Modeling the PVT Properties of Concentrated Electrolytes in Water

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Introduction

There are many practical situations where one needs to predict the densities of salt mixtures and how these densities are affected by changes of temperature and pressure. The general problem has been discussed exhaustively by Millero (1977) with regard to seawater. But the low ionic concentration of normal seawater and its low ambient temperature range has severely restricted this work. Our attention was drawn to the problem by the use of concentrated salt solutions in the "completion" of oil and gas wells (Milhone, 1983). In this technology very concentrated solutions and mixtures of salts such as NaCl, $CaCl_2$, $CaBr_2$, and $ZnBr_2$ are used to control formation pressure and provide circulation during completion. The temperature and pressure of the solutions can approach those of the formation, normally up to 150°C and 1 kbar. Inability to predict the density of the solution under these conditions can lead to excessive loss of these expensive fluids to the formation or, even worse, a well blowout. Our general approach to this problem has been based on the use of normal electrolyte solution thermodynamics and the specific interaction theoretical formalism developed in recent years by K. S. Pitzer (1979, 1980).

Theoretical Formulation

The basic approach to predicting the densities of salt solutions is through the apparent molal volume, ϕ_v, which is defined by the equation

$$\phi_v = \frac{V - (1{,}000/18.02)\bar{V}_1^\circ}{m} \tag{1}$$

where

V = volume of the solution

$\bar{V}_1^\circ$ = molar volume of the pure H_2O under the same conditions

m = molality of the solution.

ϕ_v is used instead of the partial molal volume because it is directly related to the density and because it is a thermodynamic state function.

$$\rho = \frac{1{,}000 + mM_2}{1{,}000/\rho_0 + m\phi_v} \tag{2}$$

where

M_2 = formula weight of salt

ρ_0 = density of water at same T,P

For mixtures the corresponding equations are

$$\phi_v^* = \frac{\sum_J m_J\phi_J}{\Sigma m_J} \tag{3}$$

where J is a summation over salts, and

$$\rho = \frac{1{,}000 + \sum_J m_J\phi_J}{(1{,}000/\rho_0) + \Sigma m_J\phi_J + \Delta\phi}$$

$\Delta\phi$ = a "mixing" parameter term. (4)

The Pitzer equation for the apparent molal volume of a single salt, $M\nu_M X\nu_X$, is given by

$$\phi_v = \phi_v^\circ + |Z_M Z_X|\frac{A_v}{2b}\ln(1 + bI^{1/2}) + 2\nu_M\nu_x RT[mB_{MX}^v + m^2(\nu_M\nu_X)^{1/2}C_{MX}^v] \tag{5}$$

where

$$B^{v}_{MX} = B^{(0)}_{v} + B^{(1)}_{v}\left(\frac{2}{\alpha_I^2}\right)[1 - (1 + \alpha I^{1/2})]\exp(-\alpha I^{1/2})$$

A_v = Debye-Hückel-Pitzer slope

$$B^{(0)}_{v} = \left(\frac{\phi\beta(0)}{\partial P}\right)_T$$

$$B^{(1)}_{v} = \left(\frac{\partial\beta^{(1)}}{\partial P}\right)_T$$

$$2C^{v}_{MX} = \left(\frac{\partial C^{\phi}}{\partial P}\right)_T \qquad (6)$$

(i.e., the pressure derivatives of the Pitzer parameters used for osmotic coefficients) $\alpha = 2.0$, $b = 1.2$ (same empirical parameters used by Pitzer for activity fitting).
The apparent molal compressibility ϕ_k, is given by the completely analogous equation

$$\phi_k \equiv -\left(\frac{\partial_{\phi v}}{\partial P}\right)_T$$

$$\phi_k = \phi^{\circ}_k + \nu\,|Z_M Z_x|\,\frac{A_k}{2b}\ln(1 + bI^{1/2}) + 2\nu_M\nu_X RT[mB^{k}_{Mx} + m^2(\nu_M\nu_X)^{1/2}C^{k}_{Mx}] \qquad (7)$$

and the apparent molal expansibility is given by

$$\phi_E = \left(\frac{\partial\phi_v}{\partial T}\right)_P$$

$$\phi_E = \phi^{\circ}_E + \nu\,|Z_M Z_X|\,\frac{A_E}{2b}\ln(1 + bI^{1/2}) + 2\nu_M\nu_X RT[mB^{E}_{MX} + m^2(\nu_m\nu_x)^{1/2}C^{E}_{MX}] \qquad (8)$$

