

A new equation of state for correlation and prediction of standard molal thermodynamic properties of aqueous species at high temperatures and pressures

Josef Sedlbauer ^a, John P. O'Connell ^b, Robert H. Wood ^{c,*}

^a Department of Chemistry, Technical University Liberec, Hálkova 6, 461 17 Liberec, Czech Republic

^b Department of Chemical Engineering, University of Virginia, Charlottesville, VA 22903, USA

^c Department of Chemistry and Biochemistry, and Center for Molecular and Engineering Thermodynamics, University of Delaware, Newark, DE 19716, USA

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Abstract

A new expression for partial molar volumes of aqueous solutes at infinite dilution has been developed in an empirical form based on Fluctuation Solution Theory for use over wide ranges of temperature and pressure. The solvent density and compressibility characterize the solvent properties, providing a much better description, especially in the critical region, than do models based on the solvent dielectric constant. The formulation has been integrated and differentiated to obtain analytic expressions for the Gibbs energy of hydration and Henry's constant, as well as the infinite dilution partial molar enthalpy and heat capacity of hydration at supercritical temperatures. For partial molar heat capacities at subcritical temperatures, an additional temperature-dependent function is used. Using newly established comprehensive databases of experimental V_2^0 and $C_{p,2}^0$ for nonelectrolytes and 1–1 electrolytes, supplemented with smaller databases for $\Delta_{\text{hyd}} H_2^0$ and $\Delta_{\text{hyd}} G_2^0$ for nonelectrolytes and κ_2^0 for electrolytes, it is shown that accurate correlations of all available data are obtained with the new model. For nonelectrolytes, the accuracy of predictions for all hydration and derivative properties at densities greater than 250 kg m^{-3} and at temperatures from ambient to over 700 K using only data at 298 K is almost as good as fitting the model's five parameters to all the data. For 1–1 electrolytes, predictions of $C_{p,2}^0$ near the critical temperature from V_2^0 near the critical temperature are satisfactory for NaCl(aq). © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The accurate description of chemical equilibria in aqueous solutions is crucial for understanding industrial and natural processes. In many applications, both chemical engineering and geochemical, these processes occur at elevated temperatures and pressures, where little or no experimental information is available. Under such

* Corresponding author. Fax: +1-302-831-6335; E-mail: rwood@udel.edu

circumstances reliable correlative and predictive models are needed. To obtain the desired dilute solution properties for phase equilibria, volumes and energies, the most direct route is from infinite dilution properties (with extended Debye–Hückel corrections for electrolytes), i.e., from values of chemical potential in a reference state, partial molar enthalpy and heat capacity as well as an appropriate equation of state. Fluctuation Solution Theory (Mansoori and Matteoli, 1990) suggests that a formulation of the equation of state be based on the partial molar volume which then can be integrated and/or differentiated to obtain non-ideal gas corrections to the desired thermodynamic properties.

Previous work from this laboratory has focused on experimental measurements of partial molar volumes and partial molar heat capacities of a series of model compounds (Majer et al., 1991; Hnedkovsky et al., 1996; Hnedkovsky and Wood, 1997, and references therein) at temperatures up to 725 K. With this new experimental data we hoped to be able to improve the existing equations of state or develop better ones.

Numerous correlating equations have been proposed for infinite dilution partial molar volumes, V_2^0 , and partial molar heat capacities, $C_{p,2}^0$ (see below and references given by Helgeson and Kirkham, 1976; Shock et al., 1989; Akinfiev, 1997). However, there seems to be only one predictive equation for use when few or no data are available (Shock et al., 1989; Shock and Helgeson, 1990; Shock et al., 1992; Amend and Helgeson, 1997; Shock et al., 1997; Sverjensky et al., 1997). The present paper presents a new empirical form for the infinite dilution partial molar volume based on Fluctuation Solution Theory that can be utilized to predict all of these properties for nonelectrolytes over wide ranges of conditions. For electrolytes the equation is promising and some predictions are possible. Another paper from this laboratory takes an alternate approach with an increase in accuracy at high temperatures and low densities but the equation is not appropriate for very polar substances and electrolytes (Plyasunov et al., 1999).

2. Experimental database ¹

Sixteen 1–1 electrolytes for which there are sufficient experimental results were included in this study. The source compounds were NaCl, KCl, NaOH, KOH, NaBr, CsCl, CsBr, HCl, LiBr, LiCl, KI, LiOH, HBr, HI, NH₄Cl, and NaI (ionic species involved in these compounds are Br[−], Cl[−], Cs⁺, I[−], K⁺, Li⁺, Na⁺, NH₄⁺, OH[−], and H⁺). The database on V_2^0 results includes about 1200 experimental points, the database on $C_{p,2}^0$ has about 300 points and the database on isothermal partial molar compressibilities, κ_2^0 , has some 70 points. The range of experimental results covers 273.15 K < T < 725 K and 0.1 MPa < P < 1000 MPa. For each data point, we estimated the uncertainty from the experimental method and concentration range of the measurements, the uncertainty of finite concentration values given in the original source, the extrapolation technique used, and the agreement with other estimates. Older results obtained by means of the empirical Mason equation were omitted from consideration. Experimental results on apparent molar heat capacities reported in the literature are of very diverse quality (see the discussion by Hepler and Hovey, 1996). The result is that our estimates of the errors are often somewhat larger than stated in the original sources.

Experimental results on several nonelectrolytes, CH₄, CO₂, H₂S, NH₃, H₃BO₃, Ar, and C₂H₄ were taken from three principal sources (Biggerstaff and Wood, 1988; Hnedkovsky and Wood, 1997; Hnedkovsky et al., 1996) from which there are about 300 experimental points on V_2^0 and about 75 on $C_{p,2}^0$. The temperature and pressure ranges of the data are 298.15 K < T < 716 K and 0.1 MPa < P < 35 MPa. In estimating the uncertainties we considered it necessary to note difficulties connected with results for the partial molar heat capacities at infinite dilution at supercritical temperatures (Hnedkovsky and Wood, 1997). The authors

¹ All experimental results treated in this study, including their estimated uncertainties, and also a complete list of references are available by sending an e-mail request to josef.sedlbauer@vslib.cz or may be downloaded directly from the Internet URL, <http://www.kfy.vslib.cz/aqueous/download.html>

approximate the values of $C_{p,2}^0$ by the experimental values of the apparent molar heat capacities $C_{p,\phi}$ at the lowest experimental molality, which is typically $m = 0.15\text{--}0.2 \text{ mol kg}^{-1}$. Additional uncertainty in $C_{p,2}^0$ introduced by this assumption may be estimated in the cases of ammonia and boric acid, for which there are experimental results at several molalities and extrapolations to infinite dilution may be performed. As reported by Hnedkovsky and Wood (1997), the slopes $(\partial C_{p,2}^0/\partial m)$ are qualitatively proportional to the slopes $(\partial C_{p,2}^0/\partial T)$ at the same state point, the latter quantity being very high in the vicinity of extrema of $C_{p,2}^0$. This observation and our experience with the attempts for extrapolation to infinite dilution for ammonia and boric acid show that while the values of partial molar heat capacities at lower and higher temperatures do not seem to be severely affected by extrapolation, in the region of extrema in heat capacity (e.g., at $P = 28 \text{ MPa}$ from $T \approx 662 \text{ K}$ to $T \approx 672 \text{ K}$), the effects of extrapolation may be very large (Hnedkovsky and Wood, 1997). Uncertainties were therefore estimated from these effects, experimental settings and problems with maintaining constant temperature in the course of measurements, as reported by Hnedkovsky and Wood (1997). We have also used in our calculations 21 experimental results on $\Delta_{\text{hyd}}H_2^0$ (Wagman et al., 1982; Dec and Gill, 1984, 1985; Olofsson et al., 1984; Naghibi et al., 1986) and about a hundred smoothed results for $\Delta_{\text{hyd}}G_2^0$ at P_{sat} from Wilhelm et al. (1977); Wagman et al. (1982); Fernandez-Prini and Crovetto (1989); Crovetto (1990) and Suleimenov and Krupp (1994).

3. Equation of state for partial molar volumes

3.1. Review of previous equations

Among the volumetric equations of the recent literature, the revised equation of Helgeson, Kirkham and Flowers (HKF) (Tanger and Helgeson, 1988; Shock and Helgeson, 1990; Shock et al., 1989, 1992) is the best known and most comprehensive. These equations and the literature results have been incorporated into an excellent software used widely by the chemical and geochemical communities: SUPCRT92 (Johnson et al., 1992). The HKF program includes predictive methods for both traditional aqueous inorganic nonelectrolyte and electrolyte systems and, more recently, predictions for aqueous metal complexes, hydroxide complexes and organic compounds (Sverjensky et al., 1997; Shock et al., 1997; Amend and Helgeson, 1997, respectively). The HKF equation was designed primarily for aqueous ions and some deficiencies connected with its general use for nonelectrolytes became apparent recently (Hnedkovsky et al., 1996; O'Connell et al., 1996) when it was tested with recent high temperature–high pressure experimental results on aqueous solutions of nonelectrolytes (Biggerstaff and Wood, 1988; Hnedkovsky et al., 1996).

In the HKF equation the partial molar volume at infinite dilution V_2^0 is divided into two parts. One part refers to internal or nonsolvation volume, which is solute-specific, while the other part is a solvent-specific solvation contribution, based on the Born equation (Helgeson and Kirkham, 1976). The current form of the equation is

$$V_2^0 = a_1 + a_2/(\psi + P) + a_3/(T - \theta) + a_4/\{(\psi + P)(T - \theta)\} - \omega/\varepsilon^2(\partial\varepsilon/\partial P)_T + (1 - \varepsilon - 1)(\partial\omega/\partial P)_T \quad (1)$$

where a_1 to a_4 are adjustable parameters, $\psi = 2600 \text{ bar}$, $\theta = 228 \text{ K}$, ε is the solvent dielectric constant and ω is the conventional Born coefficient, which for an ion is related to the crystallographic radius. A complex temperature and pressure dependence of ω with several coefficients adjusted to experimental results on NaCl(aq) was adopted by Shock et al. (1992). For nonelectrolyte solutes ω is an additional adjustable constant (Shock et al., 1989). This equation is not recommended for electrolytes near the critical point of water, so no predictive method exists for these conditions.

Simonson et al. (1994) found the following equation useful for aqueous NaCl solutions to 523 K,

$$V_2^0 = c_1 + \kappa_0\{c_2 + c_3/(T - 227) + c_4T\} \quad (2)$$

where c_1 to c_4 are adjustable parameters and $\kappa_0 = -(1/V_0) (\partial V_0/\partial P)_T$ is the solvent compressibility so we tried it as a correlating equation for electrolytes. There is also the equation of Plyasunov (1993) for electrolytes which is based on the combined concepts of the “total equilibrium constant” (Marshall, 1970) resulting in a compressibility term, and a nonsolvation contribution which is close to the one accepted in the HKF model,

$$V_2^0 = V_i - (n_1 + n_2 T) \kappa_0 RT - aR / \{ (T - \theta)(P + \phi) \} \quad (3)$$

where $\phi = 2500$ bar, $\theta = 228$ K, V_i , n_1 , n_2 and a are adjustable parameters. This new equation was not recommended below 400 kg m^{-3} .

