVAL OF NONSOLVATION EQUATION OF STATE PARAMETERS

The species-dependent nonsolvation parameters in Eqns. (7), (17), and (31) can be obtained by regression of exper-

imental values of the standard partial molal properties of aqueous electrolytes at a series of temperatures. Previous regression and estimation calculations of equation of state parameters for the revised HKF model have been carried out for NaCl, KCl, LiCl, CsCl, HCl, NH₄Cl, MgCl₂, CaCl₂, SrCl₂, BaCl₂, NaBr, KBr, KF, KI, CsI, LiOH, NaOH, KOH, HNO₃, NaNO₃, KNO₃, NaHCO₃, and Na₂SO₄ (TANGER and HELGESON, 1988). In addition to these electrolytes, experimental volumetric and/or calorimetric data at various temperatures are reported in the literature for RbCl, CuCl₂, LaCl₃, PrCl₃, NdCl₃, GdCl₃, AlCl₃, KNO₂, NaHS, NaClO₄, NaB(OH)₄, NaAl(OH)₄, Na₂WO₄, Na₂MoO₄, Na₂SO₃, NH₄ClO₄, Cd(NO₃)₂, and Co(NO₃)₂. Standard partial molal properties for the latter electrolytes were generated in the present study by extrapolating experimental data to infinite dilution using the extended Debye-Hückel equation adopted by HELGESON *et al.* (1981).

Extrapolation strategy

Of the several models of the concentration dependence of the partial molal thermodynamic properties of aqueous electrolytes that have been proposed in recent years (PITZER, 1973; JOHNSON and PYTKOWICZ, 1979; NORDHOLM, 1983; WOOD *et al.*, 1984; HELGESON *et al.*, 1981), the latter model, which is consistent with the Hückel equation, was adopted in the present study. The Hückel equation can be written as

$$\log \bar{\gamma}_{\pm,k} = - \frac{|Z_+ Z_-| A_{\gamma} \bar{I}^{1/2}}{1 + \bar{a}_k B_{\gamma} \bar{I}^{1/2}} + \Gamma_{\gamma} + b_{\gamma,k} \bar{I} \quad (59)$$

where $\bar{\gamma}_{\pm,k}$ stands for the mean ionic activity coefficient of the k th electrolyte, \bar{a}_k refers to the ion size parameter for the electrolyte, $b_{\gamma,k}$ denotes the corresponding extended term coefficient, Γ_{γ} denotes the mole fraction/molality conversion factor given by

$$\Gamma_{\gamma} \equiv \log(1 + 0.0180153 m_k), \quad (60)$$

and \bar{I} stands for the effective ionic strength defined by

$$\bar{I} \equiv \frac{1}{2} \sum_j Z_j^2 m_j \quad (61)$$

where j designates aqueous ions, and A_{γ} and B_{γ} represent the Debye-Hückel parameters given by

$$\begin{aligned} A_{\gamma} &= \frac{(2\pi N^0)^{1/2} e^3 \rho^0{}^{1/2}}{2.302585 (1000)^{1/2} (\epsilon^0 kT)^{3/2}} \\ &= \frac{1.824829238 \times 10^6 \rho^0{}^{1/2}}{(\epsilon^0 T)^{3/2}} \end{aligned} \quad (62)$$

and

$$B_{\gamma} \equiv \left(\frac{8\pi N^0 \rho^0 e^2}{1000 \epsilon^0 kT} \right)^{1/2} = \frac{50.29158649 \times 10^8 \rho^0{}^{1/2}}{(\epsilon^0 T)^{1/2}} \quad (63)$$

where $\pi = 3.14159265$, k denotes Boltzmann's constant (1.38054×10^{-16} erg K⁻¹), and ρ^0 and ϵ^0 stand for the density and dielectric constant of H₂O, respectively.

Taking account of Eqns. (59) and (60), together with the relation between the apparent molal property of a single electrolyte solution (ϕ_{\pm}) and the corresponding partial molal property of the electrolyte given by

¹ The slopes and intercepts of the curves shown in Fig. 1 are not exactly consistent with curves generated from the slopes and intercepts of Fig. 21 of HELGESON and KIRKHAM (1976). For this reason, values of $r_{e,j}$ and S_j^0 calculated from Eqn. (57) differ slightly from those calculated from Eqn. (74) of HELGESON and KIRKHAM (1976).

Table 1. Crystal ($r_{x,j}$) and effective electrostatic ($r_{e,j}$) radii, absolute (ω_j^{abs}) and conventional (ω_j) Born coefficients and conventional standard partial molal entropies (\bar{S}°_j) and entropy functions of aqueous ions (designated by the subscript j) at 25°C and 1 bar.

| Ion | $r_{x,j}$ a,k | $r_{e,j}$ a,k | $\omega_j^{abs,b,k} \times 10^{-5}$ | $\omega_j^{b,k} \times 10^{-5}$ | \bar{S}°_j c,k | $\Delta\bar{S}^\circ_{\pi,j} - Z_j \Delta\bar{S}^\circ_{\pi,H^+}$ c,p |
|------------------|-------------------|-------------------|-------------------------------------|---------------------------------|-----------------------|---|
| Li ⁺ | 0.68 | 1.62 | 1.0249 | 0.4862 | 2.7 | 8.7 |
| Na ⁺ | 0.97 | 1.91 | 0.8693 ⁱ | 0.3305 ⁱ | 13.96 | 19.0 |
| K ⁺ | 1.33 | 2.27 | 0.7314 | 0.1927 | 24.15 | 28.4 |
| Rb ⁺ | 1.47 | 2.41 | 0.6889 | 0.1502 | 28.8 | 32.8 |
| Cs ⁺ | 1.67 | 2.61 | 0.6361 | 0.0974 | 31.75 | 35.4 |
| Tl ⁺ | 1.47 | 2.41 | 0.6889 | 0.1502 | 30.0 | 34.0 |
| Ag ⁺ | 1.26 | 2.20 | 0.7547 | 0.2160 | 17.54 | 21.9 |
| Cu ⁺ | 0.96 | 1.90 | 0.8738 | 0.3351 | 9.7 | 14.8 |
| Mg ⁺² | 0.66 | 2.54 | 2.6146 | 1.5372 | -33.0 | -17.8 |
| Ca ⁺² | 0.99 | 2.87 | 2.3140 | 1.1363 | -13.5 | -0.1 |
| Sr ⁺² | 1.12 | 3.00 | 2.2137 | 1.2366 | -7.53 | 5.3 |
| Ba ⁺² | 1.34 | 3.22 | 2.0624 ⁱ | 0.9850 ⁱ | 2.3 | 14.3 |
| Ra ⁺² | 1.43 ^d | 3.31 ^c | 2.0064 ^f | 0.9290 ^g | 13. ^h | 24.6 |
| Mn ⁺² | 0.80 | 2.68 | 2.4780 | 1.4006 | -17.6 | -3.2 |
| Fe ⁺² | 0.74 | 2.62 | 2.5348 | 1.4574 | -25.6 | -10.9 |
| Ag ⁺² | 0.89 ^d | 2.77 ^e | 2.3975 ^f | 1.3201 ^g | -21.0 ^h | -7.1 |
| Cu ⁺² | 0.72 | 2.60 | 2.5543 | 1.4769 | -23.2 | -8.4 |
| Zn ⁺² | 0.74 | 2.62 | 2.5348 | 1.4574 | -26.2 | -11.5 |
| Cd ⁺² | 0.97 | 2.85 | 2.3302 | 1.2528 | -17.4 | -3.9 |
| Pb ⁺² | 1.20 | 3.08 | 2.1562 | 1.0788 | 4.2 | 16.7 |
| Ni ⁺² | 0.69 ^d | 2.57 ^e | 2.5841 ^f | 1.5067 ^g | -30.8 ⁱ | -15.8 |
| Co ⁺² | 0.72 ^d | 2.60 ^e | 2.5543 ^f | 1.4769 ^g | -27.0 ⁱ | -12.2 |
| Hg ⁺² | 1.10 | 2.98 | 2.2286 | 1.1512 | -8.68 | 4.3 |
| Sn ⁺² | 0.93 ^d | 2.81 ^e | 2.3634 ^f | 1.2860 ^g | -3.8 ⁱ | 9.9 |
| Sm ⁺² | 1.00 ^d | 2.88 ^e | 2.3059 ^f | 1.2285 ^g | -6.2 ^m | 7.2 |
| Al ⁺³ | 0.51 | 3.33 | 4.4872 | 2.8711 | -73.6 | -47.6 |
| Fe ⁺³ | 0.64 | 3.46 | 4.3186 | 2.7025 | -66.3 | -41.2 |
| Ga ⁺³ | 0.62 | 3.44 | 4.3437 | 2.7276 | -79. | -53.8 |
| In ⁺³ | 0.81 | 3.36 | 4.1164 | 2.5003 | -63. | -39.1 |
| Tl ⁺³ | 0.95 | 3.77 | 3.9635 | 2.3474 | -46. | -23.0 |
| Co ⁺³ | 0.63 ^d | 3.45 ^e | 4.3311 ^f | 2.7150 ^g | -73. ^h | -47.9 |
| Y ⁺³ | 0.92 ^d | 3.74 ^c | 3.9953 ^f | 2.3792 ^g | -60. ^m | -36.8 |
| La ⁺³ | 1.14 | 3.96 | 3.7733 | 2.1572 | -52. | -30.1 |
| Ce ⁺³ | 1.07 ^d | 3.89 ^e | 3.8412 ^f | 2.2251 ^g | -49. ^m | -26.7 |
| Pr ⁺³ | 1.06 ^d | 3.88 ^e | 3.8511 ^f | 2.2350 ^g | -50. ^m | -27.7 |
| Nd ⁺³ | 1.04 ^d | 3.86 ^e | 3.8711 ^f | 2.2550 ^g | -49.5 ^m | -27.0 |
| Sm ⁺³ | 1.00 ^d | 3.82 ^e | 3.9116 ^f | 2.2955 ^g | -50.7 ^m | -28.0 |
| Eu ⁺³ | 0.98 ^d | 3.80 ^e | 3.9322 ^f | 2.3161 ^g | -53.0 ^m | -30.2 |
| Gd ⁺³ | 0.97 | 3.79 | 3.9426 | 2.3265 | -49.2 | -26.3 |
| Tb ⁺³ | 0.93 ^d | 3.75 ^e | 3.9846 ^f | 2.3683 ^g | -54.0 ^m | -30.9 |
| Dy ⁺³ | 0.92 ^d | 3.74 ^e | 3.9953 ^f | 2.3792 ^g | -55.2 ^m | -32.0 |
| Ho ⁺³ | 0.91 ^d | 3.73 ^e | 4.0060 ^f | 2.3899 ^g | -54.3 ^m | -31.1 |
| Er ⁺³ | 0.89 ^d | 3.71 ^e | 4.0276 ^f | 2.4115 ^g | -58.3 ^m | -34.9 |
| Tm ⁺³ | 0.87 ^d | 3.69 ^e | 4.0494 ^f | 2.4333 ^g | -58.1 ^m | -34.6 |
| Yb ⁺³ | 0.86 ^d | 3.68 ^e | 4.0604 ^f | 2.4443 ^g | -56.9 ^m | -33.3 |
| Lu ⁺³ | 0.85 ^d | 3.67 ^e | 4.0715 ^f | 2.4554 ^g | -63.1 ^m | -39.5 |
| Sc ⁺³ | 0.81 ^d | 3.63 ^e | 4.1164 ^f | 2.5003 ^g | -61. ^h | -37.1 |
| F ⁻ | 1.33 | 1.33 | 1.2483 | 1.7870 | -3.15 | 4.1 |
| Cl ⁻ | 1.81 | 1.81 | 0.9173 | 1.4560 | 13.56 | 18.9 |
| Br ⁻ | 1.96 | 1.96 | 0.8471 | 1.3858 | 19.80 | 24.7 |
| I ⁻ | 2.20 | 2.20 | 0.7547 | 1.2934 | 25.50 | 29.9 |
| OH ⁻ | 1.40 | 1.40 | 1.1859 | 1.7246 | -2.56 | 4.3 |
| HS ⁻ | 1.84 | 1.84 | 0.9023 | 1.4410 ^j | 16.3 ⁿ | 21.5 |

a. Angstroms. b. cal mol⁻¹. c. cal mol⁻¹ K⁻¹. d. Pauling radius (Bloss, 1971). e. Calculated with eq (48). f. Calculated with eq (45). g. Calculated with eq (47). h. Wagman et al. (1982). i. Corrected error in Helgeson and Kirkham (1976). j. Corrected error in Helgeson, Kirkham and Flowers (1981). k. From Helgeson and Kirkham (1976) table 7, Helgeson, Kirkham and Flowers (1981) table 18, or Tanger and Helgeson (1988) unless otherwise indicated. l. Jackson and Helgeson (1985). m. Morss (1976). n. Barbero et al. (1982). p. Calculated as described in text.

Table 2. Standard partial molal entropies (\bar{S}_j^0), effective electrostatic radii ($r_{e,j}$), and absolute (ω_j^{abs}) and conventional (ω_j) Born coefficients of aqueous ions (designated by the subscript j) at 25°C and 1 bar.

| Ion | \bar{S}_j^0 ^a | $r_{e,j}$ ^b | $\omega_j^{\text{abs}} \times 10^{-5}$ | $\omega_j \times 10^{-5}$ |
|---|----------------------------|------------------------|--|---------------------------|
| NH ₄ ⁺ | 26.57 ^c | 2.41 | 0.6889 | 0.1502 |
| VO ₂ ⁺ | -10.1 | 1.34 | 1.2390 | 0.7003 |
| Eu ²⁺ | -2.4 ^f | 3.06 | 2.1703 | 1.0929 |
| Yb ²⁺ | -11.2 ^f | 2.88 | 2.3059 | 1.2285 |
| VO ²⁺ | -32.0 | 2.53 | 2.6249 | 1.5475 |
| UO ₂ ²⁺ | -23.3 | 2.67 | 2.4873 | 1.4099 |
| Hg ₂ ²⁺ | 15.66 ^c | 3.50 | 1.8975 | 0.8201 |
| U ³⁺ | -45.9 | 3.84 | 3.8913 | 2.2752 |
| AlO ₂ ⁻ | -6.4 | 1.40 | 1.1859 | 1.7246 |
| BO ₂ ⁻ | -8.9 | 1.36 | 1.2208 | 1.7595 |
| BF ₄ ⁻ | 43. | 3.78 | 0.4392 | 0.9779 |
| HCO ₃ ⁻ | 23.53 ^g | 2.26 | 0.7346 | 1.2733 |
| CN ⁻ | 22.5 | 2.21 | 0.7513 | 1.2900 |
| NO ₂ ⁻ | 35.12 ^c | 2.97 | 0.5590 | 1.0977 |
| NO ₃ ⁻ | 29.4 | 2.57 | 0.6460 | 1.1847 |
| N ₃ ⁻ | 25.8 | 2.37 | 0.7005 | 1.2392 |
| H ₂ PO ₄ ⁻ | 21.6 | 2.18 | 0.7616 | 1.3003 |
| H ₂ P ₂ O ₇ ⁻ | 51. | 5.22 | 0.3181 | 0.8568 |
| H ₂ AsO ₄ ⁻ | 28. | 2.49 | 0.6668 | 1.2055 |
| H ₂ AsO ₅ ⁻ | 26.4 | 2.40 | 0.6918 | 1.2305 |
| Sb ₂ S ₄ ⁻ | -6.3 | 1.40 | 1.1859 | 1.7246 |
| HO ₂ ⁻ | 5.7 | 1.65 | 1.0062 | 1.5449 |
| HSO ₃ ⁻ | 33.4 | 2.84 | 0.5846 | 1.1233 |
| HSO ₄ ⁻ | 28.8 ^h | 2.54 | 0.6536 | 1.1923 |
| HSO ₅ ⁻ | 50.7 ^l | 5.15 | 0.3224 | 0.8611 |
| HSe ⁻ | 19. | 2.07 | 0.8021 | 1.3408 |
| HSeO ₃ ⁻ | 32.3 | 2.76 | 0.6015 | 1.1402 |
| HSeO ₄ ⁻ | 35.7 | 3.02 | 0.5498 | 1.0885 |
| HTeO ₃ ⁻ | 33.2 ^l | 2.83 | 0.5867 | 1.1254 |
| HF ₂ ⁻ | 22.1 | 2.20 | 0.7547 | 1.2934 |
| ClO ⁻ | 10. | 1.77 | 0.9380 | 1.4767 |
| ClO ₂ ⁻ | 24.2 | 2.29 | 0.7250 | 1.2637 |
| ClO ₃ ⁻ | 38.8 | 3.30 | 0.5031 | 1.0418 |
| ClO ₄ ⁻ | 43.5 | 3.85 | 0.4312 | 0.9699 |
| BrO ⁻ | 10. | 1.77 | 0.9380 | 1.4767 |
| BrO ₂ ⁻ | 38.65 | 3.29 | 0.5046 | 1.0433 |
| BrO ₃ ⁻ | 47.7 | 4.51 | 0.3681 | 0.9068 |
| Br ₂ ⁻ | 51.5 | 5.35 | 0.3103 | 0.8490 |
| IO ⁻ | -1.3 | 1.50 | 1.1068 | 1.6455 |
| IO ₂ ⁻ | 28.3 | 2.51 | 0.6615 | 1.2002 |
| IO ₃ ⁻ | 53. | 5.77 | 0.2877 | 0.8264 |
| I ₃ ⁻ | 57.2 | 7.41 | 0.2241 | 0.7628 |

| Ion | \bar{S}_j^0 ^a | $r_{e,j}$ ^b | $\omega_j^{\text{abs}} \times 10^{-5}$ | $\omega_j \times 10^{-5}$ |
|--|----------------------------|------------------------|--|---------------------------|
| H ₂ VO ₄ ⁻ | 29. | 2.55 | 0.6511 | 1.1898 |
| HCrO ₄ ⁻ | 44. | 3.29 | 0.4235 | 0.9622 |
| MnO ₄ ⁻ | 45.7 | 4.17 | 0.3981 | 0.9368 |
| ReO ₄ ⁻ | 48.1 | 4.59 | 0.3617 | 0.9004 |
| BeO ₂ ²⁻ | -38. | 2.45 | 2.7106 | 3.7880 |
| CO ₃ ²⁻ | -11.95 ^g | 2.87 | 2.3140 | 3.3914 |
| SiF ₆ ²⁻ | 29.2 | 3.92 | 1.6942 | 2.7716 |
| N ₂ O ₇ ²⁻ | 6.6 ^j | 3.26 | 2.0371 | 3.1145 |
| HPO ₄ ²⁻ | -8.7 | 2.93 | 2.2666 | 3.3440 |
| H ₂ P ₂ O ₇ ²⁻ | 39. | 4.30 | 1.5444 | 2.6218 |
| HAsO ₄ ²⁻ | -0.4 | 3.10 | 2.1423 | 3.2197 |
| SO ₃ ²⁻ | -7. | 2.96 | 2.2436 | 3.3210 |
| SO ₄ ²⁻ | 4.50 ^e | 3.21 | 2.0689 | 3.1463 |
| S ₂ ²⁻ | 6.8 | 3.27 | 2.0309 | 3.1083 |
| S ₂ O ₃ ²⁻ | 16. | 3.51 | 1.8920 | 2.9694 |
| S ₂ O ₄ ²⁻ | 22. | 3.69 | 1.7998 | 2.8772 |
| S ₂ O ₅ ²⁻ | 25 ^k | 3.78 | 1.7569 | 2.8343 |
| S ₂ O ₆ ²⁻ | 30 ^k | 3.95 | 1.6813 | 2.7587 |
| S ₂ O ₈ ²⁻ | 58.4 | 5.31 | 1.2507 | 2.3281 |
| S ₃ ²⁻ | 15.8 | 3.50 | 1.8975 | 2.9749 |
| S ₃ O ₆ ²⁻ | 33 ^k | 4.06 | 1.6357 | 2.7131 |
| S ₄ ²⁻ | 24.7 | 3.77 | 1.7616 | 2.8390 |
| S ₄ O ₆ ²⁻ | 61.5 | 5.52 | 1.2031 | 2.2805 |
| S ₅ ²⁻ | 33.6 | 4.08 | 1.6277 | 2.7051 |
| S ₅ O ₆ ²⁻ | 40 ^k | 4.34 | 1.5302 | 2.6076 |
| SeO ₃ ²⁻ | 3. | 3.18 | 2.0884 | 3.1658 |
| SeO ₄ ²⁻ | 12.9 | 3.42 | 1.9418 | 3.0192 |
| TeO ₃ ²⁻ | 3.2 ^l | 3.18 | 2.0884 | 3.1658 |
| HVO ₄ ²⁻ | 4. | 3.20 | 2.0753 | 3.1527 |
| CrO ₄ ²⁻ | 12. | 3.40 | 1.9533 | 3.0307 |
| Cr ₂ O ₇ ²⁻ | 62.6 | 5.59 | 1.1880 | 2.2654 |
| MnO ₄ ²⁻ | 14. | 3.45 | 1.9250 | 3.0024 |
| MoO ₄ ²⁻ | 6.5 ^m | 3.26 | 2.0371 | 3.1145 |
| WO ₄ ²⁻ | 9.7 ^m | 3.34 | 1.9883 | 3.0657 |
| PO ₄ ³⁻ | -53. | 3.74 | 3.9953 | 5.6114 |
| HP ₂ O ₇ ³⁻ | 11. | 4.93 | 3.0309 | 4.6470 |
| AsO ₄ ³⁻ | -38.9 | 3.95 | 3.7829 | 5.3990 |
| P ₂ O ₇ ⁴⁻ | -28. | 5.59 | 4.7521 | 6.9069 |

a. cal mol⁻¹ K⁻¹, taken from Wagman et al. (1982) unless otherwise indicated. b. Angstroms, calculated with eq (57). c. cal mol⁻¹, calculated with eq (45). d. cal mol⁻¹, calculated with eq (47). e. CODATA (1978). f. Morss (1976). g. Berg and Vanderzee (1978). h. From fit of log K data in present study, see text. i. Naumov et al. (1974). j. Rossini et al. (1952). k. Latimer (1952). l. Price et al. (1986). m. Jackson and Helgeson (1985).

and

$$\rho_{J,k} = \phi_{C_p} - \psi_k A_j \bar{I}^{1/2} \alpha^* + \frac{\psi_k (2A_H B_H - A_G B_J T) \beta^*}{2.303 RT^2} - \frac{2\psi_k A_j (B_H)^2 \zeta^*}{2.303 RT^2} = \bar{C}_{P,k}^0 - \frac{\nu_k b_{j,k} \bar{I}}{4}, \quad (84)$$

which can be used to extrapolate experimental values of ϕ_V and ϕ_{C_p} to infinite dilution.