In all cases $I = 1/2\Sigma_i m_i Z_i^2$.
An ionic equation for any of the three properties is then given by

$$\phi_i = \phi^{\circ}_i + \frac{Z_i^2 A}{2b}\ln(1 + bI^{1/2}) + RT\sum_i B_{ij}m_j + \frac{RT}{2|Z_i|^{1/2}}\sum_i C_{ij}m_j^2|Z_j|^{1/2} + RT\sum_k \theta_{ik}m_k \qquad (9)$$

where summations over $\underline{j}$ are over ions of opposite charge and summations over $\underline{k}$ are over ions of the same charge. The term with θ_{ik} is a binary mixing term sometimes needed for pressure-volume-temperature (PVT) properties. We have not yet found any need for the corresponding ternary mixing term. In data fitting, the sets of (ϕ, m) data for a given salt are analyzed to give the appropriate (ϕ°, $\beta^{(0)}$, $\beta^{(1)}$, C) parameters. These can then be used in Eq. 9 to give

$$\phi_J = \sum_i \nu_i\phi_i \qquad (10)$$

and in Eq. 3 to give the appropriate mean property, ϕ^*.

The appropriate slopes for the calculations have recently been published (Ananthaswamy and Atkinson, 1984).

Single-Salt Properties

Rogers and Pitzer (1982) have recently summarized the PVT properties of aqueous NaCl over the range 0–300°C and 1 atm to 1 kbar (1 kPa to 1 MPa). Additional data on NaCl up to 500°C and 4 kbar can be found in Hilbert (1979). NaCl is the only salt whose PVT properties have been measured with precision over this wide a range of conditions; fortunately, most natural brines are concentrated NaCl solutions. The required fitting parameters are thoroughly summarized in Rogers and Pitzer and will not be repeated here. It is, however, useful to examine the temperature and pressure dependence of the ϕ°_v of NaCl solutions as a clue to the behavior of a simple electrolyte.

Figure 1 shows the dependence of ϕ°_v on temperature over the range 0–150°C at 1 atm. The maximum observed here in the vicinity of 70°C is observed in essentially all simple electrolytes. By simple in this context we mean electrolytes not involved in a complex formation or acid-base equilibria to an appreciable extent in this temperature range. These curves can commonly be fitted by a quadratic equation in t

$$\phi^{\circ}_v = \phi_v(0) + at + bt^2 \qquad (11)$$

so that the expansibility is given by

$$\phi^{\circ}_E \equiv \left(\frac{\partial\phi^{\circ}_v}{\partial T}\right)_p = a + 2bt \qquad (12)$$

In the case of very good data over a wide range of t, a cubic equation can be used.

Figure 2 shows the effect of pressure on ϕ°_v over the range 1–1,000 bar at 25° and 150°C. The lines are straight lines to within the precision of the data.

$$\phi^{\circ}_v(t, P) = \phi^{\circ}_v(t, P) + cP$$

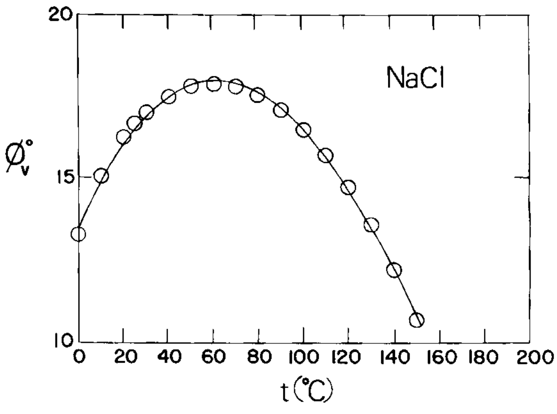

Figure 1. Temperature dependence of ϕ°_v of NaCl at 1 atm.