A different approach, based on the Fluctuation Solution Theory (Kirkwood and Buff, 1951; O’Connell, 1971, 1981, 1990, 1994, 1995) has been adopted by O’Connell et al. (1996) for nonelectrolyte solutes. The result is a correlation which is a function of $\kappa_0 RT$, the partial molar volume of a point mass (Neff and McQuarrie, 1973; Ben Naim, 1987; Wood et al., 1990). The quantity $V_2^0/(\kappa_0 RT)$ is closely related to a generalization of the Krichevskii parameter and equals $(1 - C_{21})$, where C_{21} is the dimensionless solute–solvent infinite dilution direct correlation function integral which shows only weak divergence at the solvent critical point (see, for example, Levelt Sengers, 1991).

Use of $V_2^0/(\kappa_0 RT)$ formed the basis of successful methods for estimating partial molar volumes of gases at infinite dilution in solvents (Brelvi and O’Connell, 1972) and for aqueous salts (Cooney and O’Connell, 1987). The most recent equation for aqueous nonelectrolytes is the equation of O’Connell et al. (1996) which divided V_2^0 into two parts: one was for a reference solute (water) and the other for the change in the volume when a water molecule is replaced by the solute. In the equation of O’Connell et al. (1996) the variation of $V_2^0/(\kappa_0 RT)$ was principally described by a function of the density of the solvent without any explicit pressure or temperature dependence,

$$V_2^0 = V_0 + (a + b(\exp[\vartheta\rho_0] - 1))\kappa_0 RT\rho_0 \quad (4)$$

where V_0 is the molar volume of pure water, a and b are parameters, and $\vartheta = 0.005 \text{ m}^3 \text{ kg}^{-1}$ is the same for all aqueous solutes. This form was very similar to that of Cooney and O’Connell (1987) for electrolytes,

$$V_2^0 = (a(1.0 - 7.0 \cdot 10^{-9} \exp[\chi/T])\exp[\xi\rho_0] + b)\kappa_0 RT \quad (5)$$

also with two adjustable parameters a and b and general constants $\chi = 4500$ K and $\xi = 0.00588 \text{ m}^3 \text{ kg}^{-1}$. O’Connell et al. (1996) found that Eq. (4) affords better accuracy than Eq. (1) for the description of aqueous nonelectrolytes over a wide range of temperatures and pressures. Using water as a reference is consistent with the decomposition of solute properties into local and long-range effects, as proposed by Chialvo and Cummings (1994).

3.2. Development of a new model

Theoretical (Wheeler, 1972; Levelt Sengers, 1991) and practical evidence for nonelectrolytes (Hnedkovsky et al., 1996; O’Connell et al., 1996) and electrolytes (Wood et al., 1994) suggest that the behavior of partial molar volumes in the vicinity of the critical point of pure solvent is determined by solute compressibility rather than solvent dielectric constant as implied by Eq. (1). In particular, the Born equation gives unphysical first coordination shells near the critical point of water (fifty or more water molecules in the first solvation shell) because of its neglect of changes of solvent compressibility near the ion (Wood et al., 1994). As a result, we focused on developing a model for electrolytes and nonelectrolytes by combining successful features of Eqs. (2)–(5) which are based on $\kappa_0 RT$.

As a starting point, Eq. (4) implies that a plot $(V_2^0 - V_0)/(\rho_0 \kappa_0 RT)$ vs. $\exp[\vartheta\rho_0]$ would be linear for all nonelectrolyte solutes/individual ions. Figs. 1–3 show such plots for methane as a typical nonelectrolyte, boric acid as a strongly polar nonelectrolyte and NaCl as an electrolyte. The range of experimental conditions for both nonelectrolytes covers $303 \text{ K} < T < 705 \text{ K}$ and $28 \text{ MPa} < P < 35 \text{ MPa}$ (Hnedkovsky et al., 1996), and 273.15

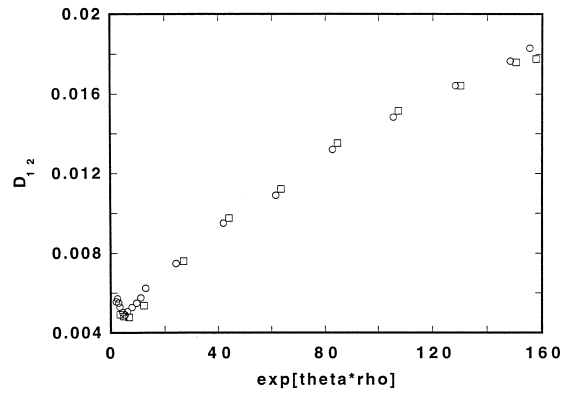


Fig. 1. $D_{12} = (V_2^0 - V_0)/(\rho_0 \kappa_0 RT)$ vs. $\exp[\vartheta \rho_0]$ for $\text{CH}_4(\text{aq})$ at $28 \text{ MPa} < P < 35 \text{ MPa}$ and $303 \text{ K} < T < 705 \text{ K}$. $\circ \circ \circ$ — $P = 28 \text{ MPa}$, $\square \square \square$ — $P = 35 \text{ MPa}$.

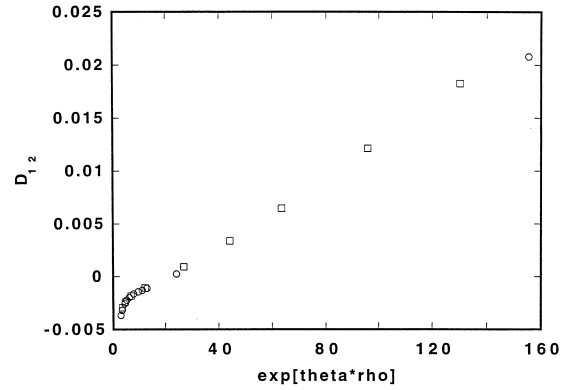


Fig. 2. $D_{12} = (V_2^0 - V_0)/(\rho_0 \kappa_0 RT)$ vs. $\exp[\vartheta \rho_0]$ for $\text{H}_3\text{BO}_3(\text{aq})$ at $28 \text{ MPa} < P < 35 \text{ MPa}$ and $303 \text{ K} < T < 705 \text{ K}$. $\circ \circ \circ$ — $P = 28 \text{ MPa}$, $\square \square \square$ — $P = 35 \text{ MPa}$.

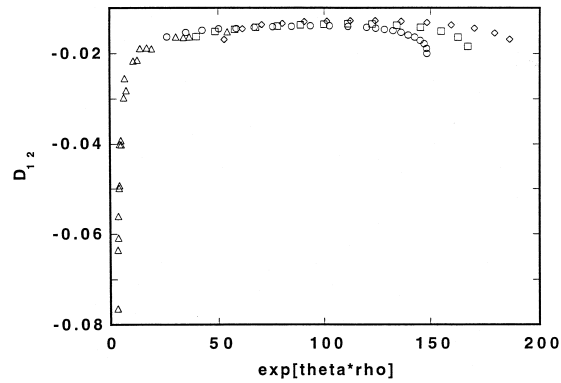


Fig. 3. $D_{12} = (V_2^0 - 2V_0)/(\rho_0 \kappa_0 RT)$ vs. $\exp[\vartheta \rho_0]$ for $\text{NaCl}(\text{aq})$ at $0.1 \text{ MPa} < P < 100 \text{ MPa}$ and $273.15 \text{ K} < T < 725 \text{ K}$. $\circ \circ \circ$ — $P = \text{saturation}$, $\square \square \square$ — $P = 50 \text{ MPa}$, $\diamond \diamond \diamond$ — $P = 100 \text{ MPa}$, $\triangle \triangle \triangle$ — $28 \text{ MPa} < P < 38 \text{ MPa}$.

$K < T < 725$ K, 0.1 MPa $< P < 100$ MPa for NaCl, for which we used the data of Archer (1992) at saturation pressure and at $P = 50$ MPa, 100 MPa, and the results of Majer et al. (1991) extrapolated to infinite dilution by Sedlbauer et al. (1998) at 550 K $< T < 725$ K and $P = 28$ MPa, 33 MPa, and 38 MPa. The figures show no apparent pressure or temperature dependence in the intermediate density range and the linear variation of Eq. (4) is appropriate. On the other hand, at low and high densities, especially for NaCl(aq), linearity cannot be assumed.

We have been able to describe the low-temperature (high density) extrema found in the experimental results for polar and ionic solutes with a term involving temperature with an additional adjustable parameter, c , and a universal coefficient, θ , found by simultaneous fit to all of the partial molar volume results. The low-density (high temperature) behavior can be correlated by the addition of another exponential function in density with an adjustable parameter, δ , and universal coefficient, λ . Finally, to improve the description of the infinite dilution partial molar compressibilities of aqueous ions, we have allowed the reference volume term to be adjusted with a single parameter, d .

Our final equation of state for the partial molar volume of a single ion or solute is

$$V_2^0 = \kappa_0 RT + d(V_0 - \kappa_0 RT) + (a + c \exp[\theta/T] + b(\exp[\vartheta\rho_0] - 1) + \delta(\exp[\lambda\rho_0] - 1))\kappa_0 RT\rho_0 \quad (6)$$

where V_0 , ρ_0 and κ_0 are molar volume, specific density and compressibility of pure water, respectively, $\vartheta = 0.005$ m³ kg⁻¹, $\lambda = -0.01$ m³ kg⁻¹ and $\theta = 1500$ K are valid for all solutes, a , b , c and d are adjustable parameters for each solute. An independent estimate of the δ parameter can be used without substantial loss of accuracy. The estimates are $\delta = 0.35a$ for aqueous nonelectrolytes, $\delta = 0$ m³ kg⁻¹ for aqueous cations, and $\delta = -0.645$ m³ kg⁻¹ for aqueous anions. In applying Eq. (6) to the individual ions it is necessary to make an arbitrary choice of V_2^0 for one ion. While it is common to set $V_2^0[\text{H}^+] = 0$, the form of Eq. (6) with its reference state term suggests we choose all adjustable parameters of H^+ to zero, yielding $V_2^0[\text{H}^+] = \kappa_0 RT$. A small formal change in Eq. (6) is needed in order to achieve a conventional scale $V_2^0[\text{H}^+] = 0$; this is further discussed in Appendix A and is implemented in equations given there. The hydrogen convention also leads to the unsymmetrical choice of δ for cations and anions.

As we shall demonstrate below, Eq. (6) provides a generally better description of infinite dilution partial molar volumes than any other equation for both nonelectrolytes and electrolytes. The improvement is very significant in the near-critical region. Further, description of experimental results on infinite dilution partial molar compressibilities at low temperatures of aqueous ions is almost within the limits of experimental error. The equation yields the correct ideal gas limit as density approaches zero, although it does not fully reflect rigorous deviations from ideal gas behavior at low densities because of its inappropriate description of temperature dependence of the second virial coefficient.