It follows from the second identities in Eqns. (83) and (84) that $\rho_{V,k}$ and $\rho_{J,k}$ are linear functions of \bar{I} in a completely dissociated electrolyte solution. Under these conditions, $\bar{I} = I = 1/2 \sum_j \nu_{j,k} Z_j^2 m_k$, and a plot of $\rho_{V,k}$ or $\rho_{J,k}$ against I at constant temperature and pressure should yield a linear curve

with an intercept of \bar{V}_k^0 or $\bar{C}_{P,k}^0$, respectively. The slopes of the curves are equal to the corresponding extended term parameters, modified by $\nu_k/4$. Departures from linearity with increasing concentration in plots of this type can be attributed to ion association (HELGESON *et al.*, 1981). Plots of ρ_V and ρ_J against I are shown in Figs. 3 through 5 for many of the electrolytes considered in the present study. It can be seen in these figures that in every case the distribution of the experimental data is consistent with Eqn. (83) or (84), except at ionic strengths where ion association apparently becomes significant ($I \geq 1$ to 10, depending on the electrolyte). The intercepts of the curves shown in Figs. 3 through 5 are tabulated in the Appendix² (NAPS, 1988).

Regression calculations

The values of the standard partial molal volumes and heat capacities of aqueous electrolytes at various temperatures summarized in the Appendix (NAPS, 1988) were regressed graphically with Eqns. (7) and (31) to obtain the nonsolvation species-dependent equation of state parameters in the revised HKF model by first subtracting the solvation contributions

² See NAPS document No. 04597 for 37 pages of supplementary material. Order from NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10163-3513. Remit in advance, in U.S. funds only, \$12.85 for photocopies or \$4.00 for microfiche. Outside the U.S. and Canada, add postage of \$4.50 for the first 20 pages and \$1.00 for each of 10 pages of material thereafter, or \$1.50 for microfiche postage.

Table 3. Crystal ($r_{c,j}$) and effective electrostatic ($r_{e,j}$) radii, absolute (ω_j^{abs}) and conventional (ω_j) Born coefficients and conventional standard partial molal entropies (\bar{S}_j^0) of aqueous ions (designated by the subscript j) at 25°C and 1 bar.

| Ion | $r_{c,j}^a$ | $r_{e,j}^b$ | \bar{S}_j^c | $\omega_j^{abs,d} \times 10^{-5}$ | $\omega_j^e \times 10^{-5}$ |
|------------------|-------------|-------------|--------------------|-----------------------------------|-----------------------------|
| Au ⁺ | 1.37 | 2.31 | 24.5 ^f | 0.7187 | 0.1800 |
| Fr ⁺ | 1.80 | 2.74 | 32.0 | 0.6059 | 0.0672 |
| Be ⁺² | 0.35 | 2.23 | -55.7 | 2.9781 | 1.9007 |
| Ge ⁺² | 0.73 | 2.61 | -27.0 | 2.5445 | 1.4671 |
| Pd ⁺² | 0.80 | 2.68 | -22.6 | 2.4780 | 1.4006 |
| Pt ⁺² | 0.80 | 2.68 | -22.6 | 2.4780 | 1.4006 |
| V ⁺² | 0.88 | 2.76 | -17.9 | 2.4062 | 1.3288 |
| Am ⁺³ | 1.07 | 3.89 | -42.6 | 3.8412 | 2.2251 |
| As ⁺³ | 0.58 | 3.40 | -79.2 | 4.3949 | 2.7787 |
| Au ⁺³ | 0.82 | 3.67 | -57.9 ^f | 4.0715 | 2.4554 |
| B ⁺³ | 0.23 | 3.05 | -112.5 | 4.8992 | 3.2931 |
| Bi ⁺³ | 0.96 | 3.78 | -50.0 | 3.9530 | 2.3369 |
| Cr ⁺³ | 0.63 | 3.45 | -75.0 | 4.3311 | 2.7150 |
| Mn ⁺³ | 0.66 | 3.48 | -72.5 | 4.2938 | 2.6777 |
| Np ⁺³ | 1.10 | 3.92 | -40.7 | 3.8118 | 2.1957 |
| Pa ⁺³ | 1.13 | 3.95 | -38.8 | 3.7829 | 2.1668 |
| Pm ⁺³ | 1.06 | 3.88 | -43.3 | 3.8511 | 2.2350 |
| Pu ⁺³ | 1.08 | 3.90 | -42.0 | 3.8314 | 2.2153 |
| Rh ⁺³ | 0.68 | 3.50 | -70.9 | 4.2693 | 2.6532 |
| Sb ⁺³ | 0.76 | 3.58 | -64.6 | 4.1739 | 2.5578 |
| Ti ⁺³ | 0.76 | 3.58 | -64.6 | 4.1739 | 2.5578 |
| V ⁺³ | 0.74 | 3.56 | -66.2 | 4.1973 | 2.5812 |
| Am ⁺⁴ | 0.92 | 4.68 | -88.8 | 5.6761 | 3.5213 |
| Ce ⁺⁴ | 0.94 | 4.70 | -87.2 | 5.6520 | 3.4972 |
| Ge ⁺⁴ | 0.53 | 4.29 | -122.9 | 6.1921 | 4.0373 |
| Hf ⁺⁴ | 0.78 | 4.54 | -100.4 | 5.8512 | 3.6964 |
| Ir ⁺⁴ | 0.68 | 4.44 | -109.1 | 5.9830 | 3.8282 |
| Mn ⁺⁴ | 0.60 | 4.36 | -116.3 | 6.0927 | 3.9379 |

| Ion | $r_{c,j}^a$ | $r_{e,j}^b$ | \bar{S}_j^c | $\omega_j^{abs,d} \times 10^{-5}$ | $\omega_j^e \times 10^{-5}$ |
|------------------|-------------|-------------|---------------|-----------------------------------|-----------------------------|
| Mo ⁺⁴ | 0.70 | 4.46 | -107.3 | 5.9561 | 3.8013 |
| Nb ⁺⁴ | 0.74 | 4.50 | -103.8 | 5.9032 | 3.7484 |
| Np ⁺⁴ | 0.95 | 4.71 | -86.4 | 5.6400 | 3.4852 |
| Os ⁺⁴ | 0.69 | 4.45 | -108.2 | 5.9695 | 3.8147 |
| Pa ⁺⁴ | 0.98 | 4.74 | -84.1 | 5.6043 | 3.4495 |
| Pb ⁺⁴ | 0.84 | 4.60 | -95.3 | 5.7749 | 3.6201 |
| Pd ⁺⁴ | 0.65 | 4.41 | -111.8 | 6.0237 | 3.8689 |
| Pr ⁺⁴ | 0.92 | 4.68 | -88.8 | 5.6761 | 3.5213 |
| Pt ⁺⁴ | 0.65 | 4.41 | -111.8 | 6.0237 | 3.8689 |
| Pu ⁺⁴ | 0.93 | 4.69 | -88.0 | 5.6640 | 3.5092 |
| Re ⁺⁴ | 0.72 | 4.48 | -105.6 | 5.9295 | 3.7747 |
| Ru ⁺⁴ | 0.68 | 4.44 | -109.1 | 5.9830 | 3.8282 |
| S ⁺⁴ | 0.37 | 4.13 | -138.7 | 6.4320 | 4.2772 |
| Se ⁺⁴ | 0.50 | 4.26 | -125.8 | 6.2358 | 4.0810 |
| Si ⁺⁴ | 0.42 | 4.18 | -133.7 | 6.3551 | 4.2003 |
| Sn ⁺⁴ | 0.71 | 4.47 | -106.4 | 5.9428 | 3.7880 |
| Tb ⁺⁴ | 0.81 | 4.57 | -97.8 | 5.8128 | 3.6580 |
| Te ⁺⁴ | 0.70 | 4.46 | -107.3 | 5.9561 | 3.8013 |
| Th ⁺⁴ | 1.02 | 4.78 | -81.0 | 5.5574 | 3.4026 |
| Ti ⁺⁴ | 0.68 | 4.44 | -109.1 | 5.9830 | 3.8282 |
| U ⁺⁴ | 0.97 | 4.73 | -84.9 | 5.6161 | 3.4613 |
| V ⁺⁴ | 0.63 | 4.39 | -113.6 | 6.0511 | 3.8963 |
| W ⁺⁴ | 0.70 | 4.46 | -107.3 | 5.9561 | 3.8013 |
| Zr ⁺⁴ | 0.79 | 4.55 | -99.5 | 5.8383 | 3.6835 |

a. Angstroms, Pauling radii (Bloss, 1971). b. Angstroms, calculated from equation (48). c. cal mol⁻¹ K⁻¹, calculated from equation (58). d. cal mol⁻¹, calculated from equation (45). e. cal mol⁻¹, calculated from equation (47). f. Note that as a consequence of the revised \bar{S}_j^0 estimation procedure, these values differ from those given in table 3 of Helgeson, Kirkham and Flowers (1981).

from the standard partial molal properties. These contributions were calculated from Eqns. (5) and (35) using the values of ω_j given in Tables 1, 2, and 3, together with values of the Born functions Q , X , and Y taken from HELGESON and KIRKHAM (1974a), and SHOCK *et al.* (1988b). The resulting nonsolvation volume ($\Delta\bar{V}_n^0$) and heat capacity ($\Delta\bar{C}_{P,n}^0$) values are plotted in Figs. 6 and 7 against $1/(T - \Theta)$ and $1/(T - \Theta)^2$, respectively. It follows from Eqns. (7) and (31) that the intercepts of the linear curves shown in Figs. 6 and 7 correspond to either σ or c_1 and the slopes to ξ or c_2 , depending on the partial molal property that is plotted on the ordinate. Taking account of Eqns. (3), (7) and (31), equation of state parameters were then computed for individual ions from those for the electrolytes. Values of σ , ξ , c_1 , and c_2 for the ionic species generated in this way are shown in Table 4, along with those for other ions obtained from regression of experimental data by TANGER and HELGESON (1988). As shown below, the equation of state parameters listed in Table 4 can be correlated with one another, and in certain instances they can be calculated from the standard partial molal properties of the ions at 25°C and 1 bar. These correlations provide a means of estimating parameters for ions and electrolytes for which experimental data are not available at more than one temperature.

CORRELATIONS AMONG STANDARD PARTIAL MOLAL PROPERTIES AND EQUATION OF STATE PARAMETERS

The nonsolvation standard partial molal properties of aqueous ions ($\Delta\bar{\xi}_n^0$) represent a summation of intrinsic

($\bar{\xi}_n^0$) and collapse ($\Delta\bar{\xi}_c^0$) contributions to the standard partial molal property ($\bar{\xi}_n^0$). The intrinsic contributions are taken to be independent of temperature and pressure, but the collapse contributions change in response to the effect of increasing or decreasing temperature and pressure on the local solvent structure. In terms of the revised HKF equations of state summarized above, the a_1 and c_1 parameters correspond to \bar{V}_i^0 , and $\bar{C}_{P,i}^0$, respectively, and $\Delta\bar{V}_n^0$ and $\Delta\bar{C}_{P,n}^0$ are represented by the remainder of the $\Delta\bar{\xi}_n^0$ expressions given by Eqns. (10) and (33) for $\Delta\bar{V}_n^0$ and $\Delta\bar{C}_{P,n}^0$, respectively. Values of $\Delta\bar{V}_n^0$, computed from Eqn. (10) using the parameters shown in Table 4 are given in Table 5. Because $\bar{\kappa}_i^0 = 0$ in the revised HKF model, Eqn. (17) and the values of $\Delta\bar{\kappa}_n^0$ in Tables 6 and 7 refer entirely to $\Delta\bar{\kappa}_c^0$. The values of a_1 , a_2 , a_3 , and a_4 for Na⁺, K⁺, Mg⁺², Cl⁻, and Br⁻ in Table 6 were taken from TANGER and HELGESON (1988).

The intrinsic standard partial molal volumes of aqueous ions represented by the values of a_1 in Table 6 are plotted in Fig. 8 against the corresponding values in Table 5 of $\Delta\bar{V}_n^0$ at 25°C and 1 bar. It can be seen in this figure that they exhibit a linear distribution. The linear curve in Fig. 8 is consistent with

$$a_1 = 1.3684 \times 10^{-2} \Delta\bar{V}_n^0 + 0.1765. \quad (85)$$

A linear correlation is also evident in Fig. 9 between the values of a_2 and $\Delta\bar{\kappa}_n^0$ in Table 6. The equation of the curve shown in Fig. 9 is given by

$$a_2 = 17.19 \Delta\bar{\kappa}_n^0 \times 10^4 + 421.1. \quad (86)$$

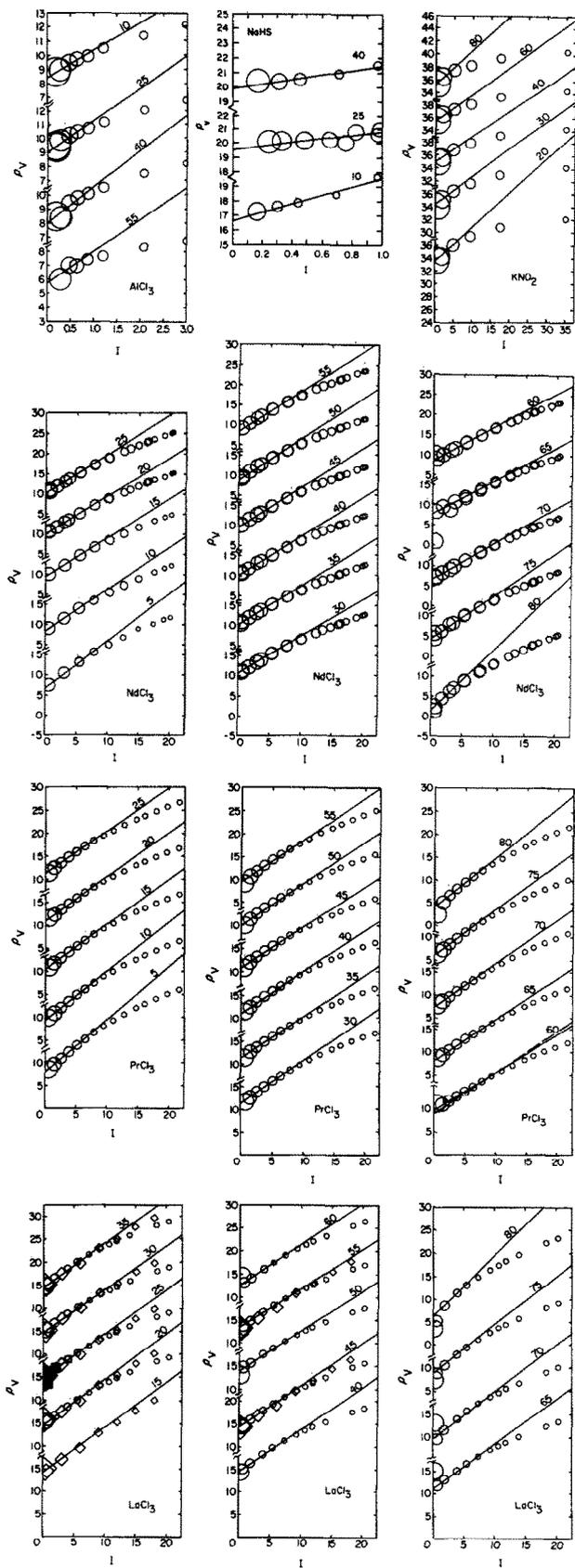


FIG. 3. ρ_V (Eqn. 83) in $\text{cm}^3 \text{mol}^{-1}$ as a function of stoichiometric ionic strength at various temperatures and P_{SAT} (see Appendix). The symbols shown above and those in Fig. 4 represent experimental data

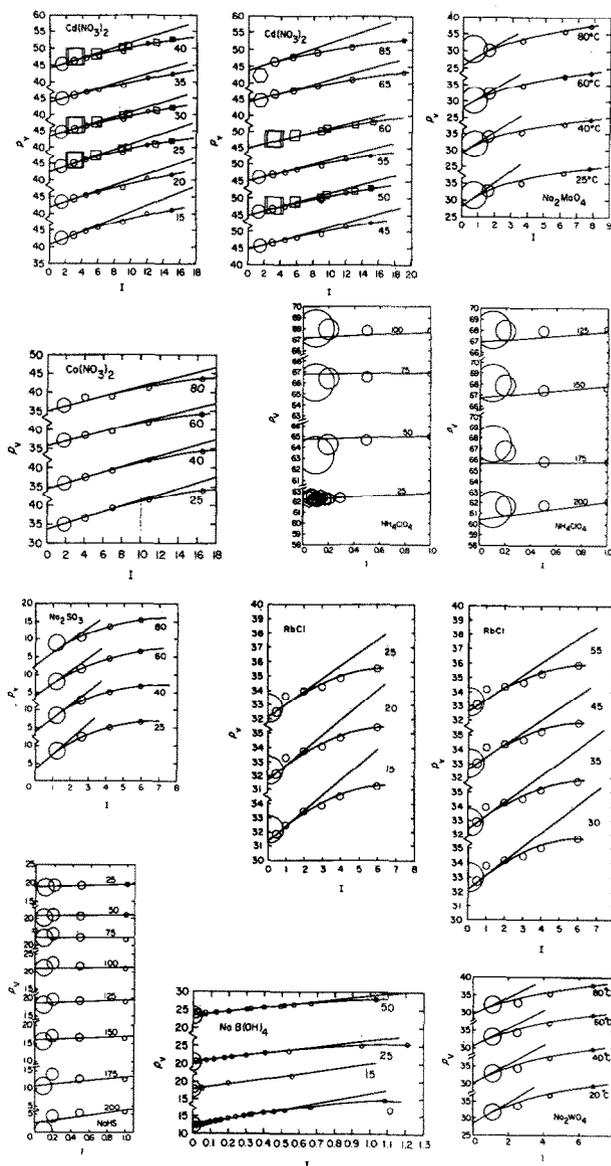


FIG. 4. ρ_V (Eqn. 83) in $\text{cm}^3 \text{mol}^{-1}$ as a function of stoichiometric ionic strength at various temperatures and P_{SAT} (see caption of Fig. 3).