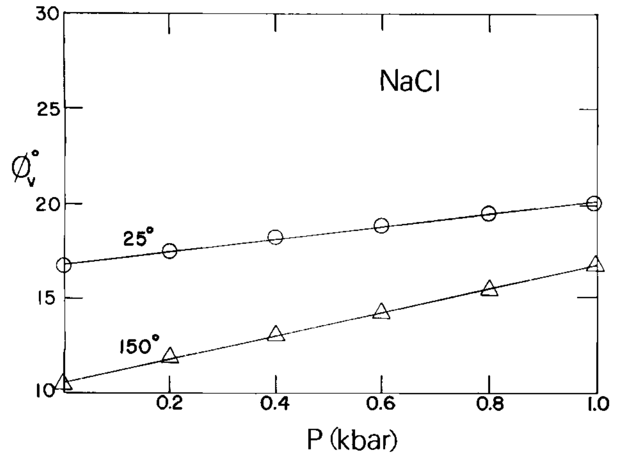

Figure 2. Effect of pressure on ϕ_v° of NaCl.

since

$$\phi_k^\circ \equiv -\left(\frac{\partial \phi_v^\circ}{\partial P}\right)_T = -c \tag{13}$$

But, clearly, ϕ_k° is strongly temperature-dependent. We will discuss behavior at more extreme conditions of T, P later in this paper.

Figure 3 shows the dependence of ϕ_v° on temperature for $CaCl_2$, another rather simple salt. Additional data on a variety of salts in the temperature range 0–200°C can be found in the reworking by Helgeson et al. (1981) of the original data of Ellis and McFadden (1972). Some more precise data over a much more limited temperature range are given by Millero and Knox (1973).

Figure 4 shows the temperature dependence of ϕ_v° for $ZnBr_2$. The maximum exhibited by simple salts is clearly absent. The Zn^{2+} ion is well known to form complexes with halide ions. The typical analyses of complexation data suggest that $ZnBr^+$, $ZnBr_2$, $ZnBr_3^-$, and $ZnBr_4^{2-}$ would all be present in concentrated solutions (Short and Morris, 1961). However, there is little agreement on the stability constants for the different complex ions (Constable, 1984), and such complex ion-forming processes are invariably endothermic (Gerding, 1969). Therefore, as we go to higher temperatures complex formation will be favored. Including complex formation explicitly in the Pitzer formalism creates equations of unwieldly proportions containing far too many undetermined parameters. We have chosen to ignore the complexes and simply include them implicity in the Pitzer parameters.

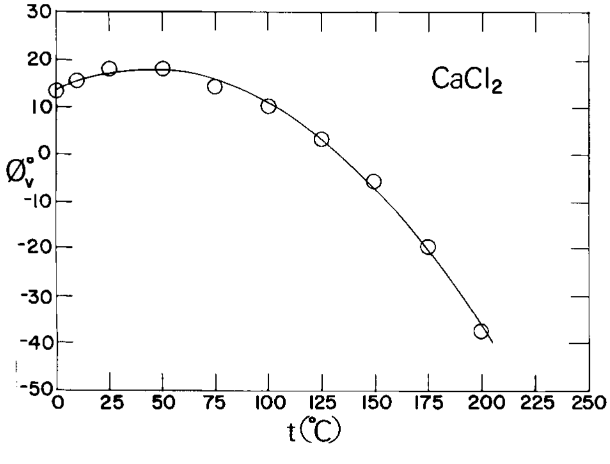

Figure 3. Temperature dependence of ϕ_v° of $CaCl_2$.

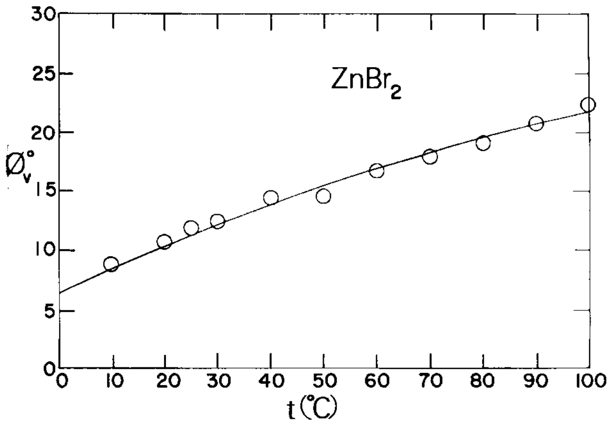

Figure 4. Temperature dependence of ϕ_v° of $ZnBr_2$.