3.3. Correlation of partial molar volume data

The first test of the equation is whether it gives an adequate fit to the experimental data. We compared the new equation of state, Eq. (6), with the other equations by performing regressions with weighted least-squares to find all adjustable parameters. These are listed in Tables 1 and 2. The weights were equal to $1/\sigma^2$, where σ is the estimated uncertainty of a given experimental result. Table 1 summarizes the results for aqueous nonelectrolytes from Eqs. (1), (4) and Eq. (6) which are the only ones applicable to nonelectrolyte solutes. The results of the overall electrolyte fits are given in Table 2. We tried Eqs. (2) and (3) even though they were not recommended in all of this region to see if they fit the new data. Ionic additivity was enforced in the case of aqueous electrolytes, with the parameters of hydrogen ion set to zero in all equations. In addition to the average value of Δ/σ , where Δ is the absolute value of the difference between calculated and experimental V_2^0 , Table 2 also gives the unweighted standard deviation of the fit. This value, although not used as a criterion of

Table 1

Test of equations of state for correlating partial molar volumes of aqueous nonelectrolytes. Eq. (6) was also fitted simultaneously to partial molar volumes, hydration Gibbs energies, hydration enthalpies and partial molar heat capacities. The results of this fit are given in the last column of the table.

Substance	$\langle \Delta/\sigma \rangle_{av}^a$			
	Eq. (1) (HKF)	Eq. (4) (OSW)	Eq. (6) (this work)	Eq. (6) (all properties) ^b
CH ₄	10.0	1.6	1.0	0.9
CO ₂	9.8	1.6	0.6	0.6
H ₂ S	7.8	1.6	0.6	0.6
NH ₃	6.5	1.6	0.6	1.0
H ₃ BO ₃	7.4	4.5	2.1	1.9
C ₂ H ₄	4.1	0.6	0.3	0.8
Ar	5.1	1.0	0.7	1.3

^aThe table gives $\langle \Delta/\sigma \rangle_{av}$, the average value of Δ/σ , where Δ is the absolute value of the difference between experimental and calculated V_2^0 and σ is the estimated uncertainty of a given experimental point.

^bSimultaneous fit of Eqs. (6), (A2), (A4) and (A5) to the V_2^0 , $\Delta_{hyd}G_2^0$, $\Delta_{hyd}H_2^0$, and $\Delta_{hyd}C_{p,2}^0$ data.

adjustment of the parameters, provides a good indication of error distribution. It is mainly influenced by results at very high temperatures, where both the absolute values of V_2^0 and their uncertainties are very high. The same impression of error distribution can be obtained from Fig. 4, which shows the performance of several equations at temperatures $T > 600$ K for NaCl(aq). The only equation which is able to account for the behavior of experimental results on V_2^0 at these conditions both qualitatively and quantitatively is Eq. (6). We note that Eq. (1) is not recommended for use in this region (Johnson et al., 1992) and not surprisingly fails to describe the results at $T > 625$ K. Our conclusion, based on Tables 1 and 2, is that using the new experimental data we have developed an equation which is generally more accurate in describing all of the experimental results than the previous equations. We found that: (a) the average value of Δ/σ is the lowest for Eq. (6) in all cases, which indicates very good description of experimental results at all experimental conditions, and (b) the value of the unweighted standard deviation is the lowest for Eq. (6) in all cases, which indicates the best description of the experimental results at near-critical and over-critical regions. The unweighted standard deviation is especially important for comparisons of aqueous electrolytes, since most of the experimental results were measured at low temperatures, which are in absolute values several orders of magnitude smaller than experimental results at high

Table 2

Test of equations of state for correlating partial molar volumes of aqueous ions. Eq. (6) was also fitted simultaneously to partial molar volumes, partial molar heat capacities and partial molar compressibilities. The result of this fit is given in the last column of the table

	$\langle \Delta/\sigma \rangle_{av}^a$					
	Eq. (1) ^{b,c} (HKF)	Eq. (2) (Simonson)	Eq. (3) (Plyasunov)	Eq. (5) (Cooney)	Eq. (6) (this work)	Eq. (6) (all properties) ^d
$\langle \Delta/\sigma \rangle_{av}$	0.44	0.62	0.45	1.20	0.44	0.69
σ_u^e (cm ³ mol ⁻¹)		397	254	144	118	

^aThe table gives $\langle \Delta/\sigma \rangle_{av}$, the average value of Δ/σ , where Δ is the absolute value of the difference between experimental and calculated V_2^0 and σ is the estimated uncertainty of a given experimental point.

^bValues of ω calculated from ionic radii.

^cNo experimental results at $T > 625$ K are included in the regression because this is the stated limit of applicability of the equation.

^dSimultaneous fit of Eqs. (6), (A5) and (12) to the V_2^0 , $\Delta_{hyd}C_{p,2}^0$, and κ_2^0 data.

^e σ_u is the unweighted standard deviation of the fit so it mainly reflects deviations at high temperatures.

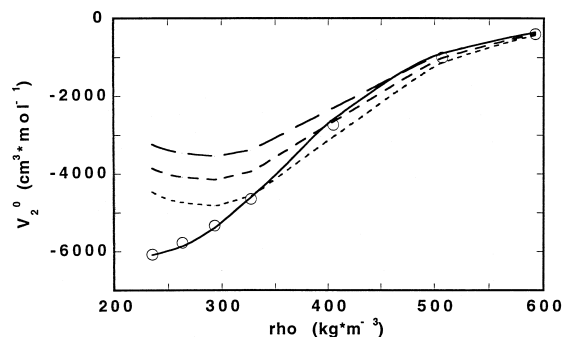


Fig. 4. Infinite dilution partial molar volume of NaCl(aq) vs. water density at $P = 38$ MPa and $600 \text{ K} < T < 725 \text{ K}$. $\circ \circ \circ$ — extrapolations to infinite dilution of Sedlbauer et al. (1998) using the experimental data of Majer et al. (1991), — — — Eq. (6), — — — Eq. (2), — — — Eq. (3), ... — Eq. (5). The equations were fit to the experimental V_2^0 over the whole temperature range from 273.15 K.

temperatures. Because of this, the description of low-temperature results makes the major contribution to the average value of Δ/σ , but does not dominate the value of the unweighted standard deviation.

4. Equation of state for other partial molar properties

4.1. Equations

The correlation of the partial molar volumes proposed in the previous section is able to describe experimental volumetric results even at densities below the critical density and has the correct ideal gas limit at $\rho_0 \rightarrow 0$ although not the correct temperature dependence of the second virial coefficient. If the expression is reasonably accurate, integration and differentiation of this function can yield equations for all thermodynamic properties relative to the ideal gas. The full expressions for infinite dilution partial molar Gibbs energy, entropy, enthalpy and isobaric heat capacity of hydration from Eq. (6) are given in Appendix A. We list here only the general thermodynamic relations and the equation for the fugacity coefficient.

The solute infinite dilution fugacity coefficient is

$$\begin{aligned} \ln[\varphi_2^0] = & \int_0^{\rho_0} \left(V_2^0 / (\kappa_0 RT) - 1 \right) \frac{d\rho_0}{\rho_0} - \ln[PM_0 / (\rho_0 RT)] = \ln[\rho_0 RT / (PM_0)] \\ & + d \left(\ln[\varphi_0] - \ln[\rho_0 \cdot RT / (PM_{H_2O})] \right) + (a + c \exp[\theta/T] - b - \delta) \rho_0 + b / \vartheta (\exp[\vartheta \rho_0] - 1) \\ & + \delta / \lambda (\exp[\lambda \rho_0] - 1) \end{aligned} \quad (7)$$

where φ_0 is the fugacity coefficient and M_0 the molar mass of water. The partial molar Gibbs energy of hydration from the ideal gas standard state (hypothetical 0.1 MPa) to the hypothetical 1 mol kg^{-1} standard state at pressure P may be calculated directly from Eq. (7),

$$\Delta_{\text{hyd}} G_2^0 = RT (\ln[\varphi_2^0 P / P^0] + \ln[M_0 m^0]) \quad (8)$$

where $P^0 = 0.1$ MPa and $m^0 = 1$ mol kg^{-1} . Note that $\Delta_{\text{hyd}} G_2^0$ is a function of P and T since the hypothetical 1m standard state pressure is not 0.1 MPa. Differentiating Eq. (8) with respect to temperature or pressure leads

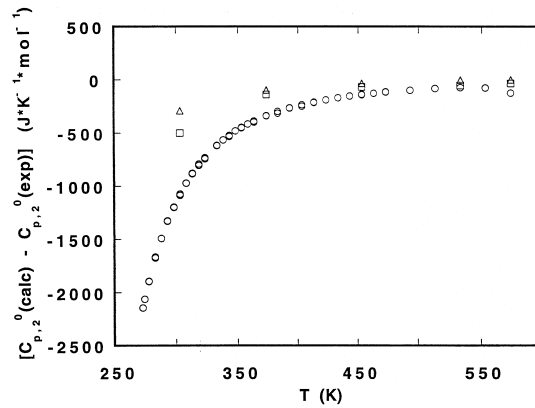


Fig. 5. Deviations from experiment of $C_{p,2}^0$ below water's critical predicted from Eq. (A5) with parameters from fitting the partial molar volume data to Eq. (6). ○○○ — NaCl(aq), □□□ — CH₄(aq), △△△ — NH₃(aq).

to equations for the infinite dilution partial molar entropy, hydration enthalpy, hydration heat capacity and partial molar isothermal compressibility,

$$\Delta_{\text{hyd}} S_2^0 = -\left(\partial \Delta_{\text{hyd}} G_2^0 / \partial T\right)_p \quad (9)$$

$$\Delta_{\text{hyd}} H_2^0 = \Delta_{\text{hyd}} G_2^0 + T \Delta_{\text{hyd}} S_2^0 \quad (10)$$

$$\Delta_{\text{hyd}} C_{p,2}^0 = -T \left(\partial^2 \Delta_{\text{hyd}} G_2^0 / \partial T^2 \right)_p \quad (11)$$

$$\kappa_2^0 = -\left(\partial V_2^0 / \partial P\right)_T. \quad (12)$$

Full expressions for these properties from Eq. (6) are given in the Appendix A.

As will be seen below when these equations were tested it was found that Eq. (11) was reasonably accurate for both nonelectrolytes and electrolytes when used above the critical point but not accurate below the critical point. This failure should probably be ascribed to the expected inadequacy of our simple volumetric model when used in the two phase region. However, comparisons of calculated $C_{p,2}^0$ values with data (see Fig. 5) showed

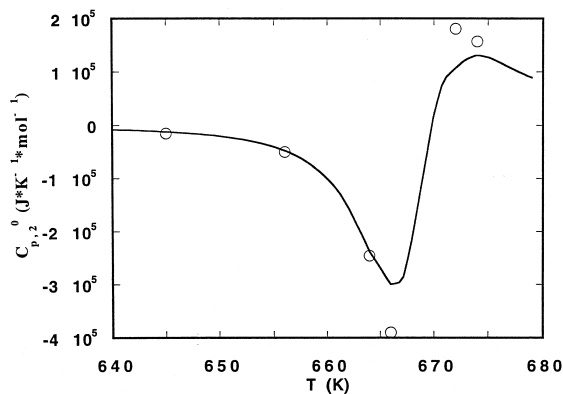


Fig. 6. Infinite dilution partial molar heat capacities for NaCl(aq) at $P = 28$ MPa and $640 \text{ K} < T < 680 \text{ K}$. ○○○ — experimental results of Carter (1992), provisionally corrected for ionic association, —, predictions at $T \geq T_c$ from Eqs. (A5) and (A12) with parameters obtained from volumetric experiments.