A similar correlation of the σ equation of state parameter with $\Delta \bar{V}_n^0$ is shown in Fig. 10, which was generated with the aid of Tables 4 and 5. The correlation curve shown in Fig. 10 is consistent with

$$\sigma = 1.11\Delta \bar{V}_n^0 + 1.8. \tag{87}$$

It can be seen in Fig. 10 that the correlation curve shown in the figure falls within the uncertainty limits of the values of

taken from EWING and HÉRTY (1953), DUNN (1966), SPEDDING *et al.* (1966), ELLIS (1968), ELLIS and MCFADDEN (1972), WARD and MILLERO (1974), GILDSETH *et al.* (1975), ROUX *et al.* (1978), ISONO (1980, 1984), BARBERO *et al.* (1982), SÖHNEL (1984), and BARTA and HEPLER (1986).

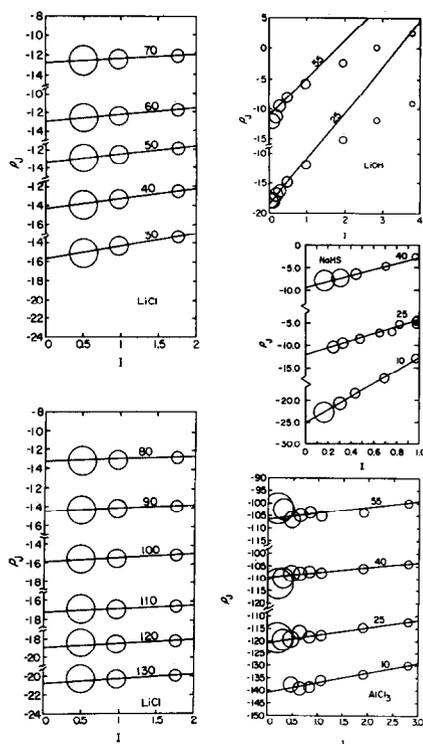


FIG. 5. ρ_j (Eqn. 84) in $\text{cal mol}^{-1} \text{K}^{-1}$ as a function of stoichiometric ionic strength at various temperatures and P_{SAT} . The symbols represent experimental data taken from RÜTERJANS *et al.* (1969), BARBERO *et al.* (1982), ROUX *et al.* (1984), and HOVEY and TREMAINE (1986).

σ and $\Delta \bar{V}_n^0$ (represented by the symbol size) for all of the aqueous ions except ClO_4^- and BO_3^- .

The correlation of intrinsic and nonsolvation standard partial molal volumes shown in Fig. 8 is consistent with observations made by AKITT (1980), who demonstrated that the absolute standard partial molal volumes (\bar{V}_i^{obs}) of ions of similar crystallographic radius can be correlated with their charge. By extrapolating to zero charge, Akitt obtained what he termed the absolute intrinsic volumes (\bar{V}_i^{abs}) of ions, which include implicitly all local structural contributions of the solvent. Akitt's intrinsic volumes correspond conceptually in the revised HKF model to the nonsolvation contribution ($\Delta \bar{V}_n^0$) to \bar{V}^0 at 25°C and 1 bar. In accord with Akitt's conclusion, the correlations of $\Delta \bar{V}_n^0$ with a_1 and σ shown in Figs. 8 and 10 are independent of ion charge.

The values of a_2 and a_4 in Table 6 are plotted against each other in Fig. 11. Note that these parameters also exhibit a linear dependence on one another consistent with

$$a_4 = -4.134a_2 - 27790. \quad (88)$$

This correlation, together with Eqns. (17), (20), (22), and (86) requires that the slopes of curves representing $\Delta \bar{V}_n^0$ as a function of $1/(T - \Theta)$ be linearly related to their intercepts. This constraint is consistent with the solid curves shown in Fig. 12. The dashed curves in this figure correspond to TANGER and HELGESON's (1988) regression curves of the experimental data represented by the symbols, which were not so constrained. It can be seen in Fig. 12 that the differences

between the dashed and solid curves fall within the experimental uncertainty represented by the sizes of the symbols. Because the solid curves are consistent with the correlations shown in Figs. 9 and 11, they were adopted in the present

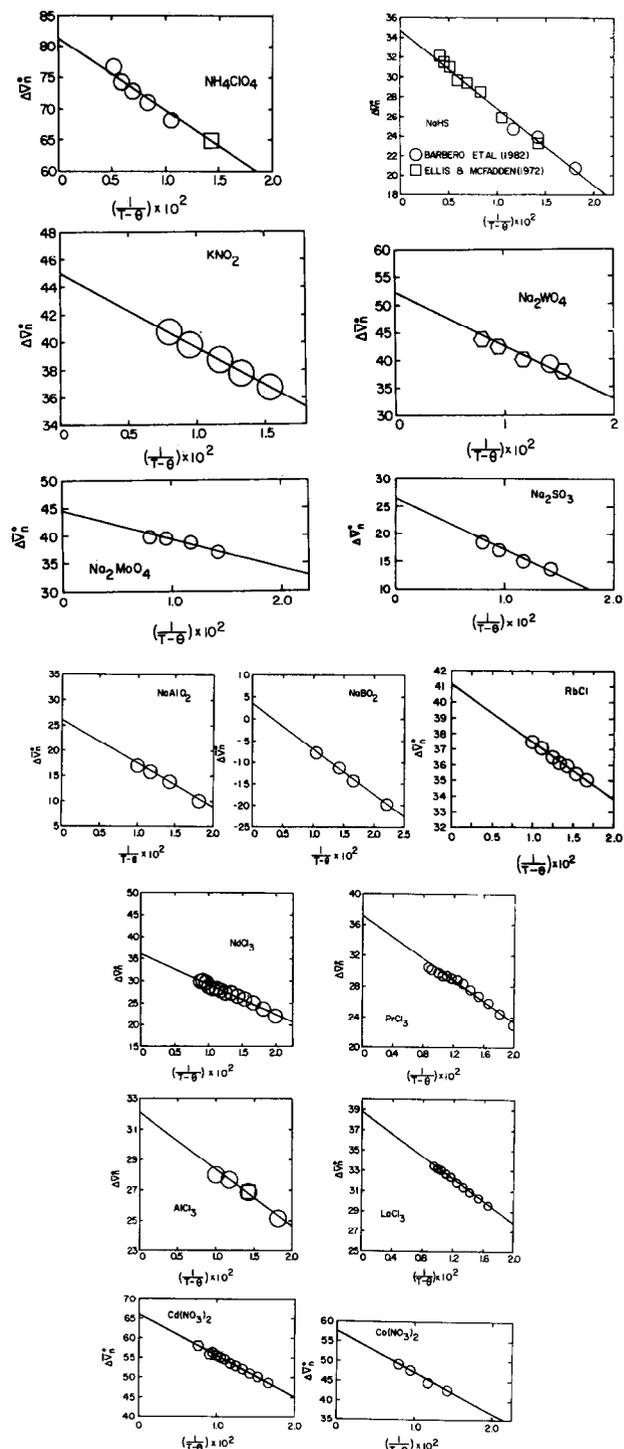


FIG. 6. Graphic representation of Eqn. (7) for the nonsolvation contributions to the standard partial molal volumes ($\Delta \bar{V}_n^0$) of aqueous electrolytes in $\text{cm}^3 \text{mol}^{-1}$ at P_{SAT} . The symbols represent experimental data (see caption of Fig. 4), but the curves correspond to regression values (see text).

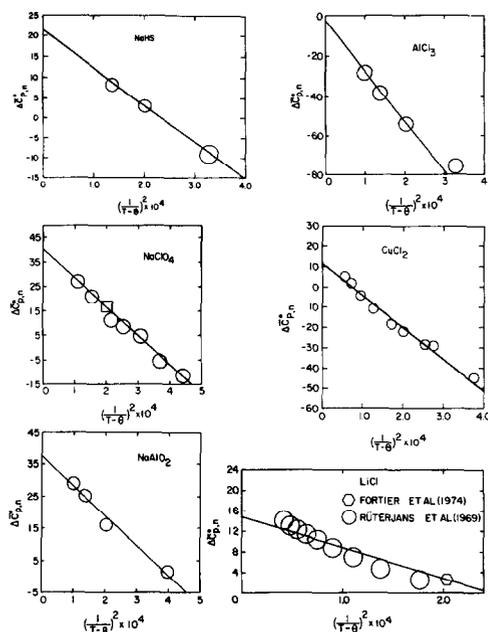


FIG. 7. Graphic representation of Eqn. (31) for the nonsolvation contributions to the standard partial molal heat capacities ($\Delta\bar{C}_{P,n}^0$) of aqueous electrolytes in $\text{cal mol}^{-1} \text{K}^{-1}$ at P_{SAT} . The symbols represent experimental data taken from MASTROIANNI and CRISS (1972), COBBLE *et al.* (1982), and the references given in the caption to Fig. 5, but the curves correspond to regression values (see text).

study in preference to their regression counterparts. Values of a_2 and a_4 computed from Eqns. (14), (15), (86), and (88) are shown in Table 7, together with the standard partial molal compressibilities and values of $\Delta\bar{\kappa}_{n,j}^0$ and $\Delta\bar{\kappa}_{s,j}^0$ used in the calculations. Estimates can be made of the c_2 parameter by taking account of the linear correlation in Fig. 13 of the values of c_2 in Tables 4 and 6 with those of \bar{C}_P^0 in Table 5. The linear curve shown in this figure is consistent with

$$c_2 \times 10^{-4} = 0.2037\bar{C}_P^0 - 3.0346. \quad (89)$$

Estimation of equation of state parameters

The various correlations shown in Figs. 8 through 11 and 13 afford estimates of all of the equation of state parameters that are required to calculate the standard partial molal properties of aqueous ions and electrolytes at high pressures and temperatures for which little or no experimental data are available at temperatures $> 25^\circ\text{C}$. Estimates made with these correlation algorithms are most reliable if the estimation strategy is designed to avoid magnification of uncertainties in the estimated equation of state parameters. An optimum strategy of this kind was adopted in the present study, which is summarized in Table 8. The procedure for calculating Born coefficients from effective electrostatic radii obtained from crystallographic radii or estimated from values of \bar{S}^0 is summarized at the top of Table 8, which is followed by procedures used to estimate \bar{C}_P^0 and \bar{V}^0 at 25°C and 1 bar if these properties cannot be generated from experimental data. The equations used to calculate values of $\Delta\bar{V}_n^0$, $\Delta\bar{\kappa}_{s,j}^0$, $\Delta\bar{C}_{P,s}^0$, $\Delta\bar{V}_n^0$, $\Delta\bar{\kappa}_n^0$, and $\Delta\bar{C}_{P,n}^0$ are then shown, below which are given the numbers of the correlation expressions and other equations used to estimate all of the nonsolvation parameters for

four alternate cases. Which of these cases is appropriate for a given ion depends on the type of experimental data available. For example, an ion would be represented by case 1 if values of σ at 1 bar and $\Delta\bar{V}_n^0$, $\Delta\bar{\kappa}_n^0$ and \bar{C}_P^0 at 25°C and 1 bar are available for the ion, but the estimation procedure corresponding to case 4 would apply if only $\Delta\bar{V}_n^0$ and \bar{C}_P^0 at 25°C and 1 bar are known. The procedures for estimating values of c_2 and calculating values of c_1 are shown at the bottom of Table 8. Most of the equation of state parameters for aqueous ions given in Table 11, as well as all of the parameters shown in Table 12 were generated using the estimation strategies summarized in Table 8.

Uncertainties in estimated equation of state parameters can be minimized if the parameters are calculated in a manner consistent with Table 8. Note that it is possible to obtain all of the equation of state parameters without experimental values of $\bar{\kappa}^0$ at 25°C and 1 bar. However, in such cases the uncertainties in the estimated volumetric parameters are greater than they would otherwise be (see below). Uncertainties in estimated equation of state parameters generated from Table 8 can be assessed by taking account of the maximum difference between the symbols and curves in Figs. 8–11 and 13. However, it should be emphasized in this regard

Table 4. Summary of fit coefficients generated by regression of nonsolvation contributions to the standard partial molal volumes and heat capacities of aqueous electrolytes as a function of temperature at 1 bar with equations (7) and (31).

| Ion | σ^a | $\xi^b \times 10^{-2}$ | c_1^c | $c_2^d \times 10^{-4}$ |
|--------------------------------|---------------------|------------------------|--------------------|------------------------|
| Li ⁺ | -0.21 ^e | 0.378 ^e | 19.2 | -0.24 |
| Na ⁺ | 4.02 ^e | -3.023 ^e | 18.18 ^e | -2.981 ^e |
| K ⁺ | 12.52 ^e | -2.088 ^e | 7.40 ^e | -1.791 ^e |
| Rb ⁺ | 16.5 | -1.35 | ... | ... |
| Cs ⁺ | 25.51 | -2.700 ^e | 6.27 ^e | -5.736 ^e |
| NH ₄ ⁺ | 19.99 ^e | -0.990 ^e | 17.45 ^e | -0.021 ^e |
| Mg ⁺² | -17.27 ^e | -0.334 ^e | 20.80 ^e | -5.892 ^e |
| Ca ⁺² | -12.48 ^e | -1.766 ^e | 9.00 ^e | -2.522 ^e |
| Sr ⁺² | -13.37 ^e | -0.860 ^e | ... | ... |
| Ba ⁺² | -4.72 ^e | -3.816 ^e | 3.80 ^e | -3.450 ^e |
| Cd ⁺² | -17.0 | 3.26 | ... | ... |
| Co ⁺² | -25.4 | 3.21 | ... | ... |
| Cu ⁺² | ... | ... | 20.3 | -4.39 |
| Al ⁺³ | -41.5 | 3.00 | 10.70 | -8.06 |
| La ⁺³ | -34.8 | 1.30 | ... | ... |
| Pr ⁺³ | -36.4 | 0.86 | ... | ... |
| Nd ⁺³ | -37.5 | -0.04 | ... | ... |
| F ⁻ | 5.06 ^e | -1.380 ^e | 4.46 ^e | -7.488 ^e |
| Cl ⁻ | 24.59 ^e | -2.253 ^e | -4.40 ^e | -5.714 ^e |
| Br ⁻ | 32.65 ^e | -3.071 ^e | -3.80 ^e | -6.811 ^e |
| I ⁻ | 45.79 ^e | -4.413 ^e | -6.27 ^e | -4.944 ^e |
| OH ⁻ | 5.36 ^e | -3.698 ^e | 4.15 ^e | -10.346 ^e |
| NO ₂ ⁻ | 41.52 ^e | -6.828 ^e | 7.70 ^e | -6.725 ^e |
| HCO ₃ ⁻ | 33.49 ^e | -3.978 ^e | ... | ... |
| BO ₂ ⁻ | -0.6 | -7.4 | ... | ... |
| AlO ₂ ⁻ | 22.0 | -5.7 | 19.1 | -6.2 |
| HS ⁻ | 30.7 | -4.86 | 3.42 | -6.27 |
| ClO ₄ ⁻ | 61.9 | -10.6 | 22.3 | -8.9 |
| NO ₃ ⁻ | 32.4 | -3.58 | ... | ... |
| SO ₄ ⁻² | 31.54 ^e | -6.854 ^e | 1.64 ^e | -17.998 ^e |
| WO ₄ ⁻² | 44.3 | -3.65 | ... | ... |
| SO ₃ ⁻² | 15.8 | -1.05 | ... | ... |
| MoO ₄ ⁻² | 33.5 | 2.30 | ... | ... |

a. $\text{cm}^3 \text{mol}^{-1}$. b. $\text{cm}^3 \text{K mol}^{-1}$. c. $\text{cal mol}^{-1} \text{K}^{-1}$. d. cal K mol^{-1} . e. Tanger and Helgeson (1988).

Table 5. Standard partial molal heat capacities (C_p^0) and nonsolvation contributions to the standard partial molal volumes ($\Delta\bar{V}_n^0$) of aqueous ions at 25°C and 1 bar.

| Ion | $\Delta\bar{V}_n^0$ a | C_p^0 b |
|-------------------------------|-----------------------|---------------------|
| Li ⁺ | 0.33 ^c | 14.2 |
| Na ⁺ | -0.29 ^c | 9.06 ^c |
| K ⁺ | 9.54 ^c | 1.98 ^c |
| Rb ⁺ | 14.6 | |
| Cs ⁺ | 21.66 ^c | -6.29 ^c |
| NH ₄ ⁺ | 18.58 ^c | 15.74 ^c |
| Mg ²⁺ | -17.75 ^c | -5.34 ^c |
| Ca ²⁺ | -15.00 ^c | -7.53 ^c |
| Sr ²⁺ | -14.60 ^c | -10.05 ^c |
| Ba ²⁺ | -10.16 ^c | -12.30 ^c |
| Co ²⁺ | -21.0 | |
| Cd ²⁺ | -12.4 | |
| Al ³⁺ | -37.1 | -32.5 |
| La ³⁺ | -33.1 | |
| Pr ³⁺ | -36.4 | |
| Nd ³⁺ | -37.3 | |
| OH ⁻ | 0.09 ^c | -32.79 ^c |
| HS ⁻ | 24.39 ^c | -22.17 ^c |
| F ⁻ | 3.09 ^c | -27.23 ^c |
| Cl ⁻ | 21.33 ^c | -29.44 ^c |
| Br ⁻ | 28.27 ^c | -30.42 ^c |
| I ⁻ | 39.50 ^c | -28.25 ^c |
| NO ₂ ⁻ | 27.87 | |
| NO ₃ ⁻ | 31.79 ^c | -16.4 ^c |
| BO ₂ ⁻ | -11.0 | |
| AlO ₂ ⁻ | 14.3 | -11.9 |
| SO ₄ ²⁻ | 21.77 ^c | -64.38 ^c |
| SO ₃ ²⁻ | 14.6 | |
| WO ₄ ²⁻ | 39.8 | |

a. cm³ mol⁻¹. b. cal mol⁻¹ K⁻¹. c. Tanger and Helgeson (1988).

that the scatter of data points in these figures is not necessarily indicative of *experimental* uncertainty. The correlations are two-dimensional approximations of what in reality is almost certainly a complicated interdependence of the equation of state parameters. Nevertheless, the fact that they are close approximations suggests that the influences on the correlations of variables other than those shown on the abscissas of Figs. 8–11 and 13 are second order. In the ensuing discussion, an effort is made to assess the sensitivities of estimated equation of state parameters to uncertainties in the positions and slopes of the curves in the correlation plots. Overall uncertainties are calculated also for predicted apparent standard partial molal Gibbs free energies of formation at elevated temperatures and pressures.

Table 6. Summary of volumetric fit coefficients and nonsolvation contributions to the standard partial molal compressibility ($\Delta\bar{\kappa}_n^0$) of aqueous ions at 25°C and 1 bar taken from Tanger and Helgeson (1988).

| Ion | $\Delta\bar{\kappa}_n^0$ a × 10 ⁴ | $\left(\frac{\partial\sigma}{\partial P}\right)_T$ b × 10 ³ | $\left(\frac{\partial\xi}{\partial P}\right)_T$ c | a ₁ e × 10 | a ₂ c × 10 ⁻² | a ₃ f | a ₄ d × 10 ⁻⁴ |
|------------------|--|--|---|-----------------------|-------------------------------------|------------------|-------------------------------------|
| Na ⁺ | -32.8 | 1.413 | 0.1686 | 1.8390 | -2.2850 | 3.2560 | -2.726 |
| K ⁺ | -33.0 | 0.911 | 0.1677 | 3.5590 | -1.4730 | 5.4350 | -2.712 |
| Mg ²⁺ | -74.2 | 5.318 | 0.1478 | -0.8217 | -8.5990 | 8.3900 | -2.390 |
| Cl ⁻ | 4.6 | -2.969 | 0.1761 | 4.0320 | 4.8010 | 5.5630 | -2.847 |
| Br ⁻ | 13.0 | -4.078 | 0.1944 | 5.2690 | 6.5940 | 4.7450 | -3.143 |

a. cm³ mol⁻¹ bar⁻¹. b. cm³ K² mol⁻¹ bar⁻¹. c. cal mol⁻¹. d. cal K mol⁻¹. e. cal mol⁻¹ bar⁻¹. f. cal K mol⁻¹ bar⁻¹.