Table 1 gives the Pitzer parameters as a function of temperature for three important 2–1 electrolytes. The parameters are all smoothed with a polynomial of the form $Y = a + bt + ct^2$ where a is the value of Y at 0°C. The fit of the Pitzer equation, Eq. 5, to the $CaCl_2$ and $CaBr_2$ data is quite good over the range of temperatures 0–140°C. The RMSD (root mean square deviation) for $CaCl_2$ is 0.08 and for $CaBr_2$ 0.12. The fit for $ZnBr_2$ is substantially worse (RMSD = 0.86) and a close examination of the fit shows clearly that the simple Pitzer equation used here has the wrong shape to fit the ϕ_v of $ZnBr_2$ well. No amount of parameter adjustment will remove this problem.

Figure 5 shows the thermodynamic cycle we have used for correcting ϕ_v for the effects of both temperature and pressure. The apparent molal volume for any salt as a function of temperature and pressure is given by the equation

$$\phi_v = \phi_v(m) + \int_{T_0}^{T} \phi_E(m, T)\,dT - \int_{1}^{P} \phi_k(m, T)\,dP \tag{14}$$

For the ϕ_E and ϕ_k corrections we can use the Pitzer equations. However, the lack of high-precision density data as a function of

Table 1. Pitzer Parameters for Some 2-1 Salts

Parameter	Salt	a	b	c
ϕ_v^0	$CaCl_2$	14.01	0.1438	−0.0015
	$CaBr_2$	27.29	0.1932	−0.0017
	$ZnBr_2$	6.267	0.2101	−0.0006
$10^5 \times B_v^{(o)}$	$CaCl_2$	2.922	−0.0705	0.0006
	$CaBr_2$	3.729	−0.0568	0.0004
	$ZnBr_2$	5.342	−0.0617	0.0002
$10^4 \times B_v^{(1)}$	$CaCl_2$	−1.2903	0.0927	−0.0016
	$CaBr_2$	−1.3248	0.0080	−0.0007
	$ZnBr_2$	27.05	−0.117	0
$10^6 \times C^v$	$CaCl_2$	−3.972	0.1686	−0.0016
	$CaBr_2$	−4.5570	0.0634	−0.0005
	$ZnBr_2$	−5.532	0.0417	0

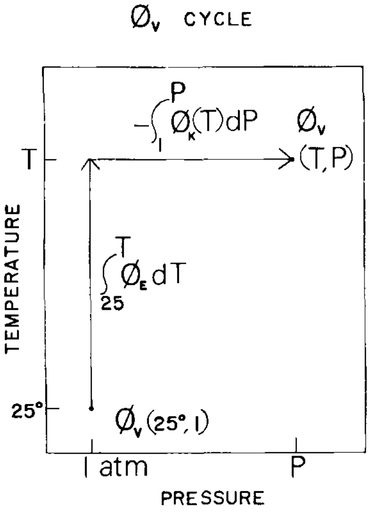

Figure 5. Correction cycle for ϕ_v.

temperature and pressure for salts other than NaCl makes this too complex in most cases. In a recent paper we have shown that expansibility data can easily be fitted to equations of the form $\phi_E(m, T) = (D + Em^{1/2}) + (F + Gm^{1/2})T$, where D, E, F, G are empirical parameters for a given salt and

$$\phi_k(m, T) = H + Im^{1/2}$$
$$H = H_0 + H_1T + H_2T^2$$
$$I = I_0 + I_1T + I_2T^2$$

where all the parameters are empirical. This approach predicts the densities of concentrated brine mixtures to within 0.3% up to 125°C and 1,500 bar.

Mixtures

In two recent papers (Kumar et al., 1982; Kumar and Atkinson, 1983) we examined the need for mixing parameters in the system NaCl–CaCl$_2$. We examined the temperature range 5–35°C and mixtures ranging from pure NaCl to pure CaCl$_2$ up to ionic strength 5. The use of a single mixing parameter θ_{NaCa} for apparent molal volumes only improved the ϕ_v fit from 0.03 to 0.01%, a negligible practical consequence. The analogous fit for ϕ_k improved the fit from 3.0% to 0.7%, and so seemed to be useful. In practice, a good value for a mixing parameter can be determined by making one precise measurement on the system at the highest ionic strength with a salt ratio at which the two salts contribute equally to the ionic strength.