Table 3
Parameters of Eqs. (6) and (13) for aqueous nonelectrolytes

Solute	(10 ³ <i>a</i>)/ (m ³ kg ^{−1} mol ^{−1})	(10 ⁴ <i>b</i>)/ (m ³ kg ^{−1} mol ^{−1})	(10 ⁵ <i>c</i>)/ (m ³ kg ^{−1} mol ^{−1})	<i>d</i>	<i>e</i> /(J K ^{−2} mol ^{−1})
CH ₄	4.21345	1.76721	−0.69122	0.41610	−0.13768
CO ₂	3.39209	1.48009	−1.38796	0.55582	−0.26387
H ₂ S	1.99299	1.54007	−1.91120	0.59693	−0.38816
NH ₃	1.32548	0.49738	−0.80535	0.88078	−0.18104
H ₃ BO ₃	−0.61428	0.38857	0.86324	1.82268	0.12002
C ₂ H ₄	3.80910	2.16619	−1.63335	0.58783	−0.33402
Ar	4.96236	1.30750	0.20640	0.33230	0.04698

consistent differences below the critical point that depended only on temperature. A function that describes these differences for nonelectrolytes is

$$C_{p,2}^{\text{corr}} = e(T - T_c)^2 / - (T - \Theta) \text{ at } T < T_c$$

$$C_{p,2}^{\text{corr}} = 0 \text{ at } T \geq T_c, \quad (13)$$

where a new parameter for each solute, *e*, has been introduced and $\Theta = 228$ K is a universal characteristic temperature (Helgeson and Kirkham, 1976). Using this corrected $C_{p,2}^0$ for nonelectrolytes with reference values of $\Delta_{\text{hyd}}G_2^0$, $\Delta_{\text{hyd}}S_2^0$, $\Delta_{\text{hyd}}H_2^0$, and $\Delta_{\text{hyd}}C_{p,2}^0$ above the critical temperature (predicted from integrating Eq. (6)) allows equations to be derived for $\Delta_{\text{hyd}}G_2^0$, $\Delta_{\text{hyd}}H_2^0$, $\Delta_{\text{hyd}}S_2^0$ and $\Delta_{\text{hyd}}C_{p,2}^0$ which are valid under all conditions (see Appendix A Eqs. (A2), (A3), (A4), (A5), (A6), (A7), (A8), (A9), (A10) and (A11)).

For electrolytes a different correction has to be used. Fig. 6 shows predictions of partial molar heat capacities of NaCl(aq) from volumetric measurements using Eq. (2) compared with experimental heat capacities. As with nonelectrolytes the predictions are very close to the experimental measurements at near-critical and supercritical temperatures for NaCl(aq), for which there are a few experimental results (Carter, 1992). The correction for electrolytes below the critical temperature is somewhat different in shape and of larger magnitude than for nonelectrolytes (see Fig. 5 for comparison), requiring two new parameters for each ion, *e* and *g*

$$C_{p,2}^{\text{corr}} = (T - T_c)(e/(T - \Theta) + g) \text{ at } T < T_c$$

$$C_{p,2}^{\text{corr}} = 0 \text{ at } T \geq T_c. \quad (14)$$

Unlike the nonelectrolytes, for electrolytes the values of $\Delta_{\text{hyd}}G_2^0$, $\Delta_{\text{hyd}}S_2^0$ and $\Delta_{\text{hyd}}H_2^0$ calculated from Eqs. (8)–(10) were found inaccurate by a constant. This is presumably due to the very strong hydration of electrolytes even at low densities which is not accurately described by Eq. (6) for V_2^0 so the integral in Eq. (7)

Table 4
Parameters of Eqs. (6) and (14) for aqueous ions

Ion	(<i>a</i>)/ (m ³ kg ^{−1} mol ^{−1})	(10 ⁴ <i>b</i>)/ (m ³ kg ^{−1} mol ^{−1})	(10 ⁵ <i>c</i>)/ (m ³ kg ^{−1} mol ^{−1})	<i>d</i>	(10 ^{−2} <i>e</i>)/ (J K ^{−1} mol ^{−1})	(<i>g</i>)/ (J K ^{−2} mol ^{−1})
H ⁺	0	0	0	0	0	0
Li ⁺	−0.0071394	1.84661	−0.82402	−1.27172	0.97971	−0.51155
Na ⁺	−0.0071136	2.31260	−3.02894	−1.52032	2.94922	−1.14565
K ⁺	−0.0075291	2.18516	−2.57981	−0.80917	2.49692	−0.79125
Cs ⁺	−0.0058022	1.90946	−2.55954	0.06822	2.52611	−0.69451
NH ₄ ⁺	−0.0027026	1.08730	−0.95674	0.28730	0.99682	−0.36821
Cl [−]	−0.656755	−0.86168	−0.30967	2.56146	0.16432	0.26063
Br [−]	−0.654326	−1.20912	−0.84933	3.19590	0.64270	0.11044
I [−]	−0.650966	−1.56554	−1.43758	4.05431	1.04893	0.09678
OH [−]	−0.661106	0.50154	−1.88666	0.40718	1.88351	−0.59552

Table 5

Predictions of partial molar volumes of $\text{NH}_3(\text{aq})$ at $P = 28$ MPa using Eq. (6). Comparison with experimental results (Hnedkovsky et al., 1996)

$(T)/(\text{K})$	$(\rho_0)/(\text{kg m}^{-3})$	$(V_2^0(\text{exp}))/(\text{cm}^3 \text{mol}^{-1})$	$(V_2^0(\text{calculated 705}))/(\text{cm}^3 \text{mol}^{-1})^a$	$< \Delta/\sigma >_{\text{av}}^{\text{a,c}}$	$(V_2^0(\text{calculated 298}))/(\text{cm}^3 \text{mol}^{-1})^b$	$< \Delta/\sigma >_{\text{av}}^{\text{b,c}}$
298.15	1010	24	23.6	−0.82	24.2	0.37
623.15	637	63	64	0.82	61	−1.08
653.08	513	134	142	1.70	132	−0.37
657.11	483	165	184	3.14	170	0.90
660.28	453	220	243	2.68	223	0.40
663.38	415	314	343	2.25	313	−0.08
666.19	369	458	471	0.66	428	−1.56
668.22	331	542	535	−0.31	484	−2.43
670.10	299	552	517	−1.44	468	−3.40
674.59	246	434	390	−2.38	356	−4.23
678.85	217	347	315	−2.27	290	−4.08
685.41	189	285	261	−2.23	243	−3.97
705.28	150	221	218	−0.56	206	−2.32

^aCalculated with parameters from Table 3 obtained from fitting all experimental data at $283 < T < 705$ K.

^bCalculated with parameters obtained from experimental V_2^0 , $\Delta_{\text{hyd}}G_2^0$, $\Delta_{\text{hyd}}H_2^0$, and $C_{\text{p},2}^0$ at 298.15 K and 0.1 MPa.

^cAverage value of Δ/σ where Δ is the absolute value of the difference between experimental and calculated V_2^0 , and σ is the estimated uncertainty of a given point.

is not accurate. The result for electrolytes is that we have good equations for V_2^0 and $\Delta_{\text{hyd}}C_{\text{p},2}^0$ (Eqs. (6) and (A5)) but no reference values of $\Delta_{\text{hyd}}G_2^0$, $\Delta_{\text{hyd}}S_2^0$ and $\Delta_{\text{hyd}}H_2^0$ above the critical temperature from Eqs. (A2), (A3) and (A4). Therefore we use experimentally determined reference values at some state point, e.g., at 298.15

Table 6

Predictions of partial molar heat capacities of $\text{NH}_3(\text{aq})$ at $P = 28$ MPa using Eq. (A12). Comparison with experimental results (Hnedkovsky et al., 1996)

$(T)/(\text{K})$	$(C_{\text{p},2}^0(\text{experimental}))/(\text{kJ mol}^{-1})$	$(C_{\text{p},2}^0(\text{calculated 705}))/(\text{kJ mol}^{-1})^a$	$< \Delta/\sigma >_{\text{av}}^{\text{a,c}}$	$(C_{\text{p},2}^0(\text{calculated 298}))/(\text{kJ mol}^{-1})^b$	$< \Delta/\sigma >_{\text{av}}^{\text{b,c}}$
303.79	78	78	0.01	73	−2.11
373.56	88	89	0.60	97	3.61
448.44	108	106	−0.40	107	−0.27
523.31	144	127	−2.36	121	−3.20
576.10	191	165	−2.79	154	−3.93
623.23	386	341	−0.77	313	−1.25
648.75	1390	1246	−0.69	1129	−1.25
661.95	6432	5926	−0.13	5306	−0.29
665.95	5764	5304	−0.12	4710	−0.28
669.15	−3468	−6283	−0.93	−5632	−0.71
671.15	−6639	−8205	−0.39	−7315	−0.17
674.05	−4909	−5441	−0.15	−4828	0.02
679.15	−2390	−2200	0.40	−1935	0.95
688.65	−905	−592	1.73	−508	2.19
703.75	−212	−119	2.18	−93	2.85

^aCalculated with parameters from Table 3 obtained from fitting all experimental data at $283 < T < 705$ K.

^bCalculated with parameters obtained from experimental V_2^0 , $\Delta_{\text{hyd}}G_2^0$, $\Delta_{\text{hyd}}H_2^0$, and $C_{\text{p},2}^0$ at 298.15 K and 0.1 MPa.

^cAverage value of Δ/σ where Δ is the absolute value of the difference between experimental and calculated $C_{\text{p},2}^0$, and σ is the estimated uncertainty of a given point.

Table 7

Predictions of partial molar heat capacities of $\text{H}_3\text{BO}_3(\text{aq})$ at $P = 28 \text{ MPa}$ using Eq. (A12). Comparison with experimental results (Hnedkovsky et al., 1996)

$(T)/(\text{K})$	$(C_{p,2}^0(\text{experimental}))/(\text{kJ mol}^{-1})$	$(C_{p,2}^0(\text{calculated 705}))/(\text{kJ mol}^{-1})^a$	$< \Delta/\sigma >^{a,c}$	$(C_{p,2}^0(\text{calculated 298}))/(\text{kJ mol}^{-1})^b$	$< \Delta/\sigma >^{b,c}$
303.48	121.2	117.9	−0.90	118.5	−0.73
373.56	152	170	3.94	183	6.70
448.44	159	165	1.25	162	0.73
523.31	159	149	−1.18	135	−3.03
576.11	130	118	−1.85	92	−5.85
623.22	−54	−64	−1.16	−140	−10.50
648.75	−1118	−1301	−1.09	−1659	−3.22
661.95	−8511	−11246	−0.60	−13176	−1.02
665.95	−14570	−16488	−0.30	−18269	−0.58
669.15	−2477	5521	2.91	7761	3.73
671.15	7711	13942	1.44	16875	2.12
674.05	9580	11971	0.49	14007	0.91
679.15	6378	6178	−0.16	7061	0.53
688.65	2666	2423	−0.45	2714	0.09
703.75	1141	1020	−0.53	1121	−0.09

^aCalculated with parameters from Table 3 obtained from fitting all experimental data at $273 < 705 \text{ K}$.