Table 7. Standard partial molal compressibilities ($\bar{\kappa}^0$), solvation ($\Delta\bar{\kappa}_n^0$) and nonsolvation ($\Delta\bar{\kappa}_s^0$) contributions, and a₂ and a₄ parameters calculated with equations (86) and (88) which are consistent with the correlations shown in figures 9 and 11.

| Ion | $\bar{\kappa}^0$ a, d × 10 ⁴ | $\Delta\bar{\kappa}_s^0$ a × 10 ⁴ | $\Delta\bar{\kappa}_n^0$ a × 10 ⁴ | a ₂ b × 10 ⁻² | a ₄ c × 10 ⁻⁴ |
|---------------------------------|---|--|--|-------------------------------------|-------------------------------------|
| Li ⁺ | -28.6 | -3.7 | -24.9 | -0.0690 | -2.7761 |
| Rb ⁺ | -30.9 ^e | -1.1 | -29.8 | -0.9041 | -2.7416 |
| Cs ⁺ | -26.0 | -0.7 | -25.3 | -0.1309 | -2.7736 |
| NH ₄ ⁺ | -12.0 | -1.4 | -10.6 | 2.3448 | -2.8759 |
| Ca ²⁺ | -76.1 | -9.4 | -66.7 | -7.2520 | -2.4792 |
| Sr ²⁺ | -92.2 | -8.6 | -83.6 | -10.1508 | -2.3544 |
| Ba ²⁺ | -90.5 | -7.5 | -83.0 | -10.0565 | -2.3633 |
| F ⁻ | -30.2 | -13.6 | -16.6 | 1.3588 | -2.9287 |
| I ⁻ | 13.8 | -9.8 | 23.6 | 8.2762 | -3.1211 |
| HS ⁻ | -6.5 | -11.0 | 4.5 | 4.9799 | -2.9849 |
| OH ⁻ | -37.2 | -13.1 | -24.1 | 0.0738 | -2.7821 |
| NO ₂ ⁻ | 6.6 | -8.6 | 15.2 | 6.7824 | -3.0594 |
| HCO ₂ ⁻ | -27.5 | -10.1 | -17.4 | 1.1505 | -2.8266 |
| B(OH) ₂ ⁻ | -57.5 ^e | -9.8 | -47.7 | 15.7412 | -3.4297 |
| SO ₄ ²⁻ | -60.0 | -24.2 | -35.8 | -1.9846 | -2.6970 |
| CO ₃ ²⁻ | -73.5 ^e | -24.2 | -35.8 | -3.9844 | -2.6143 |

a. cm³ mol⁻¹ xbar⁻¹. b. cal mol⁻¹. c. cal K mol⁻¹. d. Tanger and Helgeson (1988). e. Millero (1982).

Uncertainties in estimated equation of state parameters

Uncertainties in the values of $\Delta\bar{V}_n^0$, $\Delta\bar{\kappa}_n^0$, and \bar{C}_P^0 given in Tables 5, 6 and 7 can be regarded as the sum of reported experimental uncertainties and those arising from extrapolation of the experimental data to infinite dilution. These total uncertainties in $\Delta\bar{V}_n^0$, $\Delta\bar{\kappa}_n^0$, and \bar{C}_P^0 at 25°C and 1 bar can be used to assess corresponding uncertainties in equation of state parameters obtained from the regression calculations summarized above. The results of these calculations permit evaluation of the extent to which the correlation curves represent accurately the data from which they were generated. An example of the procedure followed in the uncertainty analysis is described below.

The values of $\bar{\kappa}^0$ shown in Table 6 range from 15×10^{-4} to -95×10^{-4} cm³ mol⁻¹ bar⁻¹. A conservative estimate of the total uncertainty in these values of $\bar{\kappa}^0$ is $\pm 3 \times 10^{-4}$ cm³ mol⁻¹ bar⁻¹. If all this uncertainty is attributed to the nonsolvation contribution to $\bar{\kappa}^0$ ($\Delta\bar{\kappa}_s^0$), the maximum uncertainty in a₂ can be assessed by assuming no uncertainty in

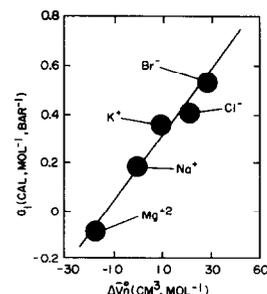


FIG. 8. Correlation of the intrinsic volume equation of state parameter (a_1) with the nonsolvation standard partial molal volumes ($\Delta\bar{V}_n^0$) of aqueous ions at 25°C and 1 bar. The symbols represent values taken from Tables 5 and 6. The curve shown is consistent with Eqn. (85).

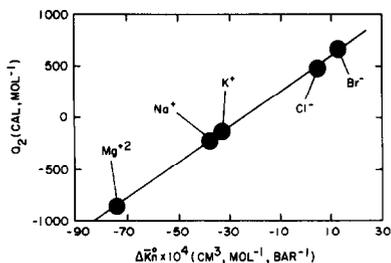


FIG. 9. Correlation of the a_2 parameter with the nonsolvation standard partial molal compressibilities ($\Delta\bar{\kappa}_n^0$) of aqueous ions at 25°C and 1 bar. The symbols represent values taken from Table 6. The curve is consistent with Eqn. (86).

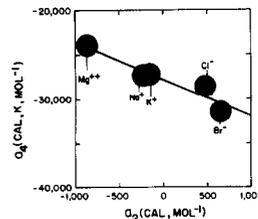


FIG. 11. Correlation of a_4 in cal K mol⁻¹ with a_2 in cal mol⁻¹ for aqueous ions. The symbols represent values taken from Table 6. The curve is consistent with Eqn. (88).

a_4 . Taking the finite difference derivative (δ) of Eqn. (17) and holding a_4 constant leads to

$$\delta a_2 = (\Psi + P)^2 \delta \Delta\bar{\kappa}_n^0, \tag{90}$$

which can be combined with the uncertainty represented by $\delta\Delta\bar{\kappa}_n^0$ ($\pm 3 \times 10^{-4}$ cm³ mol⁻¹ bar⁻¹) to give a maximum uncertainty in the a_2 parameter of ± 48.5 cal mol⁻¹. The curve drawn through the symbols shown in Fig. 9 falls within this maximum uncertainty, which yields a maximum uncertainty in estimates of a_4 from a_2 using the correlation shown in Fig. 11 of $\sim \pm 200$ cal K mol⁻¹. The latter uncertainty is about equivalent to the thickness of the curve shown in Fig. 11. Uncertainties in a_2 and a_4 of ~ 50 cal mol⁻¹ and 200 cal K mol⁻¹ have an insignificant effect on calculated values of \bar{V}^0 , \bar{S}^0 , $\Delta\bar{H}^0$ and $\Delta\bar{G}^0$ at elevated pressures and temperatures.

The symbols shown in Fig. 8 representing correlation of the a_1 parameter with $\Delta\bar{V}_n^0$ differ from the curve in the figure by as much as ± 0.05 cal mol⁻¹ bar⁻¹, which corresponds to

an uncertainty in $\Delta\bar{V}_n^0$ of ± 2.1 cm³ mol⁻¹. This value compares well with combined experimental and extrapolative uncertainties in \bar{V}^0 , which are typically of the order of ± 2 cm³ mol⁻¹ (AKITT, 1980). Average uncertainties in values of σ generated from the correlations shown in Fig. 10 are also ± 2 cm³ mol⁻¹, although the distribution of some of the symbols indicates that in certain cases the uncertainty may reach as much as ± 5 cm³ mol⁻¹. The scatter of symbols around the linear curve in Fig. 10 results in similar uncertainties in predicted values of $\Delta\bar{V}_n^0$.

The distribution of data points along the correlation curve in Fig. 13 indicates an average uncertainty in the c_2 parameter of $\pm 1.5 \times 10^4$ cal K mol⁻¹ and a maximum uncertainty of $\pm 3.5 \times 10^4$ cal K mol⁻¹. These differences correspond to uncertainties in calculated values of \bar{C}_p^0 at 25°C or c_1 of ± 3.1 cal mol⁻¹ K⁻¹ and ± 7.1 cal mol⁻¹ K⁻¹, respectively. Experimental uncertainties in ϕ_{C_p} at temperatures $> 25^\circ\text{C}$ typically range up to ± 2 or 3 cal mol⁻¹ K⁻¹ (HOVEY and TREMAINE, 1986), although overall uncertainties in \bar{C}_p^0 may be greater, owing to uncertainties arising from extrapolation of ϕ_{C_p} to infinite dilution. Hence, uncertainties in c_2 parameters estimated from Eqn. (89) correspond roughly to those associated with generation of c_2 parameters by regression of experimental data.

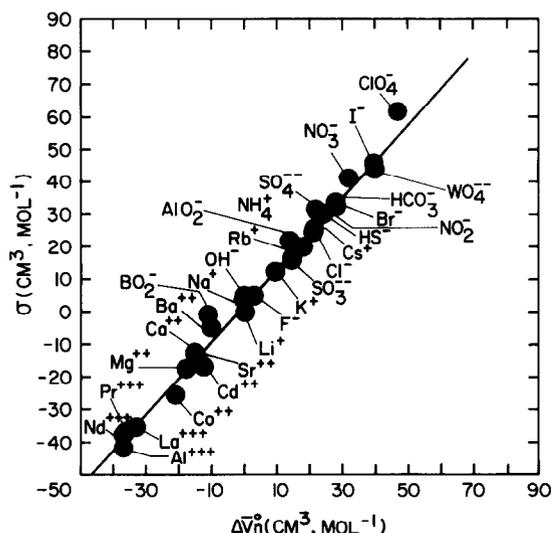


FIG. 10. Correlation of the σ equation of state parameter in cm³ mol⁻¹ at 1 bar with the nonsolvation standard partial molal volumes ($\Delta\bar{V}_n^0$) of aqueous ions in cm³ mol⁻¹ at 25°C and 1 bar. The symbols represent values taken from Tables 4, 5, and 6. The curve is consistent with Eqn. (87).

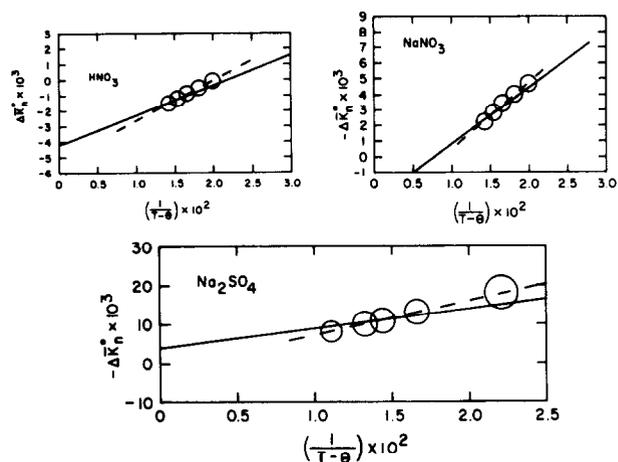


FIG. 12. Graphic representation of the second identity in Eqn. (17) for the nonsolvation contribution to the standard partial molal compressibility ($\Delta\bar{\kappa}_n^0$) of aqueous electrolytes in cm³ mol⁻¹ bar⁻¹ at various temperatures and 1 bar. The symbols represent experimental data taken from KEARNS (1966), and MILLERO *et al.* (1974). The dashed curves correspond to regression values taken from TANGER and HELGESON (1988), but the solid curves are constrained by the correlations described in the text.

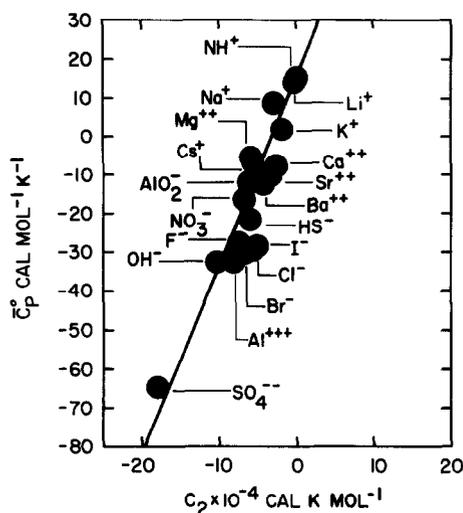


FIG. 13. Correlation of the c_2 parameter with the standard partial molal heat capacities (\bar{C}_p^0) of aqueous ions at 25°C and 1 bar. The symbols represent values taken from Tables 4, 5, and 6. The curve is consistent with Eqn. (89).

Uncertainties in calculated values of \bar{C}_p^0 , \bar{V}^0 , \bar{S}^0 , and $\Delta\bar{H}^0$ at high pressures and temperatures

The uncertainties in estimated equation of state parameters discussed above are manifested by corresponding uncertainties in calculated standard partial molal properties at high pressures and temperatures. For example, it follows from Eqn. (36) that the average uncertainty of $\pm 2 \times 10^4$ cal K mol⁻¹ in estimated c_2 parameters assessed above contributes ± 4 cal mol⁻¹ K⁻¹ uncertainty to calculated values of \bar{C}_p^0 at 25°C. However, this uncertainty decreases with increasing temperature, diminishing to a value of ± 0.02 cal mol⁻¹ K⁻¹ at 1000°C. Likewise, the uncertainty in calculated values of \bar{C}_p^0 arising from uncertainties in estimates of the a_4 parameter decrease with increasing temperature and decreasing pressure from ± 0.5 cal mol⁻¹ K⁻¹ at 25°C and 5 kb to $\pm 6 \times 10^{-4}$ cal mol⁻¹ K⁻¹ at 1000°C and 5 kb, and to ± 0.1 cal mol⁻¹ K⁻¹ at 25°C and 1 kb.

The estimated uncertainty of ± 0.05 cal mol⁻¹ bar⁻¹ in the a_1 parameter computed above contributes an uncertainty of ± 2.1 cm³ mol⁻¹ to calculated values of \bar{V}^0 , regardless of the temperature and pressure. Taking account of Eqn. (11), the average uncertainty of ± 48.5 cal mol⁻¹ in estimates of the a_2 parameter from the correlation shown in Fig. 9 contributes an uncertainty of ± 0.78 cm³ mol⁻¹ to calculated values of \bar{V}^0 at any temperature and 1 bar, which decreases to ± 0.27 cm³ mol⁻¹ at 5 kb. The uncertainty in calculated values of \bar{V}^0 arising from the average uncertainty of ± 200 cal K mol⁻¹ in estimated values of the a_4 parameter decrease with increasing pressure and temperature from ± 0.05 cm³ mol⁻¹ at 25°C and 1 bar to ± 0.02 cm³ mol⁻¹ at 25°C and 5 kb and $\pm 1 \times 10^{-3}$ cm³ mol⁻¹ at 1000°C and 5 kb.

It can be deduced from Eqn. (38) that uncertainties in calculated values of \bar{S}^0 at high pressures and temperatures arise from uncertainties in estimates of both the c_2 and a_4 parameters. The average uncertainty of $\pm 2 \times 10^4$ cal K mol⁻¹ in estimates of the c_2 parameter resulting from the correlation

shown in Fig. 13 leads to a pressure-independent uncertainty of ± 0.45 cal mol⁻¹ K⁻¹ in \bar{S}^0 at 100°C, which increases to ± 0.7 cal mol⁻¹ K⁻¹ at 1000°C. The uncertainty in calculated values of \bar{S}^0 caused by the average uncertainty in estimates of the a_4 parameter assessed above as ± 200 cal K mol⁻¹ decreases with increasing temperature and decreasing pressure from ± 0.04 cal mol⁻¹ K⁻¹ at 25°C and 5 kb to $\pm 2 \times 10^{-4}$ cal mol⁻¹ K⁻¹ at 1000°C and 5 kb, and to ± 0.01 cal mol⁻¹ K⁻¹ at 25°C and 1 kb.

Uncertainties in high pressure/temperature values of $\Delta\bar{H}^0$ computed from Eqn. (43) can be assessed in terms of uncertainties in estimated values of the a_1 , a_2 , a_4 , and c_2 parameters in the equations of state. For example, the average uncertainty of ± 0.05 cal mol⁻¹ bar⁻¹ in values of the a_1 pa-

Table 8. Outline of the strategy used in the present study to minimize uncertainty in estimated equation of state parameters for aqueous ions (see discussion in text). Note that in the case of the volumetric properties and parameters shown below, conversion to or from volumetric or caloric units may or may not be required in the estimation procedure using 1 cal mole⁻¹ bar⁻¹ = 41.8393 cm³ mole⁻¹.

| Estimation Strategy | | | |
|---------------------------------------|--|---------------------|--|
| Parameter or Property to be Estimated | Known Property | Equation to be Used | Parameter or Property to be Calculated |
| | r_x | 48 | r_c |
| | r_x, \bar{S}^0 | | |
| r_c | \bar{S}^0 | 57 | |
| \bar{S}^0 | r_x | 58 | |
| | r_c | 45 | ω^{abs} |
| | ω^{abs} | 47 | ω |
| \bar{C}_p^0 | \bar{S}^0 | 91 | |
| \bar{V}^0 | | 92 | |
| | ω | 5 | $\Delta\bar{V}_s^0$ |
| | | 15 | $\Delta\bar{K}_s^0$ |
| | | 35 | $\Delta\bar{C}_{p,s}^0$ |
| | $\bar{V}^0, \Delta\bar{V}_s^0$ | 4 | $\Delta\bar{V}_n^0$ |
| | $\bar{K}^0, \Delta\bar{K}_s^0$ | 14 | $\Delta\bar{K}_n^0$ |
| | $\bar{C}_p^0, \Delta\bar{C}_{p,s}^0$ | 29 | $\Delta\bar{C}_{p,n}^0$ |
| a_2 | $\Delta\bar{V}_n^0, \Delta\bar{K}_n^0, \sigma$ | 86 | |
| | (Case 1) | 8 | a_1 |
| a_2 | $\Delta\bar{V}_n^0, \Delta\bar{K}_n^0$ | 86 | |
| σ | | 87 | |
| | (Case 2) | 8 | a_1 |
| a_1 | $\Delta\bar{V}_n^0, \sigma$ | 85 | |
| | (Case 3) | 8 | a_2 |
| σ | $\Delta\bar{V}_n^0$ | 87 | |
| a_1 | | 85 | |
| | (Case 4) | 8 | a_2 |
| a_4 | a_2 | 88 | |
| | $\Delta\bar{V}_n^0, a_1, a_2, a_4$ | 10 | a_3 |
| c_2 | \bar{C}_p^0 | 89 | |
| | | 31 | c_1 |

parameter estimated from the correlation shown in Fig. 8 leads to an uncertainty of $\pm 25 \text{ cal mol}^{-1}$ in $\Delta \bar{H}^0$ at 500 bars, which increases to $\pm 250 \text{ cal mol}^{-1}$ at 5 kb. The temperature-independent uncertainty in calculated values of $\Delta \bar{H}^0$ arising from the average uncertainty of $\pm 48.5 \text{ cal mol}^{-1}$ in estimates of the a_2 parameter assessed above also increases with increasing pressure (for example, from $\pm 16 \text{ cal mol}^{-1}$ at 1 kb to $\pm 52 \text{ cal mol}^{-1}$ at 5 kb). The average computed uncertainty in estimates of the a_4 parameter of $\pm 200 \text{ cal K mol}^{-1}$ contributes $\pm 16 \text{ cal mol}^{-1}$ uncertainty in calculated values of $\Delta \bar{H}^0$ at 25°C and 5 kb, which decreases with increasing temperature and decreasing pressure to $\pm 0.5 \text{ cal mol}^{-1}$ at 1000°C and 5 kb, and to $\pm 5 \text{ cal mol}^{-1}$ at 25°C and 1 kb. The pressure-independent uncertainty in calculated values of $\Delta \bar{H}^0$ caused by the average uncertainty in estimated values of the c_2 parameter ($\pm 2 \times 10^4 \text{ cal K mol}^{-1}$) increase with increasing temperature from $\pm 150 \text{ cal mol}^{-1}$ at 100°C to $\pm 226 \text{ cal mol}^{-1}$ at 1000°C.