We have recently extended this work to a variety of systems when mixture densities have been published (Kumar and Atkinson, 1985a) and to the three-salt system NaCl–MgCl$_2$–CaCl$_2$ at 25°C (Kumar and Atkinson, 1985b).

Table 2. Pitzer Parameters at 25°C

Salt	ϕ_v^0 cm^3 · mol^{-1}	$10^5 \times B_v^{(o)}$	$10^5 \times B_v^{(o)}$	$10^6 \times C^v$	σ cm^3 · mol^{-1}
NaCl					
0–6m	16.58	1.14	1.15	−1.11	0.005
CaCl$_2$					
0–7.5m	18.53	1.56	−10.48	−0.88	0.30
MgCl$_2$					
0–5.25m	14.16	1.78	−6.38	−1.82	0.02

Table 3. Prediction of Mixture Densities at 25°C

Mixture	Ionic Strength	$10^3 \times \sigma$ · in $(\rho - \rho_o)$
NaCl–MgCl$_2$	1	0.026
	2	0.01
	5	0.10
MgCl$_2$–CaCl$_2$	1	0.008
	2	0.008
	5	0.008
NaCl–CaCl$_2$	1	0.07
	2	0.13
	5	0.27
NaCl–MgCl$_2$–CaCl$_2$	1	0.01
	2	0.02
	3	0.03

In this latter work we examined the apparent molal volumes of the two-salt systems NaCl–MgCl$_2$ and MgCl$_2$–CaCl$_2$ at 25°C and ionic strengths 1, 2, and 5, then looked at the N three-salt systems. Table 2 summarizes the Pitzer parameters for the different salts. Again we find that the shape of the Pitzer equation is not quite right for the Ca^{2+} salt.

Table 3 summarizes the results of using the single-salt data to predict the properties of the two-salt and three-salt mixtures. It is clear that density predictions can be made in systems of this type with very high precision using single-salt data and no mixing parameters.

Some preliminary work on mixtures containing ZnBr$_2$ shows that mixing parameters are definitely needed in such cases. However, before this can be settled definitively we must modify the formalism so that a better fit can be obtained with "pure" ZnBr$_2$. That is, an electrolyte that has an appreciable concentration of complexes present in fast equilibria behaves as if it were a mixture. It is not clear at this time that systems with multiple complexes at high concentrations can be handled gracefully with the Pitzer formalism. At the same time, there is no other theoretically sound approach that looks any better.

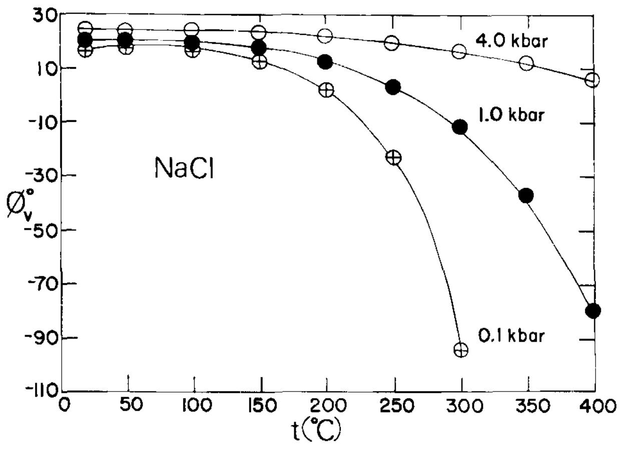

Figure 6. Effect of temperature on ϕ_v° of NaCl at selected pressures.

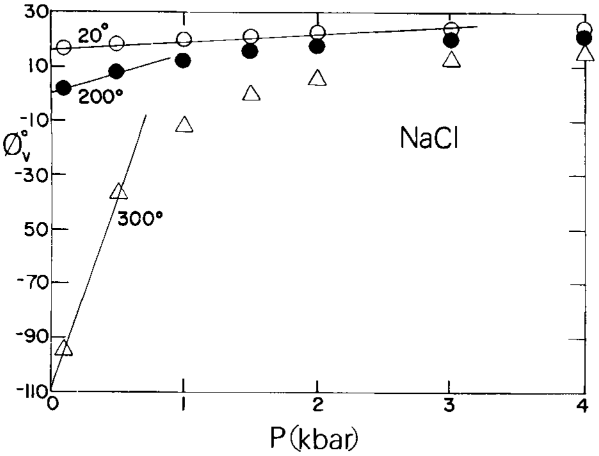

Figure 7. Effect of pressure on ϕ_v° of NaCl at selected temperatures.