^bCalculated with parameters obtained from experimental V_2^0 , $\Delta_{\text{hyd}}G_2^0$, $\Delta_{\text{hyd}}H_2^0$, and $C_{p,2}^0$ at 298.15 K and 0.1 MPa .

^cAverage value of Δ/σ where Δ is the absolute value of the difference between experimental and calculated $C_{p,2}^0$, and σ is the estimated uncertainty of a given point.

K and 0.1 MPa for the resulting equations which are given in Appendix A (Eqs. (A14a), (A14b), (A15a), (A15b) and (A16)).

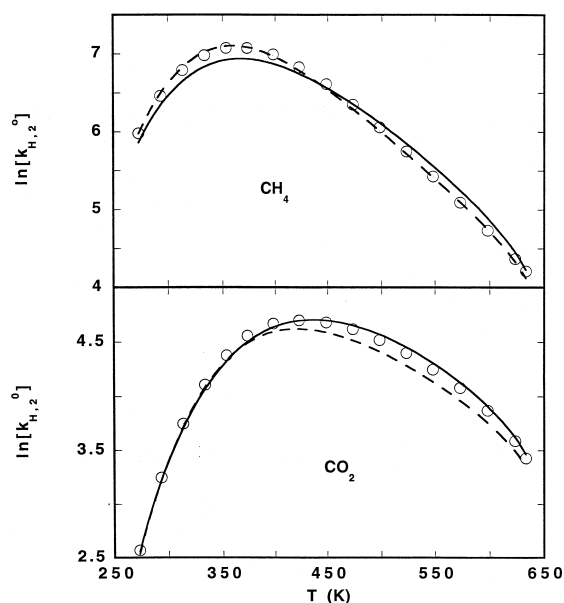


Fig. 7. Predicted Henry's constants at saturation pressure for $\text{CH}_4(\text{aq})$ and $\text{CO}_2(\text{aq})$ in water from Eq. (A6). $\circ\circ\circ$ — smoothed experimental data (Fernandez-Prini and Crovetto (1989) for $\text{CH}_4(\text{aq})$ and Crovetto (1990) for $\text{CO}_2(\text{aq})$), — — — Eq. (A6) with parameters from Table 3 obtained from fitting all experimental data, — — — Eq. (A6) with parameters from data only at $T = 298.15 \text{ K}$ and $P = 0.1 \text{ MPa}$.

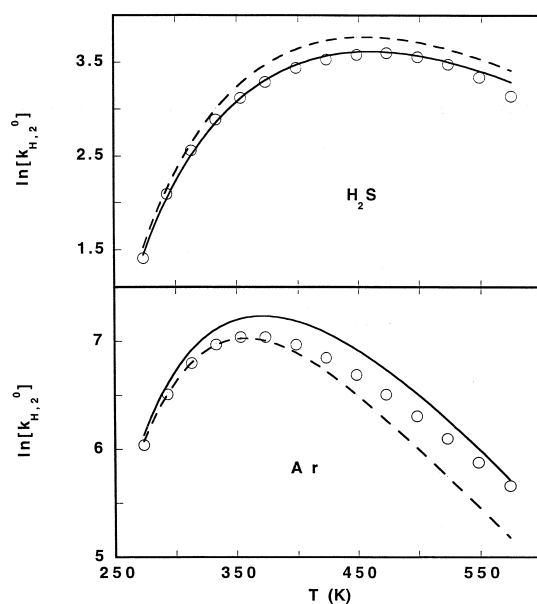


Fig. 8. Predicted Henry's constants at saturation pressure for $\text{H}_2\text{S}(\text{aq})$ and $\text{Ar}(\text{aq})$ in water from Eq. (A6). $\circ\circ\circ$ — smoothed experimental data (Suleimenov and Krupp (1994) for $\text{H}_2\text{S}(\text{aq})$ and Fernandez-Prini and Crovetto (1989) for $\text{Ar}(\text{aq})$), — — — Eq. (A6) with parameters from Table 3 obtained from fitting all experimental data, - - - Eq. (A6) with parameters from data only at $T = 298.15$ K and $P = 0.1$ MPa.

4.2. Parameter regressions

The parameters of Eq. (6) were retrieved along with parameter e of Eq. (13) from simultaneous regressions of V_2^0 , $C_{p,2}^0$, $\Delta_{\text{hyd}}G_2^0$ and $\Delta_{\text{hyd}}H_2^0$ in case of nonelectrolytes and parameters of Eq. (6) and e and g of Eq. (14) were found from regressions of V_2^0 , $C_{p,2}^0$ and κ_2^0 for the ions. Final parameters are given in Tables 3 and 4. The weighted least-squares procedure was the same as described above for the partial molar volume regressions. The average values of Δ/σ for these overall fits are given in the last columns of Tables 1 and 2. There is relatively little change from the best fit to V_2^0 alone given in the next to last columns of the tables. As for the best fits, the average values of Δ/σ are close to unity for all solutes except boric acid, so the deviations are close to the limits of experimental error. Tables 5–7 show representative detailed comparison of V_2^0 and $C_{p,2}^0$ for ammonia and boric acid at 28 MPa. The agreement with experimental results is quite acceptable. The same can be concluded from Figs. 7 and 8, which show Henry's constants at saturation pressures from Eq. (6) for several solutes. The larger inaccuracy for argon is probably due to the fact that most experimental data for this solute are available at near-critical conditions, which has a negative effect on the description at lower temperatures. In any case, we have an equation capable of representing a variety of thermodynamic properties for all types of solutes.

5. Predictions

5.1. Nonelectrolytes

Next we give a preliminary exploration of predictions of properties of nonelectrolytes in regions far removed from the experimental data used to obtain the parameters in Eqs. (A1), (A2), (A3), (A4), (A5), (A6), (A7), (A8), (A9), (A10) and (A11) assuming that integration of Eq. (6) to get Eq. (7) is accurate for $T \geq T_c$.

With Eqs. (A1), (A2), (A3), (A4), (A5), (A6), (A7), (A8), (A9), (A10) and (A11), if enough experimental measurements or empirical correlations are available we can determine the necessary parameter values and predict thermodynamic properties under all conditions. Typically the values of partial molar volumes and heat capacities in aqueous solution together with enthalpies and Gibbs energies of hydration are available at 298.15 K and 0.1 MPa, providing information to calculate four of the five parameters needed for nonelectrolytes. Additionally, an approximate linear correlation of the “*a*” parameter with $\Delta_{\text{hyd}}G_2^0$ at 298.15 K and 0.1 MPa has been observed for the nonelectrolyte solutes,

$$a = 1.79045 \cdot 10^{-3} \text{ m}^3 \text{ kg}^{-1} \text{ mol}^{-1} + 7.23543 \cdot 10^{-5} \text{ m}^3 \text{ kg}^{-1} \text{ kJ}^{-1} \cdot \Delta_{\text{hyd}}G_2^0(298.15 \text{ K}, 0.1 \text{ MPa}). \quad (15)$$

The coefficients in this equation were derived by a global least squares fit to all of the experimental results for nonelectrolytes to Eq. (6) with Eq. (15) for the “*a*” parameter. This allows all five adjustable parameters in Eqs. (A1), (A2), (A3), (A4), (A5), (A6), (A7), (A8), (A9), (A10) and (A11) (*a*, *b*, *c*, *d*, and *e*) to be found from experimental data at ambient conditions by solving simultaneously Eq. (15) and the four equations linking experimental data at ambient conditions ($\Delta_{\text{hyd}}H_2^0$, $\Delta_{\text{hyd}}G_2^0$, $C_{\text{p},2}^0$, and V_2^0) to the 5 parameters. We have used this method to make predictions of different properties at high temperatures for all our solutes. The required experimental results at 298.15 K and 0.1 MPa have been taken from NBS Tables (Wagman et al., 1982) in the case of $\Delta_{\text{hyd}}H_2^0$ and $\Delta_{\text{hyd}}G_2^0$ and from Shock et al. (1989); Shock and Helgeson (1990) in the case of $C_{\text{p},2}^0$, and V_2^0 . For boric acid an estimate ($C_{\text{p},2}^0(298) = 120 \text{ J K mol}^{-1}$) which is close to the result of Hnedkovsky and Wood (1997) at 303 K and 28 MPa was adopted rather than the value $C_{\text{p},2}^0(298) = 50 \text{ J K mol}^{-1}$ from Shock et al. (1989)).

For ammonia, which can be considered a “typical” solute in terms of polarity and quality of description, the predictions of partial molar volumes and heat capacities in water at $P = 28 \text{ MPa}$ are compared to the experimental data (Hnedkovsky et al., 1996; Hnedkovsky and Wood, 1997) in Tables 5 and 6. Table 7 summarizes predictions of partial molar heat capacities at $P = 28 \text{ MPa}$ compared to the experimental results (Hnedkovsky and Wood, 1997) for the most polar solute and also the worst fit of our set, boric acid. In Figs. 7 and 8 the predictions of Henry’s constant for methane, carbon dioxide, hydrogen sulfide and argon are compared with the smoothed experimental data at saturation pressure from Fernandez-Prini and Crovetto (1989), Crovetto (1990), and Suleimenov and Krupp (1994). Except very close to the critical point, predictions of V_2^0 , $C_{\text{p},2}^0$ and Henry’s constant are not far from the experimental results. Larger deviations of predicted and experimental values occur in the case of Henry’s constant for argon. Generally, the predictions are quite good considering the amount of information used: only a single low-temperature state point with Eq. (15) is enough to obtain reasonable predictions at temperatures as high as 700 K, even if the experimental results or estimates of thermodynamic properties at ambient conditions have large uncertainties, as in case of boric acid.

In order to assess further the limits of reliability of this new approach for nonelectrolytes we have also considered the predictions for methane (Lin and Wood, 1996) using Molecular Dynamics simulations at temperatures from 873 K to 1478 K. In Table 8 comparisons with the simulations are summarized for the predictions based on parameters from: (1) thermodynamic properties at standard conditions and Eq. (15), (2) on parameters in Table 3 obtained from fitting all experimental data for methane at $298 < T < 705 \text{ K}$. Both predictions are within the limits of estimated uncertainties at most conditions. Taking into account all of the results with an analysis of error distribution for correlation of the experimental results, we conclude that the range of applicability of the nonelectrolyte equations is up to 1000 K with solvent densities greater than 250 kg m^{-3} . Predictions from data at ambient conditions based on these equations are good for all solutes on which they have been tested. It should be noted that only limited predictions have been made on strongly polar nonelectrolytes.