Uncertainties in calculated values of $\Delta \bar{G}^0$ at high pressures and temperatures

The impact of uncertainties in estimated equation of state parameters on calculated apparent standard partial molal Gibbs free energies of formation at elevated temperatures and pressures is particularly relevant to geochemical calculations of mineral equilibria in hydrothermal systems. Taking account of Eqn. (44) and the scatter of data points in Fig. 9 it can be shown that the uncertainty associated with the a_2 parameters in Table 6 contributes up to $\pm 18 \text{ cal mol}^{-1}$ to the overall uncertainty in $\Delta \bar{G}^0$ at 5 kb, which is greater than that at any lower pressure. If the a_2 values were instead estimated from the correlation shown in Fig. 11 (Eqn. 88), the average uncertainty in calculated values of $\Delta \bar{G}^0$ arising from uncertainties in a_2 increases to $\sim \pm 270 \text{ cal mol}^{-1}$ at 5 kb. The uncertainties in the estimated values of a_4 computed above lead to an uncertainty in $\Delta \bar{G}^0$ at 5 kb and 25°C computed from Eqn. (44) of $\sim \pm 23 \text{ cal mol}^{-1}$, which decreases to $\sim \pm 2 \text{ cal mol}^{-1}$ at 5 kb and 1000°C. The uncertainty in a_1 values estimated from Eqn. (85) contribute a maximum uncertainty of $\pm 250 \text{ cal mol}^{-1}$ to $\Delta \bar{G}^0$ at 5 kb. Pressure-independent uncertainties in $\Delta \bar{G}^0$ arising from those in the c_2 parameters generated from Eqn. (89) range up to $\pm 2 \text{ kcal mol}^{-1}$ at 1000°C, but the average uncertainty in c_2 results in an uncertainty in $\Delta \bar{G}^0$ of only $\sim \pm 940 \text{ cal mol}^{-1}$ at 1000°C and $\sim \pm 470 \text{ cal mol}^{-1}$ at 500°C. In the unlikely event that all average uncertainties in the estimated parameters for a given ion lead to uncertainties of the same sign in calculated values of $\Delta \bar{G}^0$, the combined uncertainties would be of the order of $\pm 1500 \text{ cal mol}^{-1}$ at 1000°C and 5 kb, but only $\pm 700 \text{ cal mol}^{-1}$ at 500°C and 2 kb.

CALCULATION OF THE STANDARD PARTIAL MOLAL PROPERTIES OF AQUEOUS IONS AT 25°C AND 1 BAR

The procedure summarized above for estimating equation of state parameters requires values of \bar{S}^0 , \bar{V}^0 and \bar{C}_P^0 at 25°C and 1 bar for the species of interest. Values of \bar{V}^0 and \bar{C}_P^0 are

shown in Tables 9 and 10 for a wide variety of aqueous electrolytes. These values were generated from the intercepts of the linear curves in the plots of ρ_V and ρ_f as a function of ionic strength shown in Figs. A-1 through A-12 in the Appendix (NAPS, 1988). Values of \bar{V}^0 and \bar{C}_P^0 for individual ions computed from those of the electrolytes in Tables 9 and 10 with the aid of Eqn. (3) are given in Table 11. Experimental values of the standard partial molal entropy (\bar{S}^0) and the standard partial molal enthalpy and Gibbs free energy of formation at the reference temperature and pressure ($\Delta \bar{H}_f^0$ and $\Delta \bar{G}_f^0$, respectively) are also shown in Table 11 for these ions, together with equation of state parameters for the ions estimated from the values of \bar{S}^0 , \bar{V}^0 , and \bar{C}_P^0 in the table and the correlation equations shown in Table 8. In addition, experimental values of $\Delta \bar{G}_f^0$, $\Delta \bar{H}_f^0$, \bar{S}^0 , \bar{V}^0 , and \bar{C}_P^0 , are shown in Table 11 for several aqueous ions for which experimental equation of state parameters are listed in Tables 4 and 6. These parameters are repeated in Table 11, which also contains estimated values of the other equation of state parameters for the latter ions. The data and parameters in Table 11 can be used with the equations of state summarized above to predict the standard partial molal properties of the ions shown to 1000°C and 5 kb.

Correlations among standard partial molal properties at 25°C and 1 bar

For many aqueous electrolytes of geochemical interest, only volumetric and/or calorimetric data which cannot be interpreted unambiguously are available, or none at all. As a consequence, estimation of equation of state parameters for the ionic species in these electrolytes from the correlation algorithms in Table 8 requires estimates of \bar{V}^0 and \bar{C}_P^0 for the ionic species at 25°C and 1 bar. A number of methods for estimating absolute or conventional standard partial molal volumes and heat capacities have been proposed. Perhaps the most widely used of these is the \bar{C}_P^0 correlation with \bar{S}^0 introduced by CRISS and COBBLE (1964b), which is

Table 9. Summary of standard partial molal volumes (\bar{V}^0) of aqueous electrolytes at 25°C and 1 bar generated from experimental data, equation (83), and the ρ_V plots given in the Appendix.

| Electrolyte | \bar{V}^0 -a | Electrolyte | \bar{V}^0 -a | Electrolyte | \bar{V}^0 -a | Electrolyte | \bar{V}^0 -a |
|--|---------------------|---|---------------------|------------------------------------|---------------------|------------------------------------|--------------------|
| NaClO ₃ | 35.5 ^b | KClO ₃ | 46.25 ^b | K ₂ CrO ₄ | 38.5 ^c | BeCl ₂ | 19.3 ^d |
| CoCl ₂ | 10.8 ^e | Al(NO ₃) ₃ | 43.2 ^f | RbBr | 38.9 ^g | RbF | 12.7 ^h |
| RbI | 50.2 ⁱ | NaIO ₃ | 24.8 ^b | KIO ₃ | 35.0 ^b | Mg(ClO ₄) ₂ | 66.9 ^c |
| K ₂ S ₂ O ₈ | 97.1 ^c | Na ₂ S ₂ O ₈ | 76.8 ^c | NaBrO ₃ | 34.3 ^b | KBrO ₃ | 44.5 ^b |
| NaClO ₄ | 43.1 ^b | KMnO ₄ | 51.0 ^h | MnCl ₂ | 18.5 ^g | Mn(NO ₃) ₂ | 40.9 ^g |
| Zn(NO ₃) ₂ | 33.7 ^g | Zn(ClO ₄) ₂ | 64.1 ^f | Cu(ClO ₄) ₂ | 63.1 ^c | Cu(NO ₃) ₂ | 33.4 ^g |
| YCl ₃ | 12.5 ^k | EuCl ₃ | 12.1 ^k | SmCl ₃ | 11.4 ^k | DyCl ₃ | 12.7 ^l |
| Na ₂ WO ₄ | 30.0 ^c | Na ₂ MoO ₄ | 28.16 ^c | NaB(OH) ₄ | 20.5 ^m | KHCO ₃ | 33.9 ^z |
| NaH ₂ PO ₄ | 30.21 ^p | Na ₂ HPO ₄ | 3.13 ^p | Na ₃ PO ₄ | -34.12 ^p | AlCl ₃ | 9.0 ^q |
| KH ₂ PO ₄ | 40.44 ^p | K ₂ HPO ₄ | 23.57 ^p | K ₃ PO ₄ | -3.34 ^p | LaCl ₃ | 14.8 ^w |
| Ni(ClO ₄) ₂ | 58.3 ^r | Fe(ClO ₄) ₂ | -22.2 ^u | AgClO ₄ | 43.3 ^v | AgNO ₃ | 28.2 ^y |
| Co(NO ₃) ₂ | 33.6 ^k | Cd(NO ₃) ₂ | 42.4 ^{q,y} | NdCl ₃ | 10.3 ^{l,s} | NH ₄ ClO ₄ | 62.3 ^b |
| PrCl ₃ | 11.3 ^{l,s} | Na ₂ SO ₃ | 3.4 ^x | NaHSO ₃ | 32.02 ^z | KHSO ₃ | 42.69 ^z |
| NaHCO ₃ | 23.45 ⁿ | Na ₂ CO ₃ | -6.13 ⁿ | NaAl(OH) ₄ | 45.0 ^{aa} | Gd(ClO ₄) ₃ | 92.2 ^{bb} |
| Tb(ClO ₄) ₃ | 92.4 ^{bb} | Ho(ClO ₄) ₃ | 91.0 ^{bb} | Er(ClO ₄) ₃ | 89.6 ^{bb} | Tm(ClO ₄) ₃ | 89.6 ^{bb} |
| Yb(ClO ₄) ₃ | 88.1 ^{bb} | Lu(ClO ₄) ₃ | 87.6 ^{bb} | | | | |

a. cm³ mol⁻¹. b. Roux et al. (1978). c. Olofsson et al. (1978). d. Vasiliev et al. (1971). e. Spitzer et al. (1978a). f. Spitzer et al. (1978b). g. Spitzer et al. (1979a). h. Spitzer et al. (1979b). i. Hovey and Tremaine (1986). j. Desnoyers et al. (1976). k. Spedding et al. (1975a). l. Spedding et al. (1966). m. Ward and Millero (1974). n. Perron et al. (1975). p. Lo Surdo et al. (1979). q. Isono (1984). r. Dunn (1966). s. Gilseth et al. (1975). t. Barta and Hepler (1986). u. Swaddle and Mak (1983). v. Singh et al. (1978). w. data from q, l, r, and s. x. Söhnel et al. (1984). y. Ewing and Herty (1953). z. Barbero et al. (1983). aa. Hovey et al. (1987). bb. Spedding et al. (1975b).

Table 10. Summary of standard partial molal heat capacities (\bar{C}_p^0) of aqueous electrolytes at 25°C and 1 bar generated from experimental data, equation (84), and the ρ_j plots given in the Appendix.

| Electrolyte | \bar{C}_p^0 , ^a | Electrolyte | \bar{C}_p^0 , ^a | Electrolyte | \bar{C}_p^0 , ^a | Electrolyte | \bar{C}_p^0 , ^a |
|------------------------------------|------------------------------|------------------------------------|------------------------------|---|------------------------------|---|------------------------------|
| NaClO ₃ | -3.2 ^b | KClO ₃ | -10.3 ^b | NaBrO ₃ | -11.5 ^b | KBrO ₃ | -18.6 ^b |
| K ₂ CrO ₄ | -55.9 ^c | Na ₂ MoO ₄ | -29.4 ^c | Na ₂ WO ₄ | -26.4 ^c | Na ₂ S ₂ O ₈ | -39.1 ^c |
| NaCl | -7.1 ^b | KIO ₃ | -14.2 ^b | Na ₂ S ₂ O ₅ | -6.9 ^c | K ₂ S ₂ O ₈ | -21.0 ^c |
| CuCl ₂ | -61.0 ^d | Cu(ClO ₄) ₂ | -16.7 ^c | Cu(NO ₃) ₂ | -38.5 ^b | Al(NO ₃) ₃ | -78.9 ^d |
| KMnO ₄ | 0.2 ^b | NaClO ₄ | 3.6 ^b | NH ₄ ClO ₄ | 11.2 ^b | Pb(NO ₃) ₂ | -45.5 ^b |
| Mg(ClO ₄) ₂ | -16.3 ^c | Mg(NO ₃) ₂ | -38.1 ^{b,n} | MnCl ₂ | -63.0 ^b | Mg(NO ₃) ₂ | -36.9 ^{b,n} |
| NiCl ₂ | -71.3 ^c | Ni(NO ₃) ₂ | -45.2 ^b | AgNO ₃ | -8.7 ^p | Cd(NO ₃) ₂ | -36.3 ^{b,n} |
| CoCl ₂ | -66.8 ^c | Co(NO ₃) ₂ | -40.7 ^{b,n} | Zn(NO ₃) ₂ | -39.1 ^{b,n} | Zn(ClO ₄) ₂ | -17.3 ^d |
| PrCl ₃ | -136.0 ^k | Pr(NO ₃) ₃ | -96.9 ^k | Pr(ClO ₄) ₃ | -64.2 ^m | GdCl ₃ | -124.2 ^l |
| Gd(NO ₃) ₃ | -85.1 ^k | Gd(ClO ₄) ₃ | -52.4 ^m | Ho(NO ₃) ₃ | -82.5 ^k | HoCl ₃ | -121.0 ^l |
| Ho(ClO ₄) ₃ | -49.8 ^m | Dy(NO ₃) ₃ | -80.9 ^k | Dy(ClO ₄) ₃ | -48.2 ^m | Tb(ClO ₄) ₃ | -54.0 ^m |
| Tb(NO ₃) ₃ | -86.7 ^k | TbCl ₃ | -125.8 ^l | EuCl ₃ | -124.9 ^l | Eu(ClO ₄) ₃ | -53.1 ^m |
| Nd(NO ₃) ₃ | -92.4 ^k | Nd(ClO ₄) ₃ | -59.7 ^m | La(NO ₃) ₃ | -86.4 ^k | La(ClO ₄) ₃ | -53.7 ^m |
| Sm(NO ₃) ₃ | -92.5 ^k | SmCl ₃ | -131.6 ^l | Sm(ClO ₄) ₃ | -59.8 ^m | Er(NO ₃) ₃ | -83.5 ^k |
| Lu(NO ₃) ₃ | -82.0 ^k | LuCl ₃ | -121.1 ^l | Lu(ClO ₄) ₃ | -49.3 ^m | Er(ClO ₄) ₃ | -50.8 ^m |
| Yb(NO ₃) ₃ | -85.6 ^k | Yb(ClO ₄) ₃ | -52.9 ^m | Tm(NO ₃) ₃ | -83.5 ^k | TmCl ₃ | -122.6 ^l |
| Tm(ClO ₄) ₃ | -30.8 ^m | NaH ₂ PO ₄ | 2.1 ^q | Na ₂ HPO ₄ | -40.2 ^q | Na ₂ PO ₄ | -87.7 ^q |
| Na ₂ CO ₃ | -51.4 ⁿ | NaHCO ₃ | -0.6 ^r | KHCO ₃ | -9.2 ^r | Na ₂ SO ₄ | 8.8 ^s |
| NaHSO ₃ | 8.1 ^r | KHSO ₃ | 0.3 ^r | NaAl(OH) ₄ | 33.2 ^t | | |

a. cal mol⁻¹ K⁻¹. b. Roux et al.(1978). c. Olofsson et al.(1978). d. Vasiliev et al.(1974). e. Spitzer et al.(1978a). f. Spitzer et al.(1978b). g. Spitzer et al.(1979a). h. Spitzer et al.(1979b). i. Hovey and Tremaine (1986). j. Desnoyers et al.(1976). k. Spedding et al.(1979). l. Spedding et al.(1975d). m. Spedding et al.(1975c). n. Drakin et al.(1967). o. Singh et al.(1978). p. Larson et al.(1982). q. Barbero et al.(1983). r. Ahluwalia and Cobble (1964). s. Hovey et al.(1987).

represented by the curve in Fig. 14. However, it can be seen in this figure that their curve fails to represent adequately all of the more recent experimental data, especially those for divalent and trivalent ions. In contrast, the correlations of \bar{C}_p^0 with \bar{S}^0 at 25°C and 1 bar in Figs. 15 and 16 for similar ions of the same charge affords close representation of all the data. The curves shown in these figures represent a revision and extension of those described by HELGESON *et al.* (1981). The equation consistent with these curves is given by

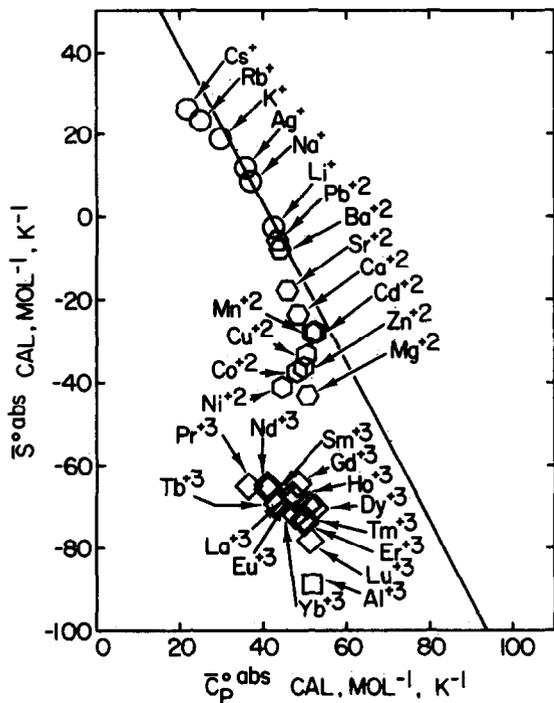


FIG. 14. Correlation of the absolute standard partial molal entropies (\bar{S}^0_{obs}) of aqueous ions with their absolute standard partial molal heat capacities ($\bar{C}_p^0_{obs}$) at 25°C and 1 bar. The symbols represent values calculated from appropriate analogs of Eqn. (2) using the values of \bar{S}^0 and \bar{C}_p^0 given in Table 11. The curve represents the correlation proposed by CRISS and COBBLE (1964b)—see text.

$$\bar{C}_p^0 = \hat{a} + \hat{b}\bar{S}^0 \quad (91)$$

where \hat{a} and \hat{b} correspond to the following parameters:

| Species | \hat{a} | \hat{b} |
|---|-----------|-----------|
| Monovalent cations (Fig. 15) | 22.2 | -0.88 |
| Divalent transition metal cations (Fig. 15) | 7.5 | 0.61 |
| Alkaline earth cations and Pb ⁺² (Fig. 15) | -11.9 | -0.19 |
| Light rare earth cations (Fig. 15) | -298.8 | -4.9 |
| Heavy rare earth cations and Al ⁺³ (Fig. 15) | -51.3 | -0.26 |
| Halide anions (Fig. 15) | -28.2 | 0.0 |
| Monovalent oxyanions (Fig. 16) | -62.4 | 1.32 |
| Monovalent acid oxyanions (Fig. 16) | -37.7 | 1.32 |
| Divalent oxyanions (Fig. 16) | -70.5 | 0.8 |
| Divalent acid oxyanions (Fig. 16) | (-51.5) | (0.8) |

It can be seen in Fig. 15 that the curve for the light rare earth ions exhibits a steep trend, which is nearly perpendicular to the trend of Al⁺³ and the heavy rare earth ions. Perhaps owing to its much larger radius, Pb⁺² correlates with the alkaline earth cations, rather than with the transition metal cations of the same charge. In the case of polyatomic ions, the monovalent acid oxyanion correlation curve in Fig. 16 is parallel to, but offset toward more positive values of \bar{C}_p^0 from the curve for monovalent oxyanions. The fact that the curves in Fig. 16 are parallel for monovalent ions leads to the assumption that the curve for divalent acid oxyanions in Fig. 16 is parallel to that shown in the figure for the divalent oxyanions.

Many attempts have been made to rationalize the relative magnitudes of, and/or predict the absolute and conventional standard partial molal volumes of aqueous ions at 25°C and 1 bar using one or another set of ionic crystal radii (COUTURE and LAIDLER, 1956, 1957; HEPLER, 1957; MUKERJEE, 1961; DESNOYERS *et al.*, 1965; CONWAY *et al.*, 1965, 1966; GLUECKAUF, 1965; PANKHURST, 1969; AKITT, 1971, 1980; HELGESON and KIRKHAM, 1976; LO SURDO and MILLERO, 1980; LEYENDEKKERS, 1982). These attempts commonly involve semi-empirical calculation of the intrinsic volumes of the ions (\bar{V}^0) and/or estimates of ion hydration numbers. In general, estimates of \bar{V}^0 generated from these algorithms are unsatisfactory because they are model dependent. Other correlations have been demonstrated between $\bar{V}^0_{i,j}$ and $\Delta\bar{S}^0_{n,j} - Z_j\Delta\bar{S}^0_{s,H^+}$, as well as between \bar{V}^0 and \bar{S}^0 for various groups of ions at 25°C and 1 bar (HELGESON and KIRKHAM, 1976) which are related to correlations described by HEPLER (1965) between volumes and entropies of ionization. The observed correlations between \bar{V}^0 and \bar{S}^0 have been revised in the present study to include a larger set of \bar{V}^0 values from recent reports of experimental investigations (see below).