Extreme Conditions

Although limited good data are available, it is instructive to examine some of it to see how a normal electrolyte behaves at extreme conditions of temperature and pressure. Again we must fall back on the unique data set provided by Hilbert (1979). Figure 6 shows the effect of temperature on the ϕ_v° of NaCl as a function of temperature at some selected pressures. At the lowest pressure of 100 bar, ϕ_v° plunges to strongly negative values at the maximum temperature available. If we look at the defining equation $\phi_v = (V - n_1\bar{v}_1^\circ)/m$ and recall that by extrapolating to ϕ_v° we have extrapolated out all interionic effects, this behavior is understandable. At the high temperature and low density, we are seeing the very large effect of the ions on the water. In effect the ions are compressing the water so much that the volume of the solution is much less than the volume of the pure water. This effect giving rise to negative ϕ_v° values is apparent even at 3 kbar and 400°C. Only at 4 kbar is ϕ_v positive and here it has decreased 77% from its 20°C value.

Figure 7 shows ϕ_v° as a function of pressure at some selected temperatures. At the low temperature ϕ_v° rises monoatonically with increasing pressure but is linear only to 1 kbar. At the higher temperature ϕ_v° is probably not even linear to 500 bar. As more data under such extreme conditions become available we may find that the simple Born equation approach suggested by Wood et al. (1983) may turn out to be a valuable tool. One should also examine the suggestions put forward recently by Pitzer and Li (1983).

As we increase the temperature the dielectric constant of water drops rapidly. As a consequence, salts such as NaCl that are essentially unassociated at room temperature become weak electrolytes at high temperature. This means that the interionic forces at the basis of the Pitzer theory become less important and short-range ion-ion and ion-solvent forces dominate. Unfortunately, the lack of high-precision data on salts other than NaCl makes further analysis too speculative at this time.

Acknowledgment

This work was supported by the National Science Foundation under Grant No. CPE 8017441, and by the Amoco Production Co., Tulsa, OK.

Notation

A_v = Pitzer slope for apparent molal volume
A_E = Pitzer shape for apparent molal expansibility
A_k = Pitzer slope for apparent molal compressibility
b = constant in Pitzer theory
$B_v^{(0)}, B_v^{(1)}$ = Pitzer coefficients in ϕ_v formula
$B_E^{(0)}, B_E^{(1)}$ = Pitzer coefficients in ϕ_E formula
$B_k^{(0)}, B_k^{(1)}$ = Pitzer coefficients in ϕ_k formula
B_{ij} = Pitzer coefficient in ϕ_i formula
C_{ij} = Pitzer coefficient in ϕ_i formula
C_{MX}^v = Pitzer coefficient in ϕ_v formula
C_{MX}^E, C_{MX}^k = Pitzer coefficient in ϕ_E formula
I = ionic strength, molal
m = molality of salt
m_J = molality of salt J
m_i = molality of ion i
M_2 = formula weight of salt
n_1 = number of moles of water in the solution
P = pressure
R = gas constant
t = temperature, °C
T = temperature, K
V = volume of solution
$\bar{v}_1^\circ$ = molar volume of water
Z_M = charge on cation M
Z_X = charge on anion X

Greek letters

α = constant in Pitzer theory
σ = standard deviation
ρ = density of solution
ρ_o = density of water
ν = number of ions per formula of salt
ν_M = number of cations per formula of salt
ν_X = number of anions per formula of salt
θ_{ik} = mixing parameter in Pitzer theory
ϕ_v = apparent molal volume
ϕ_v° = apparent molal volume at infinite dilution
ϕ_v^* = mean apparent molal volume
ϕ_E = apparent molal expansibility
ϕ_k = apparent molal compressibility

Literature cited

Ananthaswamy, J., and G. Atkinson, "Pitzer-Debye-Hückel Limiting Slopes for Water from 0 to 100°C and from 1 atm to 1 kbar," *J. Chem. Eng. Data,* **29,** 81 (1984).