5.2. Electrolytes

In contrast to the nonelectrolytes, predictions for aqueous ions from Eqs. (A1), (A2), (A3), (A4), (A5), (A6), (A7), (A8), (A9), (A10) and (A11) parameterized with experimental values at 298.15 K and 0.1 MPa are not

Table 8

Comparison of the simulation results $\Delta_h^v G_2^0(\text{sim})$ (Lin and Wood (1996)) for $\text{CH}_4(\text{aq})$ at supercritical temperatures with predictions from Eq. (7), $\Delta_h^v G_2^0 = RT \ln \left[\varphi_2^0 \frac{PM_{H_2^0}}{\rho_0 RT} \right]$

$(T)/(\text{K})$	$(\rho_0)/(\text{kg m}^{-3})$	$(\Delta_h^v G_2^0(\text{sim}))/(\text{kJ mol}^{-1})$	$(\Delta_h^v G_2^0(705))/(\text{kJ mol}^{-1})^a$	$\langle \Delta/\sigma \rangle_{\text{av}}^{\text{a,c}}$	$(\Delta_h^v G_2^0(298))/(\text{kJ mol}^{-1})^b$	$\langle \Delta/\sigma \rangle_{\text{av}}^{\text{b,c}}$
873	200	4.4	5.0	0.7	3.8	−0.7
875	580	19.1	20.4	0.2	16.2	−0.5
878	960	52.7	61.0	0.8	49.6	−0.3
1173	240	8.9	9.3	0.2	6.9	−0.9
1175	630	30.7	32.3	0.2	25.0	−0.5
1177	940	71.2	86.4	1.0	69.4	−0.1
1473	260	11.9	13.1	0.6	9.7	−1.0
1475	640	39.1	43.4	0.3	33.5	−0.4
1478	930	81.3	110.4	1.7	88.3	0.4

^a Calculated with parameters from Table 3 obtained from fitting all experimental data at $298 < T < 705$ K.

^b Calculated with parameters obtained from experimental V_2^0 , $\Delta_{\text{hyd}} G_2^0$, $\Delta_{\text{hyd}} H_2^0$, and $C_{p,2}^0$ at 298.15 K and 0.1 MPa.

^c Average value of Δ/σ where Δ is the absolute value of the difference between experimental and calculated $\Delta_h^v G_2^0$ and σ is the estimated uncertainty of a given point.

possible, because $\Delta_{\text{hyd}} G_2^0[T_r, P_r]$ and $\Delta_{\text{hyd}} H_2^0[T_r, P_r]$ have to be used for evaluation of the integration constants and three experimental properties ($V_2^0[T_r, P_r]$, $\Delta_{\text{hyd}} C_{p,2}^0[T_r, P_r]$ and usually also $\kappa_2^0[T_r, P_r]$) are not enough for setting the six adjustable parameters in Eqs. (6) and (14). We might hope to find some correlations among the parameters as in Eq. (15) or another way of estimating the parameters for ions from partial information but this search has not yet been undertaken.

6. Conclusions

This paper has taken the search for an accurate and reliable equation of state for aqueous systems in a different direction. Rather than analyze free energy properties or P – V – T – x behavior, the parameterization is made at the derivative level. We have demonstrated significant simplification of form, good correlation of experiment for the whole set of infinite dilution partial molar properties of aqueous nonelectrolyte and electrolyte components over a wide range of conditions. It was found that this new approach affords better accuracy than other equations we have tested, successfully describing the data included in our databases. Five adjustable parameters are needed to describe thermodynamic properties for the nonelectrolytes and six for aqueous ions. For nonelectrolyte solutes all of the parameters can be estimated from hydration properties at one temperature and pressure. For electrolytes experimental results at ambient conditions are not sufficient to make predictions. We have found that parameters from V_2^0 for $\text{NaCl}(\text{aq})$ near the critical point reasonably predict $C_{p,2}^0$ near the critical point but the accuracy of other predictive methods for electrolytes have not been explored.

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Appendix A

The process of hydration as used in this study consists of the transfer of a solute in the ideal gas standard state (hypothetical 0.1 MPa) at a given temperature to the hypothetical 1m standard state at the solution pressure P and the same temperature (Ben Naim, 1987).

A.1. Infinite dilution thermodynamic properties from Eq. (6)

Partial molar volumes are calculated from Eq. (6)

$$V_2^0 = (1 - z) \kappa_0 RT + d(V_0 - \kappa_0 RT) + (a + c \exp[\theta/T] + b(\exp[\vartheta \rho_0] - 1) + \delta(\exp[\lambda \rho_0] - 1)) \kappa_0 RT \rho_0 \quad (\text{A1})$$

where V_0 , ρ_0 and κ_0 are molar volume, specific density and compressibility of water, the adjustable parameters are a , b , c , and d and coefficients that do not depend on the solute are $\vartheta = 0.005 \text{ m}^3 \text{ kg}^{-1}$, $\lambda = -0.01 \text{ m}^3 \text{ kg}^{-1}$ and $\theta = 1500 \text{ K}$. The coefficient δ depends on the solute type, $\delta = 0.65a$ for aqueous nonelectrolytes, $\delta = 0 \text{ m}^3 \text{ kg}^{-1}$ for aqueous cations, and $\delta = -0.645 \text{ m}^3 \text{ kg}^{-1}$ for aqueous anions. Multiplication of the standard state term, $(1 - z)$, where z is the charge of a given particle, was added in order to comply with hydrogen convention scale, which requires all thermodynamic properties of the aqueous hydrogen ion to be zero. This addition is arbitrary, cancels out for any neutral complex and does not affect derivations discussed previously.

Integrating Eq. (A1) yields φ_2^0 (Eq. (7)) and $\Delta_{\text{hyd}} G_2^0$ (Eq. (8)). Adding an empirical correction derived from Eqs. (13) and (14), $G_2^{\text{corr}}[T]$, which includes an integration constant to compensate for Eq. (A1) not being accurate for ions at low densities, we find

$$\Delta_{\text{hyd}} G_2^0 = G_2^{\text{corr}}[T] + (1 - z) RT \ln[\rho_0 RT/P^0] + d(G_0 - G_0^{\text{ig}} - RT \ln[\rho_0 RT/(P^0 M_0)]) + RT((a + c \exp[\theta/T] - b - \delta) \rho_0 + b/\vartheta(\exp[\vartheta \rho_0] - 1) + \delta/\lambda \cdot (\exp[\lambda \rho_0] - 1)) \quad (\text{A2})$$

Eq. (A2) with Eq. (9) yields the partial molar entropy of hydration,

$$\begin{aligned} \Delta_{\text{hyd}} S_2^0 = & S_2^{\text{corr}}[T] - (1 - z) R(\ln[\rho_0 RT/P^0] + 1 - T\alpha) + d(S_0 - S_0^{\text{ig}} + R(\ln[\rho_0 RT/(P^0 M_{\text{H}_2\text{O}})] \\ & + 1 - T\alpha)) - R((a + c \exp[\theta/T] - b - \delta) \rho_0 + b/\vartheta(\exp[\vartheta \rho_0] - 1) + \delta/\lambda(\exp[\lambda \rho_0] - 1)) \\ & + R\theta c \exp[\theta/T] \rho_0/T - RT(a + c \exp[\theta/T] + b(\exp[\vartheta \rho_0] - 1) \\ & + \delta(\exp[\lambda \rho_0] - 1))(\partial \rho_0/\partial T)_p \end{aligned} \quad (\text{A3})$$

Eq. (10) with Eqs. (A2) and (A3) yields the partial molar enthalpy of hydration,

$$\begin{aligned} \Delta_{\text{hyd}} H_2^0 = & H_2^{\text{corr}} + (1 - z) RT(T\alpha - 1) + d(H_0 - H_0^{\text{ig}} - RT(T\alpha - 1)) - RT^2(-\theta c \exp[\theta/T] \rho_0/T^2 \\ & + (a + b(\exp[\vartheta \rho_0] - 1) + c \exp[\theta/T] + \delta(\exp[\lambda \rho_0] - 1))(\partial \rho_0/\partial T)_p) \end{aligned} \quad (\text{A4})$$

Eq. (11) with Eq. (A2) yields the partial molar heat capacity of hydration,

$$\begin{aligned}\Delta_{\text{hyd}} C_{\text{p},2}^0 = & C_{\text{p},2}^{\text{corr}}[T] + (1-z)R(2\alpha_0 T + T^2(\partial\alpha_0/\partial T)_{\text{p}} - 1) + d(C_{\text{p},0} - C_{\text{p},0}^{\text{ig}} - R(2\alpha_0 T \\ & + T^2(\partial\alpha_0/\partial T)_{\text{p}} - 1)) - T(Rc \exp[\theta/T]\theta^2 p_0/T^3 + 2R(a + c \exp[\theta/T](1 - \theta/T) \\ & + b(\exp[\vartheta p_0] - 1) + \delta(\exp[\lambda p_0] - 1))(\partial p_0/\partial T)_{\text{p}} + RT(b\vartheta \exp[\vartheta p_0] \\ & + \delta\lambda \exp[\lambda p_0])(\partial p_0/\partial T)_{\text{p}}^2 + RT(a + c \exp[\theta/T] + b(\exp[\vartheta p_0] - 1) \\ & + \delta(\exp[\lambda p_0] - 1))(\partial^2 p_0/\partial T^2)_{\text{p}})\end{aligned}\quad (\text{A5})$$

where G_0 , S_0 , H_0 and $C_{\text{p},0}$ are molar Gibbs energy, entropy, enthalpy and heat capacity of water at T and P and G_0^{ig} , S_0^{ig} , H_0^{ig} and $C_{\text{p},0}^{\text{ig}}$ are molar Gibbs energy, entropy, enthalpy and heat capacity of water in ideal gas standard state at T and $P^0 = 0.1$ MPa. The coefficient of thermal expansion is $\alpha_0 = -1/\rho_0(\partial\rho_0/\partial T)_{\text{p}}$. Henry's constant (for the 1m standard state) can be calculated from $\Delta_{\text{hyd}} G_2^0$ of Eq. (A2),

$$\ln[k_{\text{H},2}^0] = \Delta_{\text{hyd}} G_2^0/(RT). \quad (\text{A6})$$

The empirical corrections to the properties of Eqs. (A2), (A3), (A4), (A5) and (A6) are calculated differently for nonelectrolytes ($z = 0$) and electrolytes ($z \neq 0$) where z is the charge on the particle. The correction for the heat capacity is (Eqs. (13) and (14))

$$C_{\text{p},2}^{\text{corr}} = \begin{cases} (T - T_c)(e/(T - \theta) + g) & ; T < T_c \text{ and } z \neq 0 \\ e(T - T_c)^2/(T - \theta) & ; T < T_c \text{ and } z = 0. \\ 0 & ; T \geq T_c \end{cases} \quad (\text{A7})$$

For the correction to the enthalpy and entropy of nonelectrolytes we assume H_2^{corr} and S_2^{corr} are zero at T_c and for electrolytes H_2^{corr} and S_2^{corr} are constants at $T \geq T_c$, which must be evaluated from experimental hydration properties at some reference state point. For $T < T_c$ we use

$$H_2^{\text{corr}}[T] = C_H + \int_{T_c}^T C_{\text{p},2}^{\text{corr}}[T]dT, \quad S_2^{\text{corr}}[T] = C_S + \int_{T_c}^T C_{\text{p},2}^{\text{corr}}[T]/T dT, \quad (\text{A8})$$

where for nonelectrolytes the integration constants $C_H = C_S = 0$. After some simplification the results are,

$$H_2^{\text{corr}} = \begin{cases} g(T^2 - T_c^2)/2 + (T - T_c)(e - gT_c) + e(\theta - T_c)\ln[(T - \theta)/(T_c - \theta)] + C_H & ; T < T_c, z \neq 0 \\ e((2T_c - \theta)(T_c - T) + 1/2(T^2 - T_c^2) + (T_c - \theta)^2\ln[(T - \theta)/(T_c - \theta)]) & ; T < T_c, z = 0 \\ C_H & ; T \geq T_c, z \neq 0 \\ 0 & ; T \geq T_c, z = 0 \end{cases} \quad (\text{A9})$$

$$S_2^{\text{corr}} = \begin{cases} g(T - T_c) + \ln[T/T_c](e - g\theta)T_c/\theta + \ln[(T - \theta)/(T_c - \theta)]e(\theta - T_c)/\theta + C_S & ; T < T_c, z \neq 0 \\ e(T - T_c + T_c^2\ln[T_c/T]/\theta + (T_c - \theta)^2\ln[(T - \theta)/(T_c - \theta)]/\theta) & ; T < T_c, z = 0 \\ C_S & ; T \geq T_c, z \neq 0 \\ 0 & ; T \geq T_c, z = 0 \end{cases} \quad (\text{A10})$$

$$G_2^{\text{corr}} = H_2^{\text{corr}} - TS_2^{\text{corr}}. \quad (\text{A11})$$

The properties of interest for thermodynamic analysis are the partial molar volumes, V_2^0 , partial molar heat capacities, $C_{\text{p},2}^0$, partial molar entropies, S_2^0 , and the Gibbs energies ($\Delta_f G_2^0$) and enthalpies ($\Delta_f H_2^0$) of formation of aqueous species relative to a reference temperature and pressure, typically $T_r = 298.15$ K and $P_r = 0.1$ MPa.