Correlations of \bar{V}^0 with \bar{S}^0 at 25°C and 1 bar for many of the ions listed in Table 11 and a few from Table 12 are depicted in Figs. 17 through 19. These correlations are consistent with

$$\bar{V}^0 = \hat{c} + \hat{d}\bar{S}^0 \quad (92)$$

where \hat{c} and \hat{d} stand for the following parameters

Table 11. Summary of experimental standard partial molal thermodynamic properties of aqueous ions at 25°C and 1 bar and the parameters required to calculate the corresponding properties at high pressures and temperatures from equations (11), (36), (38), (43) and (44).

| Ion | $\Delta\bar{G}^{\circ}/P,T,a$ | $\Delta\bar{H}^{\circ}/P,T,a$ | \bar{S}° ^b | \bar{C}_p° ^{b,f} | \bar{V}° ^{c,g} | a_1 ^{u,aa} × 10 | a_2 ^{a,aa} × 10 ⁻² | a_3 ^{v,aa} | a_4 ^{w,aa} × 10 ⁻⁴ | c_1 ^{b,aa} | c_2 ^{w,aa} × 10 ⁻⁴ | ω ^{a,z} × 10 ⁻⁵ |
|---|-------------------------------|-------------------------------|--------------------------------|------------------------------------|----------------------------------|----------------------------|--|-----------------------|--|-----------------------|--|--|
| H ⁺ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Li ⁺ | -69933 ^h | -66552 ^e | 2.70 ^e | 14.2 | -0.87 ^d | -0.0237 | -0.0690 | 11.5800 | -2.7761 | 19.2 | -0.24 | 0.4862 |
| Na ⁺ | -62591 ^h | -57433 ^e | 13.96 ^e | 9.06 ^d | -1.11 ^d | 1.8390 | -2.2850 | 3.2560 | -2.726 | 18.18 | -2.981 | 0.3306 |
| K ⁺ | -67510 ^h | -60270 ^e | 24.15 ^e | 1.98 ^d | 9.06 ^d | 3.5590 | -1.4730 | 5.4350 | -2.712 | 7.40 | -1.791 | 0.1927 |
| Rb ⁺ | -67800 ^h | -60020 ^e | 28.8 ^e | -3.0 | 14.26 | 4.2913 | -0.9041 | 7.4070 | -2.7416 | 5.7923 | -3.6457 | 0.1502 |
| Cs ⁺ | -69710 ^h | -61670 ^e | 31.75 ^e | -6.29 ^d | 21.42 ^d | 6.1475 | -0.1309 | 4.2094 | -2.7736 | 6.27 | -5.736 | 0.0974 |
| Mg ²⁺ | -108505 ⁱ | -111367 ^d | -33.00 ^j | -5.34 ^d | -21.55 ^d | -0.8217 | -8.5990 | 8.3900 | -2.390 | 20.80 | -5.892 | 1.5372 |
| Ca ²⁺ | -132120 ^h | -129800 ^e | -13.5 ^e | -7.53 ^d | -18.06 ^d | -0.1947 | -7.2520 | 5.2966 | -2.4792 | 9.00 | -2.522 | 1.2366 |
| Sr ²⁺ | -134760 ^k | -131670 ^k | -7.53 ^k | -10.05 ^d | -17.41 ^d | 0.7071 | -10.1508 | 7.0027 | -2.3594 | 10.7452 | -5.0818 | 1.1363 |
| Ba ²⁺ | -134030 ^j | -128500 ^j | 2.3 ^j | -12.30 ^d | -12.60 ^d | 2.7383 | -10.0565 | -0.0470 | -2.3633 | 3.80 | -3.450 | 0.9850 |
| Al ³⁺ | -115377 ^{bb} | -126012 ^{dd} | -75.6 ^{gg} | -32.5 | -44.4 | -3.3404 | -17.1108 | 14.9917 | -2.0716 | 10.7 | -8.06 | 2.8711 |
| AlO ₂ ⁻ | -198465 ^{hh} | -222261 ^{dd} | -8.4 ^{gg} | -11.9 | 10.0 | 3.7280 | 3.9800 | -1.5170 | -2.9435 | 19.1 | -6.2 | 1.7595 |
| HCO ₃ ⁻ | -140282 ^l | -164898 ^m | 23.53 ^m | -8.46 | 24.6 | 7.5621 | 1.1505 | 1.2346 | -2.8266 | 12.9395 | -4.7579 | 1.2733 |
| CO ₃ ²⁻ | -126191 ^m | -161385 ^m | -11.95 ^m | -69.5 ⁿ | -5.02 | 2.8524 | -3.9844 | 6.4142 | -2.6143 | -3.3206 | -17.1917 | 3.3914 |
| Pb ²⁺ | -5710 ^h | 220 ^e | 4.2 ^e | -12.7 | -15.6 | -0.0051 | -7.7939 | 8.8134 | -2.4568 | 8.6624 | -5.6216 | 1.0788 |
| NO ₃ ⁻ | -26507 ^h | -49429 ^e | 35.12 ^e | -16.4 ^d | 29.0 ^d | 7.3161 | 6.7824 | -4.6838 | -3.0594 | 7.70 | -6.725 | 1.0977 |
| NO ₂ ⁻ | -7700 ^j | -25000 ^j | 29.4 ^j | -23.3 | 25.0 | 5.5864 | 5.8590 | 3.4472 | -3.0212 | 3.4260 | -7.7808 | 1.1847 |
| NH ₄ ⁺ | -18990 ^h | -31850 ^e | 26.57 ^e | 15.74 ^d | 18.13 ^d | 3.8763 | 2.3448 | 8.5605 | -2.8759 | 17.45 | -0.021 | 0.1502 |
| H ₂ PO ₄ ⁻ | -270140 ^j | -309820 ^j | 21.6 ^j | -7.0 | 31.3 | 6.4875 | 8.0594 | 2.5823 | -3.1122 | 14.0435 | -4.4605 | 1.3003 |
| HPO ₄ ²⁻ | -260310 ^j | -308815 ^p | -8.0 ^j | -58.3 | 5.4 | 3.6315 | 1.0857 | 5.3233 | -2.8239 | 2.7357 | -14.9103 | 3.3363 |
| PO ₄ ³⁻ | -243500 ^j | -305300 ^j | -53 ^j | -114.9 | -30.6 | -0.5259 | -9.0654 | 9.3131 | -2.4042 | -9.4750 | -26.4397 | 5.6114 |
| OH ⁻ | -37595 ^h | -54977 ^e | -2.56 ^e | -32.79 ^d | -4.18 ^d | 1.2527 | 0.0738 | 1.8423 | -2.7821 | 4.15 | -10.346 | 1.7246 |
| HS ⁻ | 2860 ^q | -3850 ^q | 16.3 ^q | -22.17 ^d | 20.65 | 5.0119 | 4.9799 | 3.4765 | -2.9849 | 3.42 | -6.27 | 1.4410 |
| HSO ₃ ⁻ | -126130 ^j | -149670 ^j | 33.4 ^j | -1.4 | 33.3 | 6.7014 | 8.5816 | 2.3771 | -3.1338 | 15.6949 | -3.3198 | 1.1233 |
| SO ₃ ²⁻ | -177930 ^h | -217400 ^e | 4.50 ^e | -64.38 ^d | 13.88 ^d | 8.3014 | -1.9846 | -6.2122 | -2.6970 | 1.64 | -17.998 | 3.1463 |
| HSO ₄ ⁻ | -180630 ^r | -212500 ^r | 30.0 ^r | 5.3 | 35.2 | 6.9788 | 9.2590 | 2.1108 | -3.1618 | 20.0961 | -1.9550 | 1.1748 |
| S ₂ O ₃ ²⁻ | -124900 ^j | -155000 ^j | 16 ^j | -57.3 | 28.5 | 6.6685 | 12.4951 | -7.7281 | -3.2955 | -0.0577 | -14.7066 | 2.9694 |
| S ₂ O ₈ ²⁻ | -266500 ^j | -321400 ^j | 58.4 ^j | -25.0 | 79.0 | 13.3622 | 24.8454 | -4.0153 | -3.8061 | 12.9632 | -8.1271 | 2.3281 |
| F ⁻ | -67340 ^h | -80150 ^e | -3.15 ^e | -27.23 ^d | -1.32 ^d | 0.6870 | 1.3588 | 7.6033 | -2.8352 | 4.46 | -7.488 | 1.7870 |
| Cl ⁻ | -31379 ^h | -39933 ^e | 13.56 ^e | -29.44 ^d | 17.79 ^d | 4.0320 | 4.8010 | 5.5630 | -2.847 | -4.40 | -5.714 | 1.4560 |
| ClO ₃ ⁻ | -1900 ^j | -24850 ^j | 38.8 ^j | -12.3 | 36.9 | 7.1665 | 9.7172 | 1.9307 | -3.1807 | 8.5561 | -5.5401 | 1.0418 |
| ClO ₄ ⁻ | -2040 ^j | -30910 ^j | 43.5 ^j | -5.5 | 44.2 | 8.1411 | 17.3059 | -12.2254 | -3.4944 | 22.3 | -8.9 | 0.9699 |
| Br ⁻ | -24870 ^h | -29040 ^e | 19.80 ^e | -30.42 ^d | 24.85 ^d | 5.2690 | 6.5940 | 4.7450 | -3.143 | -3.80 | -6.811 | 1.3858 |
| BrO ₃ ⁻ | 4450 ^j | -16030 ^j | 38.65 ^j | -20.6 | 35.4 | 6.9617 | 9.2173 | 2.1272 | -3.1600 | 3.7059 | -7.2308 | 1.0433 |

| Species | \hat{c} | \hat{d} |
|---|-----------|-----------|
| Monovalent cations (Fig. 17) | -20.5 | 1.29 |
| Alkaline earth cations and Pb ²⁺ (Fig. 17) | -14.8 | 0.19 |
| Divalent transition cations (Fig. 17) | 0.0 | 0.92 |
| Trivalent cations (Fig. 17) | -31.5 | 0.17 |
| Halide anions (Fig. 17) | 1.8 | 1.29 |
| Monovalent polyatomic anions (Fig. 18) | 0.0 | 1.0 |
| Divalent polyatomic anions (Fig. 19) | 13.4 | 1.0 |

Many similarities exist among these correlations and those shown in Figs. 15 and 16 for \bar{C}_p° and \bar{S}° . Once again, Pb²⁺ falls on the curve for alkaline earth ions, and Al³⁺ falls on that for the heavy rare earth ions. However, in the case of Fig. 17 the latter curve coincides with that for the light rare earth ions. The available data for Fe³⁺, Cr³⁺ and Rh³⁺ are much too ambiguous to define any additional trivalent cation correlations (see Appendix in NAPS, 1988). As in the case of Fig. 15, the curve for the divalent transition metal ions in Fig. 17 falls on a cross-cutting trend to that for the alkaline earth ions. It can be seen in Fig. 17 that Li⁺ does not fall on the correlation curve for the monovalent cations, which is typical behavior for Li⁺. Finally, relations among the polyatomic anions are somewhat simpler in Figs. 18 and 19 than those observed in the heat capacity correlations shown in Fig. 16.

Estimates of \bar{V}° and \bar{C}_p° generated from the correlation algorithms described above are shown in Table 12 for a large number of aqueous ions at 25°C and 1 bar for which limited, inconclusive, or no experimental data are available in the literature. Values of $\Delta\bar{G}_f^{\circ}$, $\Delta\bar{H}_f^{\circ}$, and \bar{S}° at 25°C and 1 bar as well as estimated equation of state parameters for these ions are also given in Table 12. These parameters, together

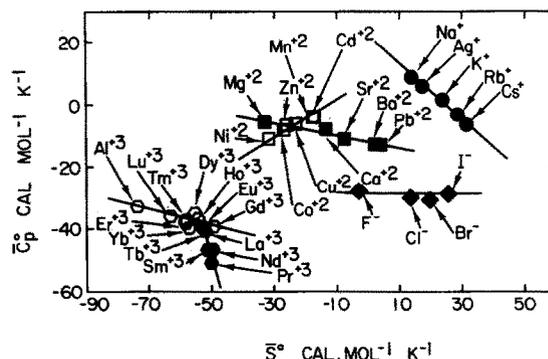


FIG. 15. Correlation of the standard partial molal heat capacities (\bar{C}_p°) and entropies (\bar{S}°) of aqueous monatomic ions at 25°C and 1 bar. The symbols represent values taken from Table 11. The curves are consistent with Eqn. (91) and the coefficients given in the text.

Table 11. (Continued)

| Ion | $\Delta\bar{G}^{\circ}_{f,P,T}$ ^a | $\Delta\bar{H}^{\circ}_{f,P,T}$ ^a | S° ^b | \bar{C}°_{p} ^{b,f} | \bar{V}° ^{c,g} | a_1 ^{u,aa} × 10 | a_2 ^{a,aa} × 10 ⁻² | a_3 ^{v,aa} | a_4 ^{w,aa} × 10 ⁻⁴ | c_1 ^{b,aa} | c_2 ^{w,aa} × 10 ⁻⁴ | ω ^{a,z} × 10 ⁻⁵ |
|--------------------------------|--|--|--------------------------|--------------------------------------|----------------------------------|----------------------------|--|-----------------------|--|-----------------------|--|--|
| I | -12410 ^h | -13600 ^e | 25.50 ^e | -28.25 ^d | 36.31 ^d | 7.7623 | 8.2762 | 1.4609 | -3.1211 | -6.27 | -4.944 | 1.2934 |
| IO ₃ | -30600 ^j | -52900 ^j | 28.3 ^j | 16.2 | 25.9 | 5.7148 | 6.1725 | 3.3240 | -3.0342 | 7.7293 | -6.3345 | 1.2002 |
| CrO ₄ ²⁻ | -173940 ^j | -210600 ^j | 12.0 ^j | -59.9 | 20.4 | 5.5808 | 5.8454 | 3.4525 | -3.0206 | -1.0175 | -15.2362 | 3.0307 |
| Mn ²⁺ | -54500 ^l | -52724 ^l | -17.6 ^l | -4.1 | -17.1 | -0.1016 | -8.0295 | 8.9060 | -2.4471 | 16.6674 | -3.8698 | 1.4006 |
| MnO ₄ ⁻ | -106900 ^j | -129400 ^j | 45.7 ^j | -1.8 | 42. | 7.8289 | 11.3346 | 1.2950 | -3.2476 | 13.7427 | -3.4013 | 0.9368 |
| Co ²⁺ | -13000 ^s | -13900 ^s | -27.0 ^s | -7.8 | -24.4 | -1.0748 | -12.9948 | 16.4112 | -2.2418 | 15.2014 | -4.6235 | 1.4769 |
| Ni ²⁺ | -10900 ^s | -12900 ^s | -30.8 ^s | -11.7 | -29.0 | -1.6942 | -11.9181 | 10.4344 | -2.2863 | 13.1905 | -5.4179 | 1.5067 |
| Cu ²⁺ | 15675 ^h | 15700 ^e | -23.2 ^c | -5.7 | -24.6 | -1.1021 | -10.4726 | 9.8662 | -2.3461 | 20.3 | -4.39 | 1.4769 |
| Zn ²⁺ | -35200 ^h | -36660 ^e | -26.2 ^e | -6.3 | -24.3 | -1.0677 | -10.3884 | 9.8331 | -2.3495 | 15.9009 | -4.3179 | 1.4574 |
| MoO ₄ ²⁻ | -199900 ^s | -238500 ^s | 6.5 ^s | -47.5 | 30.4 | 6.9775 | 9.2559 | 2.1121 | -3.1616 | 7.0224 | -12.7103 | 3.1145 |
| Ag ⁻ | 18427 ^h | 25275 ^e | 17.54 ^e | 7.9 | -0.8 | 1.7285 | -3.5608 | 7.1496 | -2.6318 | 12.7862 | -1.4254 | 0.2160 |
| Cd ²⁺ | -18560 ^h | -18140 ^e | -17.4 ^e | -3.5 | -15.6 | 0.0537 | -10.7080 | 16.5176 | -2.3363 | 15.6573 | -3.7476 | 1.2528 |
| WO ₄ ²⁻ | -219150 ⁱ | -257100 ^s | 9.7 ^s | -44.5 | 32.2 | 7.2074 | 8.7934 | 4.4896 | -3.1425 | 8.3311 | -12.0992 | 3.0657 |
| ReO ₄ ⁻ | -166000 ^j | -188200 ^j | 48.1 ^j | -0.2 | 48.1 | 8.6513 | 13.3428 | 0.5057 | -3.3306 | 14.3448 | -3.0753 | 0.9004 |
| La ⁺³ | -164000 ^t | -169600 ^t | -52.0 ^t | -37.2 | -38.6 | -2.7880 | -14.3824 | 10.9602 | -2.1844 | 4.2394 | -10.6122 | 2.1572 |
| Pr ⁺³ | -162600 ^t | -168800 ^t | -50.1 ^t | -47.7 | -42.1 | -3.2406 | -14.1998 | 8.1257 | -2.1920 | -1.1975 | -12.7511 | 2.2350 |
| Nd ⁺³ | -160600 ^t | -166500 ^t | -49.5 ^t | -43.2 | -43.1 | -3.3707 | -14.5452 | 8.3211 | -2.1777 | 1.6236 | -11.8344 | 2.2550 |
| Sm ⁺³ | -159100 ^t | -165200 ^t | -50.7 ^t | -43.3 | -42.0 | -3.2065 | -15.6108 | 11.8857 | -2.1337 | 1.9385 | -11.8548 | 2.2955 |
| Eu ⁺³ | -137300 ^t | -144700 ^t | -53.0 ^t | -36.6 | -41.3 | -3.1037 | -15.3599 | 11.7871 | -2.1440 | 6.0548 | -10.4900 | 2.3161 |
| Gd ⁺³ | -158600 ^t | -164200 ^t | -49.2 ^t | -35.9 | -40.4 | -2.9771 | -15.0506 | 11.6656 | -2.1568 | 6.5606 | -10.3474 | 2.3265 |
| Tb ⁺³ | -159500 ^{ff} | -166900 ^{ee} | -54.1 ^t | -40.5 | -40.2 | -2.9355 | -14.9491 | 11.6257 | -2.1610 | 4.2522 | -11.2844 | 2.3685 |
| Dy ⁺³ | -158700 ^t | -166500 ^t | -55.2 ^t | -31.7 | -40.7 | -3.0003 | -15.1074 | 11.6879 | -2.1545 | 9.5076 | -9.4919 | 2.3792 |
| Ho ⁺³ | -161400 ^t | -169000 ^t | -54.3 ^t | -33.3 | -41.6 | -3.1198 | -15.3992 | 11.8026 | -2.1424 | 8.6686 | -9.8178 | 2.3899 |
| Er ⁺³ | -159900 ^t | -168500 ^t | -58.3 ^t | -34.3 | -43.0 | -3.3041 | -15.8492 | 11.9794 | -2.1238 | 8.2815 | -10.0215 | 2.4115 |
| Tm ⁺³ | -159900 ^t | -168500 ^t | -58.1 ^t | -34.3 | -43.0 | -3.2967 | -15.8312 | 11.9724 | -2.1245 | 8.4826 | -10.0215 | 2.4333 |
| Yb ⁺³ | -153000 ^{ff} | -160300 ^{ee} | -56.9 ^t | -36.4 | -44.5 | -3.4983 | -16.3233 | 12.1658 | -2.1042 | 7.3533 | -10.4493 | 2.4443 |
| Lu ⁺³ | -159400 ^t | -167900 ^t | -63.1 ^t | -32.0 | -45.0 | -3.5630 | -16.4812 | 12.2279 | -2.0977 | 9.5650 | -9.7160 | 2.4554 |

a. cal mol⁻¹. b. cal mol⁻¹ K⁻¹. c. cm³ mol⁻¹. d. Tanger and Helgeson (1988). e. CODATA (1978). f. From electrolytes in table 10 unless otherwise indicated. g. From electrolytes in table 9 unless otherwise indicated. h. Calculated from $\Delta\bar{H}^{\circ}_{f,P,T}$ and \bar{S}° shown, using standard entropies of the elements from CODATA (1978). i. Calculated from $\Delta\bar{H}^{\circ}_{f,P,T}$ and \bar{S}° shown, using standard entropies of the elements from Wagman et al. (1982). j. Wagman et al. (1982). k. Buseenberg et al. (1984). l. Helgeson, Kirkham and Flowers (1981). m. Berg and Vanderzee (1978). n. From fit of log K data (see text). p. Consistent with $\Delta\bar{H}_{f,P,T}$ from fit of log K (see text). q. Barbero et al. (1982). r. Consistent with log $K_{f,P,T}$, $\Delta\bar{H}_{f,P,T}$, and $\Delta\bar{S}_{f,P,T}$ from dissociation reaction (see text). s. Jackson and Helgeson (1985). t. Morss (1976). u. cal mol⁻¹ xbar⁻¹. v. cal K mol⁻¹ xbar⁻¹. w. cal K mol⁻¹. y. From table 4. z. From table 1, 2 or 3. aa. Calculated in a manner consistent with table 8 unless otherwise indicated. bb. Calculated from data reported by Couturier et al.