Constable, E. C., "Zinc and Cadmium," *Coord. Chem. Rev.,* **58,** 1 (1984).

Ellis, A. J., and I. M. McFadden, "Partial Molal Volumes of Ions in Hydrothermal Solutions," *Geochim. Cosmochim. Acta,* **36,** 413 (1972).

Gerding, P., "Free Energy, Enthalpy, and Entropy Changes for Stepwise Formation of Zinc(II) Halide Complexes in Aqueous Solution," *Acta Chem. Scand.,* **23,** 1,695 (1969).

Helgeson, H. C., D. H. Kirkham, and G. C. Flowers, "Calculations of Activity Coefficients, Osmotic Coefficients, and Apparent Molal and Standard and Relative Partial Molal Properties to 600°C and 5 kbar," *Am. J. Science,* **281,** 1,249 (1981).

Hilbert, R., "PVT Data von Wasser und von Wässrigen Natriumchlorid-Lösungen bis 873 K, 400 bar, und 25 Gewichtesprozent NaCl," Thesis, Karlsruhe (1979).

Kumar, A., G. Atkinson, and R. D. Howell. "Densities and Compressibilities of Aqueous NaCl–CaCl$_2$ at 25°C," *J. Solution Chem.,* **11,** 857 (1982).

Kumar, A., and G. Atkinson, "Apparent Molal Volumes, Compressibilities, and Expansibilities from 5 to 35°C," *J. Phys. Chem.,* **87,** 5,504 (1983).

———, "Use of the Pitzer Formalism for Predicting Mixed Electrolyte Densities," *J. Solution Chem.* (1985a).

———, "Apparent Molal Volumes in Aqueous NaCl–MgCl$_2$–CaCl$_2$ Mixtures at 25°C," *J. Chem. Eng. Data* (1985b).

Millero, F. J., and J. H. Knox, "Apparent Molal Volume of Aqueous

NaF, Na_2SO_4, KCl, K_2SO_4, $MgCl_2$, and $MgSO_4$ Solutions at 0° and 50°C," *J. Chem. Eng. Data,* **18,** 407 (1973).

Millero, F. J., "The Use of the Specific Interaction Model to Estimate the Partial Molal Volumes of Electrolytes in Seawater," *Geochim. Cosmochim. Acta,* **41,** 215 (1977).

Millhone, R. S., "Completion Fluids for Maximizing Productivity—State of the Art," *J. Pet. Eng.,* **35,** 47 (1983).

Pitzer, K. S., "Theory: Ion Interaction Approach," *Activity Coefficients in Electrolyte Solutions,* R. M. Pytkowicz, ed., CRC Press, Boca Raton, FL, **1,** Ch. 7 (1979).

———, "Thermodynamics of Aqueous Electrolytes at Various Temperatures, Pressures, and Compositions," *Thermodynamics of Aqueous Systems with Industrial Applications,* S. A. Newman, ed., ACS 133, Washington, DC, Ch. 23 (1980).

Pitzer, K. S., and Yi-Gui, Li, "Critical Phenomena and Thermodynamics of Aqueous Sodium Chloride to 823 K," *Proc. Natl. Acad. Sci. USA,* **80,** 7,689 (1983).

Rogers, P. S. Z., and K. S. Pitzer, "Volumetric Properties of Aqueous Sodium Chloride Solutions," *J. Phys. Chem. Ref. Data,* **11,** 15 (1982).

Short, E. L., and D. F. C. Morris, "Zinc Chloride and Bromide Complexes," *J. Inorg. Nucl. Chem.,* **18,** 192 (1961).

Wood, R. H., et al., "Comparison of Experimental Values of $\bar{V}_2^\circ$, $\bar{C}_{P_2}^\circ$, and $\bar{C}_{V_2}^\circ$ for Aqueous NaCl with Predictions using the Born Equation at Temperatures from 300 to 573.15 K at 17.7 MPa," *J. Phys. Chem.,* **87,** 3,297 (1983).

Manuscript received Nov. 4, 1985.