The above equations yield these properties with straightforward derivation. The partial molar heat capacity in aqueous solution is

$$C_{p,2}^0[T, P] = \Delta_{\text{hyd}} C_{p,2}^0[T, P] + C_{p,2}^{\text{ig}}[T], \quad (\text{A12})$$

where the superscript ig denotes the ideal gas standard state. For Gibbs energies of reaction ($\Delta_{\text{R}}G$) and equilibrium constants $K[T, P]$ at T and P we use

$$\Delta_{\text{R}}G = -RT \ln K[T, P] = \sum_i \nu_i \Delta_f G_i^0[T, P] \quad (\text{A13})$$

where ν_i are the usual stoichiometric reaction coefficients for the reaction and $\Delta_f G_i^0[T, P]$ is the Gibbs energy of formation of aqueous species i at T and P from the elements in their standard states at 298.15 K and 0.1 MPa. For aqueous species we obtain $\Delta_f G_i^0[T, P]$ from $\Delta_f H_i^0[T, P]$ and $S_i^0[T, P]$. The forms of the equations depend on whether aqueous solution or ideal gas information is used. Here we give both forms

$$\Delta_f H_i^0 = \Delta_f H_i^0[T_r, P_r] + \int_{T_r}^T C_{p,i}^{\text{ig}} dT + \Delta_{\text{hyd}} H_i^0[T, P] - \Delta_{\text{hyd}} H_i^0[T_r, P_r], \quad (\text{A14a})$$

$$\Delta_f H_i^0[T, P] = \Delta_f H_i^{\text{ig}}[T_r] + \int_{T_r}^T C_{p,i}^{\text{ig}} dT + \Delta_{\text{hyd}} H_i^0[T, P], \quad (\text{A14b})$$

$$S_i^0 = S_i^0[T_r, P_r] + \int_{T_r}^T C_{p,i}^{\text{ig}}/T dT + \Delta_{\text{hyd}} S_i^0[T, P] - \Delta_{\text{hyd}} S_i^0[T_r, P_r], \quad (\text{A15a})$$

$$S_i^0[T, P] = S_i^{\text{ig}}[T_r] + \int_{T_r}^T C_{p,i}^{\text{ig}}/T dT + \Delta_{\text{hyd}} S_i^0[T, P], \quad (\text{A15b})$$

where $\Delta_f H_i^0[T_r, P_r]$, $S_i^0[T_r, P_r]$ and $\Delta_f H_i^{\text{ig}}[T_r]$, $S_i^{\text{ig}}[T_r]$ are experimental values of formation enthalpy and partial molar entropy at T_r and P_r in aqueous solution or in ideal gas state, respectively. The relation for $\Delta_f G_i^0[T, P]$ is more complicated because of the hydrogen ion convention scale (Wagman et al., 1982)

$$\Delta_f G_i^0[T, P] = \Delta_f H_i^0[T, P] - TS_i^0[T, P] + T_r \left(\sum_{\text{el}} S_{\text{el}}^0[T_r] - z/2 S_{H_2}^0[T_r] \right), \quad (\text{A16})$$

where $\sum_{\text{el}} S_{\text{el}}^0[T_r, P_r]$ is the sum of the entropies of the constituting elements in their standard states at T_r and P_r and $S_{H_2}^0[T_r]$ is the entropy of H_2 in its standard state at T_r and P_r . Note that for electrolytes the integration

Table 9
Reference state thermodynamic properties of nonelectrolyte solutes^a

Solute	($\Delta_f H_2^{\text{ig}}[298 \text{ K}]/$ (J mol ⁻¹))	($S_2^{\text{ig}}[298 \text{ K}]/$ (J K ⁻¹ mol ⁻¹))	($C_{p,2}^{\text{ig}}[T]/$ (J K ⁻¹ mol ⁻¹))
CH ₄	-74810	186.264	-5.7924 + 0.10323 · T - 2.9496 · 10 ⁻⁵ · T ² + 3955.9/T
CO ₂	-393509	213.74	32.171 + 0.036257 · T - 1.2620 · 10 ⁻⁵ · T ² - 1343.9/T
H ₂ S	-20630	205.79	22.453 + 0.028206 · T - 6.0938 · 10 ⁻⁶ · T ² + 1122.4/T
NH ₃	-46110	192.45	17.312 + 0.049637 · T - 1.1899 · 10 ⁻⁵ · T ² + 1383.1/T
H ₃ BO ₃	-994100	295.14	45.782 + 0.10849 · T - 3.7273 · 10 ⁻⁵ · T ² - 2559.6/T
C ₂ H ₄	52260	219.56	3.6876 + 0.13302 · T - 4.3467 · 10 ⁻⁵ · T ² + 1244.0/T
Ar	0	154.843	20.785

^aNBS Tables (Wagman et al., 1982). Ideal gas heat capacities were fitted to the values from JANAF Thermochemical Tables (Stull et al., 1971). The entropies of constituent elements in their standard states at 298 K and 0.1 MPa are: $S_{\text{C}}^0[298 \text{ K}, 0.1 \text{ MPa}] = 5.740 \text{ J K}^{-1} \text{ mol}^{-1}$, $S_{\text{H}_2}^0[298 \text{ K}, 0.1 \text{ MPa}] = 130.684 \text{ J K}^{-1} \text{ mol}^{-1}$, $S_{\text{O}_2}^0[298 \text{ K}, 0.1 \text{ MPa}] = 205.138 \text{ J K}^{-1} \text{ mol}^{-1}$, $S_{\text{N}_2}^0[298 \text{ K}, 0.1 \text{ MPa}] = 191.61 \text{ J K}^{-1} \text{ mol}^{-1}$, $S_{\text{B}}^0[298 \text{ K}, 0.1 \text{ MPa}] = 5.86 \text{ J K}^{-1} \text{ mol}^{-1}$, $S_{\text{Ar}}^0[298 \text{ K}, 0.1 \text{ MPa}] = 154.843 \text{ J K}^{-1} \text{ mol}^{-1}$.

Table 10

Reference state thermodynamic properties of ions^a

Ion	$(\Delta_f H_2^0[298 \text{ K}, 0.1 \text{ MPa}]) /$ (J mol ⁻¹)	$(S_2^0[298 \text{ K}, 0.1 \text{ MPa}]) /$ (J K ⁻¹ mol ⁻¹)	$(C_{p,2}^{\text{ig}}[T]) / (\text{J K}^{-1} \text{ mol}^{-1})$
H ⁺	0	0	20.785 ^b
Li ⁺	-278490	13.4	20.785
Na ⁺	-240120	59.0	20.785
K ⁺	-252380	102.5	20.785
Cs ⁺	-258280	133.05	20.785
NH ₄ ⁺	-132510	113.4	$17.312 + 0.049637 \cdot T - 1.1899 \cdot 10^{-5} \cdot T^2 + 1383.1 / T^c$
Cl ⁻	-167159	56.5	20.785
Br ⁻	-121550	82.4	20.785
I ⁻	-55190	111.3	20.785
OH ⁻	-229994	-10.75	$31.492 - 0.0063082 \cdot T + 5.7715 \cdot 10^{-6} \cdot T^2 - 293.18 / T$

^aNBS Tables (Wagman et al., 1982). Ideal gas heat capacities were fitted to the values from JANAF Thermochemical Tables (Stull et al., 1971). The $S_K^0[298 \text{ K}, 0.1 \text{ MPa}] = 64.18 \text{ J K}^{-1} \text{ mol}^{-1}$ entropies of constituent elements in their standard states at 298 K and 0.1 MPa are: $S_{\text{H}}^0[298 \text{ K}, 0.1 \text{ MPa}] = 29.12 \text{ J K}^{-1} \text{ mol}^{-1}$, $S_{\text{Na}}^0[298 \text{ K}, 0.1 \text{ MPa}] = 51.21 \text{ J K}^{-1} \text{ mol}^{-1}$, $S_{\text{Cs}}^0[298 \text{ K}, 0.1 \text{ MPa}] = 85.23 \text{ J K}^{-1} \text{ mol}^{-1}$, $S_{\text{Cl}_2}^0[298 \text{ K}, 0.1 \text{ MPa}] = 223.066 \text{ J K}^{-1} \text{ mol}^{-1}$, $S_{\text{Br}_2}^0[298 \text{ K}, 0.1 \text{ MPa}] = 152.231 \text{ J K}^{-1} \text{ mol}^{-1}$, $S_{\text{I}_2}^0[298 \text{ K}, 0.1 \text{ MPa}] = 116.135 \text{ J K}^{-1} \text{ mol}^{-1}$.

^bWhen calculating $C_{p,2}^0$ of an ion in hydrogen convention scale, $C_{p,\text{H}^+}^{\text{ig}}$ has to be added to the values of $C_{p,2}^0$ for anions and subtracted from the value of $C_{p,2}^0$ for cations.

^cIdeal gas heat capacity unknown, used the same function as for NH₃(ig).

constants C_H and C_S of Eqs. (A9) and (A10) do not appear in Eqs. (A14a) and (A15a), because they cancel out (though of course they are included in experimental values of $\Delta_f H_i^0[T_r, P_r]$ and $S_i^0[T_r, P_r]$). For nonelectrolytes it is generally convenient to start from the ideal gas properties, which are readily available for many substances from the NBS Tables (Wagman et al., 1982) or from JANAF Thermochemical Tables (Stull et al., 1971). In the JANAF Tables the ideal gas heat capacities, $C_{p,2}^{\text{ig}}[T]$, may also be found. For monatomic solutes or ions the ideal gas heat capacities are constant and for complex ions, if unknown, they may approximated by $C_{p,2}^{\text{ig}}[T]$ of the relevant neutral species, because the heat capacity change for adding/removing an electron or proton is small. For convenience, the properties needed for calculations with Eqs. (A12), (A13), (A14a), (A14b), (A15a), (A15b) and (A16) are given for all our solutes in Tables 9 and 10.