(1984) for $\text{AlO}_2 + 4\text{H}^+ = \text{Al}^{3+} + 2\text{H}_2\text{O}$ using log K = 22.20, $\Delta\bar{G}^{\circ}_{f,\text{H}_2\text{O}} = -56.687$ cal mol⁻¹, and $\Delta\bar{G}^{\circ}_{f,\text{gibbsite}} = -276,028$ cal mol⁻¹ (Hemingway and Robie, 1977). cc. Sverjensky et al. (in preparation). dd. Calculated from $\Delta\bar{G}_f$ and \bar{S}° shown, using standard entropies of the elements from CODATA (1978). ee. Bettonville et al. (1987). ff. Calculated from the values of $\Delta\bar{H}_{f,P,T}$ and \bar{S}° shown above using standard partial molal entropies of the elements taken from Morss (1976). gg. Retrieved by Sverjensky et al. (in preparation) from the temperature dependence of the dissociation constant of AlO_2 reported by Couturier et al. (1984) and the mutual solubility of albite, paragonite, and quartz reported by Woodland and Walther (1987). hh. Calculated from gibbsite solubility data reported by Kittrick (1966) for $\text{Al}(\text{OH})_{3(c)} + \text{H}_2\text{O} = \text{Al}(\text{OH})_4 + \text{H}^+$ using log K = -15.30, $\Delta\bar{G}^{\circ}_{f,\text{H}_2\text{O}} = -56.687$ cal mol⁻¹, and $\Delta\bar{G}^{\circ}_{f,\text{gibbsite}} = -276,028$ cal mol⁻¹ (Hemingway and Robie, 1977).

with the equations of state summarized above, permit prediction of the standard partial molal thermodynamic properties of all the aqueous ions shown in Table 12 to 1000°C and 5 kb. The accuracy of calculations of this kind can be tested by comparison of predicted equilibrium constants at high temperatures and pressures with their experimental counterparts reported in the literature.

COMPARISON OF PREDICTED AND EXPERIMENTAL EQUILIBRIUM CONSTANTS AT HIGH TEMPERATURES AND PRESSURES

Numerous experimental studies have been carried out at elevated temperatures and pressures of equilibrium constants (K) for reactions involving many of the ions listed in Tables 11 and 12. Values of log K can be calculated from the definition of the standard partial molal Gibbs free energy of reaction ($\Delta\bar{G}^{\circ}_r$) given by

$$\Delta\bar{G}^{\circ}_r = \sum_i \bar{n}_{i,r} \Delta\bar{G}^{\circ}_i \quad (93)$$

and the relation between $\Delta\bar{G}^{\circ}_r$ and log K represented by

$$\log K = \frac{-\Delta\bar{G}^{\circ}_r}{2.303RT}, \quad (94)$$

where $\bar{n}_{i,r}$ stands for the reaction coefficient of the i th species in the reaction, R refers to the gas constant (1.98719 cal mol⁻¹ K⁻¹) and $\Delta\bar{G}^{\circ}$ denotes the apparent standard partial molal Gibbs free energy of formation given by Eqn. (40). Comparison of experimental values of log K at elevated temperatures and pressures with those calculated from Eqns. (44), (93), and (94) using parameters taken from Tables 11 and 12 are depicted in Figs. 20 through 22 for the dissociation of HCO_3^- , H_2PO_4^- , and HSO_4^- . In all cases the symbols represent values of the equilibrium constants generated from experimental data reported in the literature, but the curves represent values calculated *independently* of the data in the present study. The close agreement of the symbols and the independently predicted curves in Figs. 20 through 22 is discussed below.



It can be seen in Fig. 20 that the predicted values of log K represented by the curve for this reaction are in close agreement with the experimental values of log K (HARNED and SCHOLLS, 1941; NÄSÄNEN, 1946; CUTA and STRAFELDA, 1954; RYZHENKO, 1963; and PATTERSON *et al.*, 1984) over the entire temperature range from 0° to 250°C at vapor-

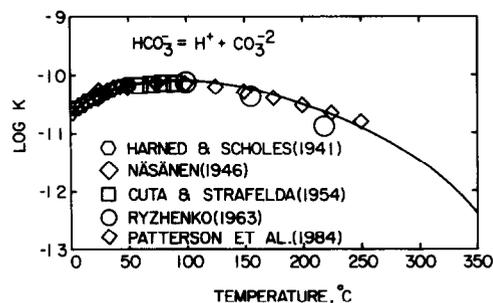


FIG. 20. Logarithm of the equilibrium constant ($\log K$) for the dissociation of the bicarbonate ion as a function of temperature at P_{SAT} . The symbols represent experimental data taken from the references given in the figure, but the curve was generated from Eqns. (44), (93), and (94) using data and parameters given in Table 11 (see text).

adopted for $\Delta\bar{G}_r^0$ and $\Delta\bar{S}_r^0$ at the reference temperature and pressure.



It can be seen in Fig. 22 that the predicted values of $\log K$ for this reaction corresponding to the curve are consistent with all of the experimental data represented by the symbols, except those above 100°C reported by MARSHALL and JONES (1966). The values of $\log K$ given by MARSHALL and JONES (1966) were retrieved from measurements of the solubility of CaSO_4 in H_2SO_4 - H_2O solutions. LIETZKE *et al.* (1961) report more negative values from similar measurements using Ag_2SO_4 . The discrepancies between MARSHALL and JONES' (1966) results and the values of $\log K$ computed in the present study may be a consequence of the formation of CaSO_4^0 and H_2SO_4^0 ion pairs in the experimental solutions. In any event, Marshall and Jones' values of $\log K$ differ significantly at 218° to 225°C from those reported by RYZHENKO (1964) and LIETZKE *et al.* (1961), both of which are in agreement with the curve generated independently in the present study.

The curve shown in Fig. 22 is consistent with $\Delta\bar{G}_r^0 = 2700 \text{ cal mol}^{-1}$, $\Delta\bar{H}_r^0 = -5300 \text{ cal mol}^{-1}$, $\Delta\bar{S}_r^0 = -25.5 \text{ cal mol}^{-1} \text{ K}^{-1}$, $\Delta\bar{C}_{p,r}^0 = -69.2 \text{ cal mol}^{-1} \text{ K}^{-1}$, and $\Delta\bar{V}_r^0 = -21.3 \text{ cm}^3$

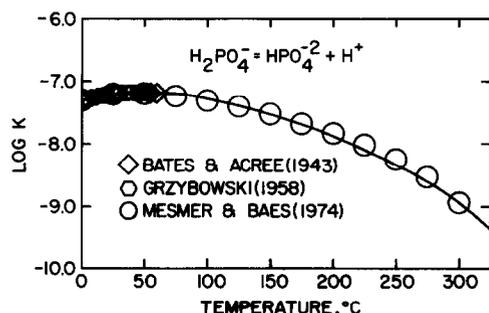


FIG. 21. Logarithm of the equilibrium constant ($\log K$) for the dissociation of H_2PO_4^- as a function of temperature at P_{SAT} . The symbols represent experimental data taken from the references given in the figure, but the curve was generated from Eqns. (44), (93), and (94) using data and parameters given in Table 11 (see text).

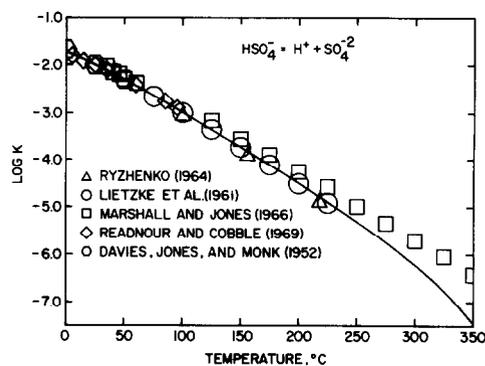


FIG. 22. Logarithm of the equilibrium constant ($\log K$) for the dissociation of the bisulfate ion as a function of temperature at P_{SAT} . The symbols represent experimental data taken from the references given in the figure, but the curve was generated from Eqns. (44), (93), and (94) using data and parameters given in Table 11 (see text).

mol^{-1} at 25°C and 1 bar. All of these values are in close agreement with those adopted by LARSON *et al.* (1982) and the relevant thermodynamic data selected by WAGMAN *et al.* (1982). However, they differ significantly from other values reported in the literature. For example, the value of $\Delta\bar{H}_r^0 = -5300 \text{ cal mol}^{-1}$ generated in the present study is more negative than that obtained by READNOUR and COBBLE (1969) ($-4124 \text{ cal mol}^{-1}$) from calorimetric measurements at 25°C and 1 bar, but less negative than the value ($-5640 \text{ cal mol}^{-1}$) determined by CHRISTENSEN *et al.* (1966) using the entropy titration method or those (-5500 and $-5700 \text{ cal mol}^{-1}$, respectively) obtained from calorimetric measure-

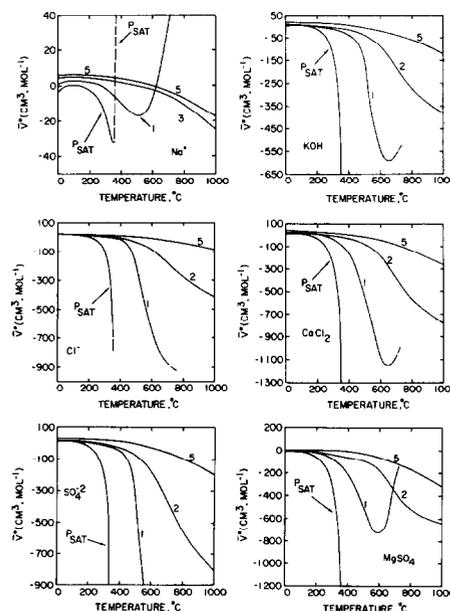


FIG. 23. Predicted values of the standard partial molal volumes (\bar{V}^0) of Na^+ , Cl^- , SO_4^{2-} , and the dissociated electrolytes KOH , CaCl_2 and MgSO_4 as a function of temperature at constant pressure (labeled in kb) computed from Eqn. (11) using parameters taken from Table 11.

Table 12. Summary of experimental and estimated standard partial molal thermodynamic properties of aqueous ions at 25°C and 1 bar and the parameters required to calculate the corresponding properties at high pressures and temperatures from equations (11), (36), (38), (43) and (44).

| Ion | $\Delta\bar{G}_{f,P,T}^{\circ}$, ^{aj} | $\Delta\bar{H}_{f,P,T}^{\circ}$, ^{aj} | \bar{S}° , ^{bj} | \bar{C}_p° , ^{b,d} | \bar{V}° , ^{c,e} | $a_1^u \times 10$ | $a_2^a \times 10^{-2}$ | a_3^v | $a_4^w \times 10^{-4}$ | c_1^b | $c_2^w \times 10^{-4}$ | $\omega^a \times 10^{-5}$ |
|--|---|---|-----------------------------------|--------------------------------------|------------------------------------|-------------------|------------------------|---------|------------------------|----------|------------------------|---------------------------|
| Be ²⁺ | -83500 ⁿ | -91500 | -55.7 ^t | -1.3 | -25.4 | -1.0684 | -10.3901 | 9.8338 | -2.3495 | 22.9152 | -3.2994 | 1.9007 |
| BeO ₂ ²⁻ | -153000 | -189000 | -38. | -100.9 | -24.6 | -0.3210 | -8.5653 | 9.1166 | -2.4249 | -18.0684 | -23.5879 | 3.7880 |
| Ra ²⁺ | -134200 | -126100 | 13. | -14.4 | -10.6 | 0.6285 | -6.2469 | 8.2053 | -2.5208 | 6.2858 | -5.9679 | 0.9290 |
| BO ₂ ⁻ | -162240 | -184600 | -8.9 | -41.0 ^{aa} | -14.5 ^f | -2.2428 | -6.2065 | -6.3216 | -2.5224 | -1.6521 | -11.3863 | 1.7595 |
| BF ₄ ⁻ | -355400 | -376400 | 43.0 | -5.6 | 43.0 | 7.9796 | 11.7027 | 1.1504 | -3.2628 | 11.8941 | -4.1753 | 0.9779 |
| Ga ³⁺ | -38000 | -50600 | -79.0 | -30.8 | -44.9 | -3.4573 | -16.2232 | 12.1264 | -2.1083 | 13.2451 | -9.3086 | 2.7276 |
| In ³⁺ | -23400 | -25000 | -63.0 ^h | -34.9 | -42.2 | -3.1646 | -15.5086 | 11.8456 | -2.1379 | 8.7476 | -10.1437 | 2.5003 |
| Tl ⁺ | -7740 | 1280 | 30.0 | -4.2 | 18.2 | 4.3063 | 2.7333 | 4.6757 | -2.8920 | 5.0890 | -3.8901 | 0.1502 |
| Tl ³⁺ | 51300 | 47000 | -46.0 | -39.3 | -39.3 | -2.8195 | -14.6658 | 11.5143 | -2.1727 | 4.7607 | -11.0400 | 2.3474 |
| CN ⁻ | 41200 | 36000 | 22.5 | -32.7 | 24.2 ⁱ | 5.5125 | 5.6786 | 3.5181 | -3.0138 | -1.1135 | -9.6956 | 1.2900 |
| SiF ₆ ²⁻ | -525700 | -571000 | 29.2 | -47.1 | 42.6 | 8.5311 | 13.0492 | 0.6211 | -3.3185 | 4.0970 | -12.6289 | 2.7716 |
| Sn ²⁺ | -6630 ^l | -2100 ^m | -3.8 ^m | -11.2 | -15.5 | 0.0786 | -7.5895 | 8.7330 | -2.4652 | 11.4502 | -5.3160 | 1.2860 |
| H ₂ P ₂ O ₇ ²⁻ | -480400 | -544600 | 39. | -20.3 | 52.4 | 9.8215 | 16.2000 | -0.6173 | -3.4487 | 18.4241 | -7.1697 | 2.6218 |
| H ₃ P ₂ O ₇ ²⁻ | -483600 | -544100 | 51. | 29.6 | 51.0 | 9.0334 | 14.2757 | 0.1391 | -3.3692 | 31.4072 | 2.9949 | 0.8568 |
| HAsO ₄ ²⁻ | -170790 | -216620 | -0.4 | -51.8 | 13.0 | 4.6321 | 3.5288 | 4.3630 | -2.9249 | 5.4710 | -13.5863 | 3.2197 |
| H ₂ AsO ₄ ⁻ | -180010 | -217390 | 28. | -0.7 | 35.1 | 6.9755 | 9.2509 | 2.1140 | -3.1614 | 16.8622 | -3.1772 | 1.2055 |
| H ₂ AsO ₃ ⁻ | -140330 | -170840 | 26.4 | -2.9 | 26.4 | 5.7934 | 6.3646 | 3.2485 | -3.0421 | 15.8032 | -3.6253 | 1.2305 |
| HO ₂ ⁻ | -16100 | -38320 | 5.7 | -30.2 | 5.7 | 3.0671 | -0.2924 | 5.8649 | -2.7669 | 2.7007 | -9.1863 | 1.5449 |
| SO ₃ ²⁻ | -116300 | -151900 | -7. | -76.1 | 5.6 | 3.6537 | 0.3191 | 7.3853 | -2.7922 | -7.8368 | -18.5362 | 3.3210 |
| HSO ₃ ⁻ | -152370 ⁿ | -185380 ^p | 50.7 ^p | 29.2 | 50.7 | 8.9938 | 14.1790 | 0.1771 | -3.3652 | 31.2126 | 2.9134 | 0.8611 |
| S ₂ ²⁻ | 19000 | 7200 | 6.8 | -65.1 | 20.2 | 5.5797 | 5.8426 | 3.4536 | -3.0205 | -3.3496 | -16.2955 | 3.1083 |
| S ₂ O ₄ ²⁻ | -143500 | -180100 | 22. | -52.9 | 35.4 | 7.5815 | 10.7306 | 1.5324 | -3.2226 | 1.6707 | -13.8103 | 2.8772 |
| S ₂ O ₅ ²⁻ | -189000 ^q | -232000 ^q | 25 ^q | -50.5 | 38.4 | 7.9775 | 11.6976 | 1.1524 | -3.2626 | 2.6824 | -13.3215 | 2.8343 |
| S ₂ O ₆ ²⁻ | -231000 ^q | -280400 ^q | 30 ^q | -46.5 | 43.3 | 8.6225 | 13.2724 | 0.5334 | -3.3277 | 4.3301 | -12.5066 | 2.7587 |
| S ₃ ²⁻ | 17600 | 6200 | 15.8 | -57.9 | 29.2 | 6.7661 | 8.7396 | 2.3150 | -3.1403 | -0.3595 | -14.8288 | 2.9749 |
| S ₃ O ₆ ²⁻ | -229000 ^q | -279000 ^q | 33 ^q | -44.1 | 46.4 | 9.0313 | 14.2706 | 0.1410 | -3.3689 | 5.3169 | -12.0178 | 2.7131 |
| S ₄ ²⁻ | 16500 | 5500 | 24.7 | -50.7 | 38.1 | 7.9381 | 11.6012 | 1.1902 | -3.2586 | 2.6081 | -13.3622 | 2.8390 |
| S ₄ O ₆ ²⁻ | -248700 | -292600 | 61.5 | -21.3 | 74.9 | 12.7850 | 23.4362 | -3.4614 | -3.7479 | 14.6933 | -7.3734 | 2.2805 |
| S ₅ ²⁻ | 15700 | 5100 | 33.6 | -43.6 | 47.0 | 9.1107 | 14.4645 | 0.0649 | -3.3770 | 5.5361 | -11.9159 | 2.7051 |
| S ₅ O ₆ ²⁻ | -229000 ^q | -281000 ^q | 40 ^q | -38.5 | 53.4 | 9.9535 | 16.5224 | -0.7440 | -3.4620 | 7.6266 | -10.8770 | 2.6076 |
| HSe ⁻ | 10500 | 3800 | 19. | -12.6 | 19.0 | 4.8181 | 3.9831 | 4.1845 | -2.9437 | 11.1345 | -5.6012 | 1.3408 |
| SeO ₃ ²⁻ | -88400 | -121700 | 3. | -68.1 | 16.4 | 5.0791 | 4.6204 | 3.9340 | -2.9700 | -4.5783 | -16.9066 | 3.1658 |
| HSeO ₃ ⁻ | -98340 | -122980 | 32.3 | 4.9 | 32.3 | 6.5703 | 8.2615 | 2.5029 | -3.1205 | 19.5432 | -2.0365 | 1.1402 |
| SeO ₄ ²⁻ | -105500 | -143200 | 12.9 | -60.2 | 20.7 | 5.6180 | 5.9362 | 3.4168 | -3.0244 | -1.2986 | -15.2973 | 3.0192 |

ments by ZIELEN (1959) and AUSTIN and MAIR (1962). In contrast, $\Delta\bar{H}_f^{\circ} = -5300 \text{ cal mol}^{-1}$ is nearly equivalent to the value calculated from WAGMAN *et al.*'s (1982) compilation ($-5241 \text{ cal mol}^{-1}$). In HEPLER and HOPKINS' (1979) review of the literature they conclude that $\Delta\bar{H}_f^{\circ}$ lies somewhere between -4800 and $-5500 \text{ cal mol}^{-1}$. More recently, LARSON *et al.* (1982) adopted $\Delta\bar{H}_f^{\circ} = -5400 \text{ cal mol}^{-1}$, based in part on the analysis by PITZER *et al.* (1977) who calculated $\Delta\bar{H}_f^{\circ} = -5610 \text{ cal mol}^{-1}$.

PREDICTION OF THE STANDARD PARTIAL MOLAL THERMODYNAMIC PROPERTIES OF AQUEOUS IONS AND ELECTROLYTES TO 5 kb AND 1000°C

The close agreement between calculated and experimental equilibrium constants depicted in Figs. 20–22 lends considerable support to the validity and generality of the equations, correlations, and parameters summarized above. Eqns. (11), (36), (38), (43), and (44), together with the equation of state parameters given in Tables 11 and 12 can be used to predict standard partial molal properties at higher tempera-

tures and pressures than those shown in Figs. 20–22. Examples of predicted standard partial molal volumes, heat capacities and entropies, together with the apparent standard partial molal enthalpies and Gibbs free energies of formation of Na⁺, Cl⁻, and SO₄²⁻, as well as the corresponding properties of the electrolytes KOH, CaCl₂, and MgSO₄ are shown in Figs. 23 through 27. The requisite values of the Born and *g* functions were taken from SHOCK *et al.* (1988b).

It can be seen in Figs. 23 and 24 that the predicted values of \bar{V}° and \bar{C}_p° of aqueous anions represented by Cl⁻ and SO₄²⁻ become much more negative than those of cations represented by Na⁺ at high temperatures and low pressures. Note that $\Delta\bar{H}_f^{\circ}$, \bar{S}° , \bar{C}_p° , and \bar{V}° for electrolytes in the liquid phase region maximize with increasing temperature at P_{SAT} and approach $-\infty$ at the critical point of H₂O (WHEELER, 1972; HELGESON and KIRKHAM, 1974b; COBBLE and MURRAY, 1977; GATES *et al.*, 1982) which is not necessarily true for the conventional standard partial molal properties of individual aqueous ions. In contrast, $\Delta\bar{H}_f^{\circ}$, \bar{S}° , \bar{C}_p° , and \bar{V}° for aqueous electrolytes at P_{SAT} in the steam phase region approach ∞ at the critical point of H₂O (GATES *et al.*, 1982;

Table 12. (Continued)

| Ion | $\Delta\bar{G}_{f,P,T}^{\circ}$, ^{a,j} | $\Delta\bar{H}_{f,P,T}^{\circ}$, ^{a,j} | \bar{S}° , ^{b,j} | \bar{C}_p° , ^{b,d} | \bar{V}° , ^{c,e} | $a_1^u \times 10$ | $a_2^a \times 10^{-2}$ | a_3^v | $a_4^w \times 10^{-4}$ | c_1^b | $c_2^w \times 10^{-4}$ | $\omega^a \times 10^{-5}$ |
|--|--|--|------------------------------------|--------------------------------------|------------------------------------|-------------------|------------------------|---------|------------------------|----------|------------------------|---------------------------|
| HSeO ₄ ⁻ | -108100 | -139000 | 35.7 | -41.9 | 31.0 | 6.3749 | 7.7844 | 2.6904 | -3.1008 | -8.3616 | -11.5696 | 1.0885 |
| HF ₂ ⁻ | -138160 | -155340 | 22.1 | -33.2 | 22.1 | 5.2263 | 4.9797 | 3.7928 | -2.9849 | -1.3751 | -9.7974 | 1.2934 |
| ClO ⁻ | -8800 | -25600 | 10. | -49.2 | 10.0 | 3.6325 | 1.0881 | 5.3224 | -2.8240 | -9.0630 | -13.0566 | 1.4767 |
| ClO ₂ ⁻ | 4100 | -15900 | 24.2 | -30.5 | 24.2 | 5.5036 | 5.6569 | 3.5266 | -3.0129 | -0.0659 | -9.2474 | 1.2637 |
| BrO ⁻ | -8000 | -22500 | 10. | -49.2 | 10.0 | 3.6325 | 1.0881 | 5.3224 | -2.8240 | -9.0630 | -13.0566 | 1.4767 |
| BrO ₄ ⁻ | 28200 | 3100 | 47.7 | 0.6 | 47.7 | 8.5987 | 13.2144 | 0.5562 | -3.3253 | 14.8727 | -2.9124 | 0.9068 |
| Br ₃ ⁻ | -25590 | -31170 | 51.5 | 5.6 | 51.5 | 9.0992 | 14.4364 | 0.0759 | -3.3758 | 17.2705 | -1.8939 | 0.8490 |
| IO ⁻ | -9200 | -25700 | -1.3 | -64.1 | -1.3 | 2.1432 | -2.5482 | 6.7516 | -2.6737 | -16.2398 | -16.0918 | 1.6455 |
| IO ₄ ⁻ | -14000 | -36200 | 53. | 7.6 | 53.0 | 9.2968 | 14.9189 | -0.1138 | -3.3957 | 18.2345 | -1.4865 | 0.8264 |
| I ₃ ⁻ | -12300 | -12300 | 57.2 | 13.1 | 57.2 | 9.8500 | 16.2697 | -0.6447 | -3.4516 | 20.8712 | -0.3661 | 0.7628 |
| VO ⁺² | -106700 | -116300 | -32. | -12.0 | -29.4 | -1.7351 | -12.0180 | 10.4736 | -2.2822 | 13.3910 | -5.4790 | 1.5475 |
| VO ₂ ⁺ | -140300 | -155300 | -10.1 | 31.1 | -33.5 | -2.5825 | -14.0871 | 11.2869 | -2.1966 | 30.8449 | 3.3005 | 0.7003 |
| HVO ₄ ⁻² | -233000 | -277000 | 4. | -48.3 | 17.4 | 5.2115 | 4.9437 | 3.8069 | -2.9834 | 6.9055 | -12.8733 | 3.1527 |
| H ₂ VO ₄ ⁻ | -244000 | -280600 | 29. | 0.6 | 29.0 | 6.1355 | 7.1997 | 2.9202 | -3.0766 | 17.4795 | -2.9124 | 1.1898 |
| HCrO ₄ ⁻ | -182800 | -209900 | 44.0 | 20.4 | 44.0 | 8.1112 | 12.0239 | 1.0241 | -3.2761 | 26.9872 | 1.1209 | 0.9622 |
| Cr ₂ O ₇ ⁻² | -311000 | -356200 | 62.6 | -20.4 | 73.0 | 12.5200 | 22.7889 | -3.2070 | -3.7211 | 15.0820 | -7.1901 | 2.2654 |
| MnO ₄ ⁻² | -119700 | -156000 | 14. | -59.3 | 27.4 | 6.5291 | 8.1609 | 2.5424 | -3.1164 | -0.9267 | -15.1140 | 3.0024 |
| Fe ⁺² | -21880 ^k | -21610 ^k | -25.6 ^k | -8.1 | -22.2 ^f | -0.7803 | -9.6867 | 9.5573 | -2.3786 | 14.8460 | -4.6846 | 1.4574 |
| Fe ⁺³ | -4078 ^k | -11821 ^k | -66.3 ^k | -34.1 | -42.8 | -3.1784 | -15.5422 | 11.8588 | -2.1365 | 11.0798 | -9.9808 | 2.7025 |
| Co ⁺³ | 32000 | 22000 | -73. | -32.3 | -43.9 | -3.3247 | -15.8994 | 11.9992 | -2.1217 | 12.2500 | -9.6141 | 2.7150 |
| Cu ⁺ | 11950 ^s | 17132 ^s | 9.7 ^s | 13.7 | -8.0 | 0.7835 | -5.8682 | 8.0565 | -2.5364 | 17.2831 | -0.2439 | 0.3351 |
| Pd ⁺² | 42200 | 42080 ^z | -22.6 ^l | -6.3 | -20.8 | -0.6079 | -9.2658 | 9.3919 | -2.3960 | 15.3780 | -4.3179 | 1.4006 |
| Ag ⁺² | 64300 | 64200 | -21.0 | -5.3 | -19.3 | 0.4299 | -8.8310 | 9.2210 | -2.4139 | 15.2224 | -4.1142 | 1.3201 |
| Au ⁺ | 39000 ^s | 47580 ^z | 24.5 ^l | 0.6 | 11.1 | 3.3448 | 0.3856 | 5.5985 | -2.7949 | 8.1768 | -2.9124 | 0.1800 |
| Au ⁺³ | 103600 ^s | 96930 ^z | -57.9 ^l | -36.2 | -41.3 | -3.0567 | -15.2450 | 11.7419 | -2.1488 | 7.5724 | -10.4085 | 2.4554 |
| Hg ⁺² | 39360 ^l | 40670 ^m | -8.68 ^m | 2.2 | -19.6 ^f | -0.5280 | -9.0707 | 9.3152 | -2.4040 | 18.0613 | -2.5865 | 1.1512 |
| Hg ₂ ⁺² | 36710 ^l | 39870 ^m | -15.66 ^m | 17.1 | 14.4 | 4.0126 | 2.0164 | 4.9575 | -2.8624 | 23.7433 | 0.4487 | 0.8201 |
| Se ⁺³ | -140200 | -146800 | -61. | -35.4 | -41.9 | -3.1236 | -15.4084 | 11.8062 | -2.1420 | 8.4546 | -10.2456 | 2.5003 |
| Y ⁺³ | -163800 ^x | -170900 ^x | -60. ^x | -35.7 | -40.8 ^f | -3.0140 | -15.1408 | 11.7010 | -2.1531 | 7.1634 | -10.3067 | 2.3792 |
| Ce ⁺³ | -161600 ^x | -167400 ^x | -49. ^x | -38.6 | -39.8 | -2.9292 | -14.9338 | 11.6196 | -2.1616 | 4.0445 | -10.8974 | 2.2251 |
| Sm ⁺² | -123000 ^x | -120500 ^x | -6.2 ^x | 3.7 | -5.7 | 1.4002 | -4.3625 | 7.4647 | -2.5987 | 19.6533 | -2.2809 | 1.2285 |
| Eu ⁺² | -129100 ^x | -126100 ^x | -2.4 ^x | 6.0 | -2.2 | 1.8333 | -3.3050 | 7.0490 | -2.6424 | 19.7516 | -1.8124 | 1.0929 |
| Yb ⁺² | -128500 ^{cc} | -126800 ^{bb} | -11.2 ^x | 0.7 | -10.3 | 0.7707 | -5.8995 | 8.0688 | -2.5351 | 17.8951 | -2.8920 | 1.2285 |

a. cal mol⁻¹. b. cal mol⁻¹ K⁻¹. c. cm³ mol⁻¹. d. Unless otherwise indicated, estimated from \bar{S}° with relations shown in figures 16 and 17 using eq (91) and coefficients given in text. e. Unless otherwise indicated, estimated from \bar{S}° with relations shown in figures 18, 19 and 20 using eq (92) and coefficients given in text. f. Calculated by additivity relations using \bar{V}° data for electrolytes from table 9 and ions from table 11. h. Corrected typographical error in Wagman et al. (1982) (see Helgeson and Kirkham, 1976). i. Akitt (1980). j. Wagman et al. (1982) unless otherwise noted. k. Helgeson (1985). l. Calculated from $\Delta\bar{H}_{f,P,T}^{\circ}$ and \bar{S}° using \bar{S}° of the elements from m. m. CODATA (1978). n. Calculated from $\Delta\bar{H}_{f,P,T}^{\circ}$ and \bar{S}° using \bar{S}° of the elements from Wag-

man et al. (1982). p. Price et al. (1986). q. Latimer (1952). r. Calculated from aqueous electrolyte volumes given by Millero (1972) using values of the ions from table 11. s. Helgeson, Kirkham and Flowers (1981). t. From table 3. u. cal mol⁻¹ bar⁻¹. v. cal K mol⁻¹ bar⁻¹. w. cal K mol⁻¹. x. Morss (1976). y. From tables 1, 2 or 3. z. Calculated from $\Delta\bar{G}_{f,P,T}^{\circ}$ and \bar{S}° in table using \bar{S}° of the elements from Wagman et al. (1982). aa. From fit of log K data. bb. Bettonvillet et al. (1987). cc. Calculated from the values of $\Delta\bar{H}_{f,P,T}^{\circ}$ and \bar{S}° shown above using standard partial molal entropies of the elements taken from Morss (1976).

WOOD and QUINT, 1982). As a consequence, the 1 and 2 kb isobars in Fig. 24 exhibit partial quasi-sinusoidal behavior, which dampens with increasing pressure. It can be seen in Figs. 25 and 26 that the effect of the critical phenomena on \bar{S}° and $\Delta\bar{H}^{\circ}$ continues to be significant at 1 and 2 kilobars but is considerably dampened at 5 kb and temperatures to 1000°C. Note that increasing pressure has little effect on $\Delta\bar{G}^{\circ}$ of the sodium ion at all temperatures, but it has a dramatic effect on $\Delta\bar{G}^{\circ}$ of Cl⁻, SO₄⁻² and the electrolytes shown in Fig. 27. The predicted values of $\Delta\bar{G}^{\circ}$ for the electrolytes exhibit three distinctly different types of behavior with increasing temperature at constant pressure. In the case of the 1:1 electrolyte KOH, the 5 kb $\Delta\bar{G}^{\circ}$ isobar becomes increasingly negative with increasing temperature. At lower pressures, the isobars for KOH tend to minimize at progressively lower

temperatures. In contrast, the isobars for $\Delta\bar{G}_{CaCl_2}^{\circ}$ minimize with increasing temperature at all of the pressures shown in Fig. 27. Unlike KOH and CaCl₂, $\Delta\bar{G}_{MgSO_4}^{\circ}$ increases monotonically with increasing temperature at all of the constant pressures shown in the figure.

CONCLUDING REMARKS

The equations, correlations and parameters summarized above can be used together with Born functions and effective electrostatic radii (HELGESON and KIRKHAM, 1974a; SHOCK et al., 1988b) to calculate \bar{V}° , \bar{C}_p° , \bar{S}° , $\Delta\bar{H}^{\circ}$ and $\Delta\bar{G}^{\circ}$ for a large number of aqueous ions and electrolytes to 5 kb and 1000°C. The correlations can also be used to estimate equation of state parameters and predict these properties at high

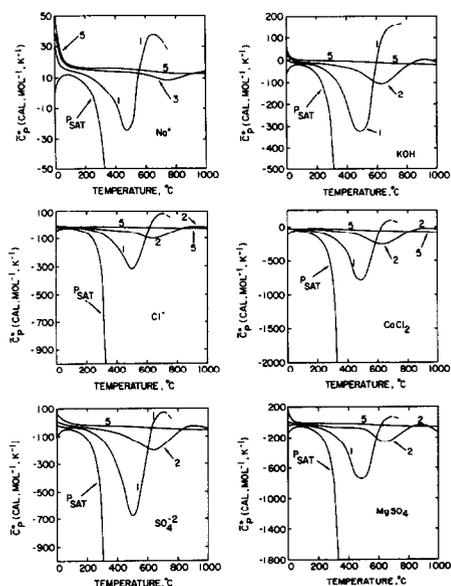


FIG. 24. Predicted values of the standard partial molal heat capacity (C_p^0) of Na^+ , Cl^- , SO_4^{2-} , and the dissociated electrolytes KOH , CaCl_2 and MgSO_4 as a function of temperature at constant pressure (labeled in kb) computed from Eqn. (36) using parameters taken from Table 11.

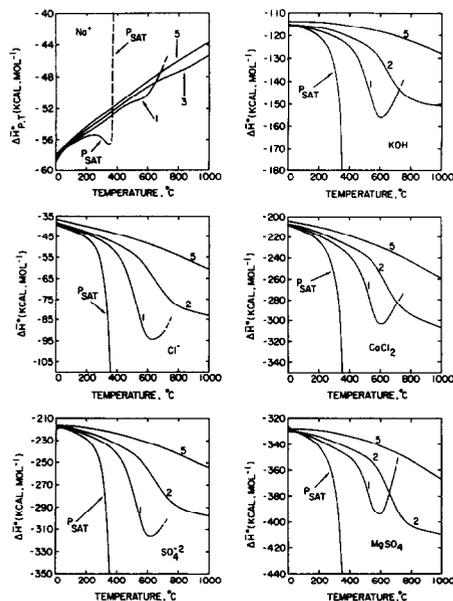


FIG. 26. Predicted values of the apparent standard partial molal enthalpy of formation (ΔH^0) of Na^+ , Cl^- , SO_4^{2-} , and the dissociated electrolytes KOH , CaCl_2 and MgSO_4 as a function of temperature at constant pressure (labeled in kb) computed from Eqn. (43) using parameters taken from Table 11.

temperatures and pressures for neutral aqueous dissolved gases and inorganic acids (SHOCK *et al.*, 1988a), aqueous organic species (SHOCK and HELGESON, 1988) and charged and neutral aqueous metal complexes (SVERJENSKY *et al.*, 1988). 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 under supercritical conditions. The standard partial molal entropies of aqueous ions at high pressures and temperatures calculated in the manner described above can

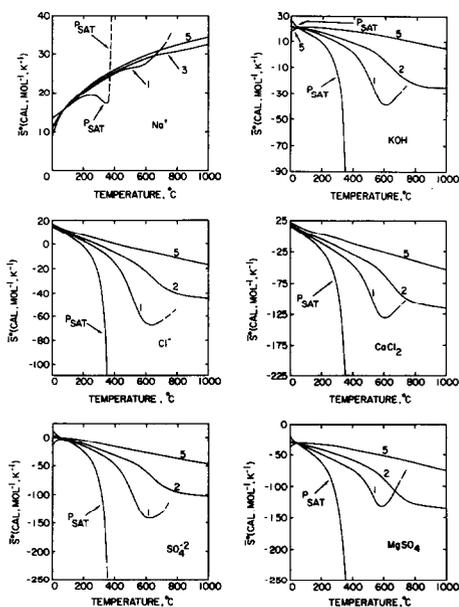


FIG. 25. Predicted values of the standard partial molal entropy (S^0) of Na^+ , Cl^- , SO_4^{2-} , and the dissociated electrolytes KOH , CaCl_2 and MgSO_4 as a function of temperature at constant pressure (labeled in kb) computed from Eqn. (38) using parameters taken from Table 11.

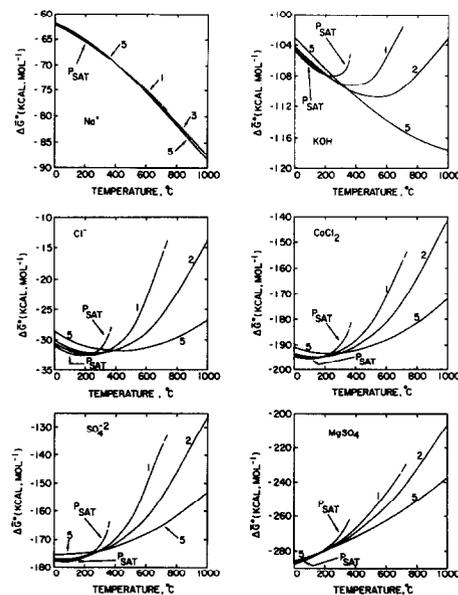


FIG. 27. Predicted values of the apparent standard partial molal Gibbs free energy of formation (ΔG^0) of Na^+ , Cl^- , SO_4^{2-} , and the dissociated electrolytes KOH , CaCl_2 and MgSO_4 as a function of temperature at constant pressure (labeled in kb) computed from Eqn. (44) using parameters taken from Table 11.

be used to calculate limiting equivalent conductances and tracer diffusion coefficients (OELKERS and HELGESON, 1988a), dissociation constants (OELKERS and HELGESON, 1988b), and other transport properties of aqueous species to 5 kb and 1000°C (OELKERS and HELGESON, 1988c). These calculations make it possible to characterize a wide variety of both heterogeneous equilibria and nonequilibria in geochemical processes at magmatic temperatures and pressures. The revised HKF equations of state and their extension to 5 kb and 1000°C have been incorporated in a revised version of the computer program SUPCRT which is available together with a new data file including all of the ions listed in Tables 11 and 12 from the Laboratory of Theoretical Geochemistry (otherwise known as Prediction Central) at the University of California, Berkeley. The Appendix to this paper is available from the National Auxiliary Publication Service (NAPS, 1988).

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