References

- Akinfiev, N.N., 1997. Thermodynamic description of H₂O-gas binary systems by means of the Redlich–Kwong equation over a wide range of parameters of state. *Geochem. Int.* 35, 188–196.
- Amend, J.P., Helgeson, H.C., 1997. Group additivity equations of state for calculating the standard molal thermodynamic properties of aqueous organic species at elevated temperatures and pressures. *Geochim. Cosmochim. Acta* 61, 11–46.
- Archer, D.G., 1992. Thermodynamic properties of the NaCl+H₂O system: II. Thermodynamic properties of NaCl(aq), NaCl·2H₂O(cr), and phase equilibria. *J. Phys. Chem. Ref. Data* 21, 793–829.
- Ben Naim, A., 1987. *Solvation Thermodynamics*. Plenum, New York.
- Biggerstaff, D.R., Wood, R.H., 1988. Apparent molar volumes of aqueous argon, ethylene, and xenon from 300 to 716 K. *J. Phys. Chem.* 92, 1988–1994.
- Brelvi, S.W., O'Connell, J.P., 1972. Corresponding states correlations for liquid compressibility and partial molal volumes of gases at infinite dilution in liquids. *AIChE J.* 18, 1239–1243.
- Carter, R.W., 1992. PhD Thesis. University of Delaware.
- Chialvo, A.A., Cummings, P.T., 1994. Solute-induced effects on the structure and thermodynamics of infinitely dilute mixtures. *AIChE J.* 40, 1558–1573.

- Cooney, W.R., O'Connell, J.P., 1987. Correlation of partial molar volumes at infinite dilution of salts in water. *J. P. Chem. Eng. Commun.* 56, 341–349.
- Crovetto, R., 1990. Evaluation of solubility data of the system $\text{CO}_2\text{--H}_2\text{O}$ from 273 K to the critical point of water. *J. Phys. Chem. Ref. Data* 20, 575–589.
- Dec, S.F., Gill, S.J., 1984. Heats of solution of gaseous hydrocarbons in water at 15, 25 and 35°C. *J. Solution Chem.* 14, 827–836.
- Dec, S.F., Gill, S.J., 1985. Heats of solution of gaseous hydrocarbons in water at 25°C. *J. Solution Chem.* 13, 27–41.
- Fernandez-Prini, R., Crovetto, R., 1989. Evaluation of data on solubility of simple apolar gases in light and heavy water at high temperature. *J. Phys. Chem. Ref. Data* 18, 1231–1243.
- Helgeson, H.C., Kirkham, D.H., 1976. Theoretical prediction of the thermodynamic properties of aqueous electrolytes at high pressures and temperatures: III. Equation of state for aqueous species at infinite dilution. *Am. J. Sci.* 276, 97–240.
- Hepler, L.G., Hovey, J.K., 1996. Standard state heat capacities of aqueous electrolytes and some related undissociated species. *Can. J. Chem.* 74, 639–649.
- Hnedkovsky, L., Wood, R.H., 1997. Apparent molar heat capacities of aqueous solutions of CH_4 , CO_2 , H_2S , and NH_3 from 304 K to 704 K at 28 MPa. *J. Chem. Thermodyn.*, submitted for publication.
- Hnedkovsky, L., Wood, R.H., Majer, V., 1996. Volumes of aqueous solutions of CH_4 , CO_2 , H_2S , and NH_3 at temperatures from 298.15 K to 705 K and pressures to 35 MPa. *J. Chem. Thermodyn.* 28, 125–142.
- Johnson, J.W., Oelkers, E.H., Helgeson, H.C., 1992. SUPCRT92: a software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000°C. *Comput. Geosci.* 18, 899–947.
- Kirkwood, J.G., Buff, F.P., 1951. The statistical mechanical theory of solutions. I. *J. Chem. Phys.* 19, 774–782.
- Levelt Sengers, J.M.H., 1991. Thermodynamics of solutions near the solvent's critical point. In: Bruno, T.J., Ely, J.F. (Eds.), *Supercritical Fluid Technology: Reviews in Modern Theory and Applications*, Chap. 1. CRC Press, Boca Raton, FL, pp. 1–56.
- Lin, C.-L., Wood, R.H., 1996. Predictions of the free energy of dilute aqueous methane, ethane, and propane at temperatures from 600 to 1200°C and densities from 0 to $1\text{ g}\cdot\text{cm}^{-3}$ using molecular dynamics simulations. *J. Phys. Chem.* 100, 16399–16409.
- Majer, V., Hui, L., Crovetto, R., Wood, R.H., 1991. Volumetric properties of aqueous 1–1 electrolyte solutions near and above the critical temperature of water: I. Densities and apparent molar volumes of NaCl(aq) from $0.0025\text{ mol}\cdot\text{kg}^{-1}$ to $3.1\text{ mol}\cdot\text{kg}^{-1}$, 604.4 K to 725.5 K, and 18.5 MPa to 38.0 MPa. *J. Chem. Thermodyn.* 23, 213–229.
- Mansoori, G.A., Matteoli, E. (Eds.), 1990. *Fluctuation Theory of Mixtures*. Taylor & Francis.
- Marshall, W.L., 1970. Complete equilibrium constants, electrolyte equilibria, and reaction rates. *J. Phys. Chem.* 74, 346–355.
- Naghbi, H., Dec, S.F., Gill, S.J., 1986. Heat of solution of methane from 0 to 50°C. *J. Phys. Chem.* 90, 4621–4623.
- Neff, R.O., McQuarrie, D.A., 1973. A statistical mechanical theory of solubility. *J. Phys. Chem.* 77, 413–418.
- O'Connell, J.P., 1971. Thermodynamic properties of solutions based on correlation functions. *Mol. Phys.* 20, 27–36.
- O'Connell, J.P., 1981. Thermodynamic properties of solutions and the theory of fluctuations. *Fluid Phase Equilib.* 6, 21–34.
- O'Connell, J.P., 1990. Thermodynamic properties of mixtures from fluctuation solution theory. In: Mansoori, G.A., Matteoli, E. (Eds.), *Fluctuation Theory of Mixtures*. Taylor & Francis, pp. 45–63.
- O'Connell, J.P., 1994. Thermodynamics and fluctuation solution theory. In: Kiran, E., Levelt Sengers, J.M.H. (Eds.), *NATO Advanced Study Institute on Supercritical Fluids*, Kemer, Turkey, Proceedings. Kluwer Academic Publishers, Dordrecht, Holland, pp. 191–230.
- O'Connell, J.P., 1995. Application of fluctuation solution theory to thermodynamic properties of solutions. *Fluid Phase Equilib.* 104, 21–39.
- O'Connell, J.P., Sharygin, A.V., Wood, R.H., 1996. Infinite dilution partial molar volumes of aqueous solutes over wide ranges of conditions. *Ind. Eng. Chem. Res.* 35, 2808–2812.
- Olofsson, G., Oshodj, A.A., Quarnström, E., Wadsö, I., 1984. Calorimetric measurements on slightly soluble gases in water. Enthalpies of solution of helium, neon, argon, krypton, xenon, methane, ethane, propane, *n*-butane, and oxygen at 288.15, 298.15, and 308.15 K. *J. Chem. Thermodyn.* 16, 1041–1052.
- Plyasunov, A.V., 1993. Description of the standard thermodynamic properties of dissolved electrolytes from the total equilibrium constant. *Geochim. Int.* 30, 52–65.
- Plyasunov, A.V., O'Connell, J.P., Wood, R.H., 1999. Infinite dilution partial molar properties of aqueous solutions of nonelectrolytes: I. Equations for V_2^0 in a wide range of state parameters and for the standard thermodynamic functions of hydration of volatile nonelectrolytes at temperatures above the critical temperature of water. *Geochim. Cosmochim. Acta*, submitted for publication.
- Sedlbauer, J., Yezdimer, E.M., Wood, R.H., 1998. Partial molar volumes at infinite dilution in aqueous solutions of NaCl , LiBr , NaBr , and CsBr at temperatures above 550 K. *J. Chem. Thermodyn.* 30, 3–12.
- Shock, E.L., Helgeson, H.C., 1990. Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: standard partial molal properties of organic species. *Geochim. Cosmochim. Acta* 54, 915–945.
- Shock, E.L., Helgeson, H.C., Sverjensky, D.A., 1989. Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: standard partial molal properties of inorganic neutral species. *Geochim. Cosmochim. Acta* 53, 2157–2183.
- Shock, E.L., Oelkers, E.H., Johnson, J.W., Sverjensky, D.A., Helgeson, H.C., 1992. Calculation of the thermodynamic properties of aqueous species at high pressures and temperatures. *J. Chem. Soc., Faraday Trans.* 88, 803–826.
- Shock, E.L., Sassani, D.C., Willis, M., Sverjensky, D.A., 1997. Inorganic species in geologic fluids: correlations among standard molal thermodynamic properties of aqueous ions and hydroxide complexes. *Geochim. Cosmochim. Acta* 61, 907–950.

- Simonson, J.M., Oakes, C.S., Bodnar, R.J., 1994. Densities of NaCl(aq) to the temperature 523 K at pressures to 40 MPa measured with a new vibrating-tube densitometer. *J. Chem. Thermodyn.* 26, 345–359.
- Stull, D.R., Prophet, H. (Project Directors), 1971. JANAF Thermochemical Tables. NSRDS-NBS 37.
- Suleimenov, O.M., Krupp, R.E., 1994. Solubility of hydrogen sulfide in pure water and in NaCl solutions, from 20 to 320°C and at saturation pressures. *Geochim. Cosmochim. Acta* 58, 2433–2444.
- Sverjensky, D.A., Shock, E.L., Helgeson, H.C., 1997. Prediction of the thermodynamic properties of aqueous metal complexes to 1000°C and 5 kb. *Geochim. Cosmochim. Acta* 61, 1359–1412.
- Tanger, J.C., Helgeson, H.C., 1988. Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: revised equations of state for the standard partial molal properties of ions and electrolytes. *Am. J. Sci.* 288, 19–98.
- Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S.M., Churney, K.L., Nuttall, R.L., 1982. The NBS tables of chemical thermodynamic properties. *J. Phys. Chem. Ref. Data* 11, Suppl. 2.
- Wheeler, J.C., 1972. Behavior of a solute near the critical point of an almost pure solvent. *Ber. Bunsenges. Phys. Chem.* 76, 308–318.
- Wilhelm, E., Battino, R., Wilcock, R.J., 1977. Low-pressure solubility of gases in liquid water. *Chem. Rev.* 77, 219–262.
- Wood, R.H., Crovetto, R., Majer, V., Quint, J.R., 1990. In: Pichal, M., Sifner, O. (Eds.), *Properties of Water and Steam. Proceedings of the 11th International Conference*. Hemisphere, New York, pp. 157–167.
- Wood, R.H., Carter, R.W., Quint, J.R., Majer, V., Thompson, P.T., Boccio, J.R., 1994. Aqueous electrolytes at high temperatures: comparison of experiment with simulation and continuum models. *J. Chem. Thermodyn.* 26, 225–249.