International Journal of Thermophysics, Vol. 19, No. 2, 1998

Aqueous Electrolytes at Near-Critical and Supercritical Temperatures[1]

K. S. Pitzer[2]

The aqueous electrolyte systems NaCl–H_2O, KCl–H_2O, and $CaCl_2$–H_2O are of great interest both geologically and industrially. Equations of state were developed recently for these systems; they are based on theoretical modeling for mixtures of hard spheres with appropriate diameters and dipole moments for H_2O, NaCl, and KCl and with a quadrupole moment for $CaCl_2$. Empirical terms are added as required to fit the available experimental data. The fit to the compositions and densities at equilibrium of the saturated vapor and liquid constitutes a severe test, in addition to properties in the single-phase regions. Temperatures range upward from 300°C for NaCl and KCl and from 250°C for $CaCl_2$ for these equations. Complications from hydrolysis and alternate equations valid at lower temperatures are discussed briefly. In addition, there is a very important theoretical aspect relating to the general phase diagrams. With the high ratio of critical temperatures of the salts to that of water, complex diagrams involving liquid–liquid phase separation near the critical point of water are expected. But no such effect is observed experimentally; instead, one finds simple type I phase diagrams. This is particularly clear in the case of NaCl–H_2O, where the database is very accurate and extends above 1000 K.

KEY WORDS: aqueous electrolytes; calcium chloride; equation of state; near-critical properties; phase-diagram type; potassium chloride; sodium chloride; supercritical properties.

1. INTRODUCTION

This presentation is concerned primarily with equations of state for industrially and geologically important aqueous electrolytes at near-critical and supercritical temperatures. Before proceeding to this high-temperature

---

[1] Invited paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22–27, 1997, Boulder, Colorado, U.S.A.

[2] Department of Chemistry and Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720, U.S.A.

range, however, a few remarks are appropriate concerning equations for lower temperatures. In a 1993 review [1] it was shown that the strong-electrolyte Gibbs energy formulation widely used at room temperature was satisfactory up to 573 or even 623 K for 1–1 electrolytes such as NaCl [2] and KCl [3]. For the 2–1 electrolytes $CaCl_2$ and $MgCl_2$, however, ion association becomes substantial by 523 K. Treatments with special terms for partial association have been presented for aqueous $CaCl_2$ [4] and $MgCl_2$ [5] for 298–523 K but their extension to temperatures in the 573–623 K range is not satisfactory. At these temperatures, the equilibrium vapor is still essentially pure steam; the very small salt impurity has been treated as a separate problem [6].

At still higher temperatures it is more satisfactory to use a Helmholtz energy formulation for both vapor and liquid at near-subcritical temperatures as well as above-critical temperatures. Also, in this range the ion association is so strong that the fully associated basis is a useful approximation. Then dissociation into ions is introduced as a special correction as the salt concentration decreases to zero. At a high salt concentration the oppositely charged ions are never far apart and the fraction dissociated is definite only with respect to an arbitrary definition of the distance of separation. On this fully associated basis, equations of state for $NaCl–H_2O$, $KCl–H_2O$, and the ternary $NaCl–KCl–H_2O$ were developed for the range above 573 K [7, 8]. A similar equation for $CaCl_2–H_2O$ is valid for the liquid above 523 K [9].

Hydrolysis is a complication that becomes more serious for the saturated vapor with a reduction of the temperature and pressure. For $NaCl–H_2O$ the reaction

$$NaCl + H_2O = NaOH + HCl \tag{A}$$

has been investigated carefully [10]. It is not serious above the three-phase pressure, but at 100 bar (10 MPa) in equilibrium with the solid the Cl^-/Na^+ ratio in the vapor exceeds unity above about 700 K. The resulting NaOH presumably dissolves in the solid NaCl.

For $CaCl_2–H_2O$ hydrolysis is much more important. Bischoff et al. [11] report that the Cl^-/Ca^{2+} ratio exceeds 2 at pressures below 250 bar at 673 K. This effect appears abruptly, and at substantially lower pressures, the vapor is nearly pure HCl. The $Ca(OH)_2$ dissolves in the liquid $CaCl_2$. For this system the three-phase pressure is below 50 bar at 673 K.

To introduce the hydrolysis equilibrium or the ion-dissociation equilibrium into the general equation of state would add great complexity. Thus, for the $CaCl_2–H_2O$ system there was no attempt to fit the vapor properties quantitatively beyond a short range below the critical pressure at any temperature. In contrast, for NaCl–H_2O the general equation represents the properties of the saturated vapor over the full range above 573 K and the three-phase pressure at each temperature. It is only at higher densities for the liquid that the absence of the ion-dissociation equilibrium is a serious deficiency.

The general pattern of the phase diagram from the critical component of one component to that of the other has been a matter of great interest. The calculations of van Konynenburg and Scott [12] with the van der Waals equation showed several types of diagrams in addition to the simple type I with a single continuous critical line from one critical point to the other. They found a maximum ratio of critical temperatures of about 3 for the type I pattern. Harvey [13] made calculations for a more appropriate model for the aqueous electrolytes and found a maximum T_c ratio of 3.56.

The critical temperature of NaCl is too high for direct experimental measurement, but different calculations indicate values in the range 3000–3300 K [14–17]. Then the ratio to the critical temperature of H_2O (647 K) is 4.6–5.1 and is well above the maximum 3.56 of the Harvey calculation. This apparent anomaly merits further research.

2. THERMODYNAMIC MODEL

In order to calculate phase equilibria and volumetric properties, we need an expression for the difference between the molar Helmholtz energy of the system and that of an ideal gas mixture at the same temperature, volume, and composition. This residual Helmholtz energy is defined as

$$a^{\mathrm{res}}(T, v, x) = a(T, v, x) - a^{\mathrm{id}}(T, v, x) \tag{1}$$

Thus, the standard state adopted in this work for the mixture as well as pure components is the ideal gas state. The Helmholtz energy is convenient as a generating function because its derivatives, with respect to volume and each of the component mole numbers, yield the pressure and the chemical potentials, respectively.

It is desirable to formulate an idealized molecular model whose properties are known from theory and provide a reasonable approximation of the real system properties. The idealized model constitutes a reference system for the computations. Any departure of the real system behavior from that of the reference system is then accounted for by a perturbation contribution which is determined from experimental data. The residual Helmholtz energy is then

$$a^{\mathrm{res}} = a^{\mathrm{ref}} + a^{\mathrm{per}} \tag{2}$$

where the superscripts ref and per denote the reference and perturbation contributions, respectively.

We define the reference system as that containing ion pairs for NaCl or KCl or ion triplets for $CaCl_2$ and solvent molecules. The a^{ref} contribution involves, then, averaged interactions between ion pairs or triplets of the solute and polar molecules of the solvent:

$$a^{\mathrm{ref}} = a_{\mathrm{solute\text{-}solute}} + a_{\mathrm{solute\text{-}solvent}} + a_{\mathrm{solvent\text{-}solvent}} \tag{3}$$

Each of these terms in the reference Helmholtz energy is a sum of a repulsive contribution a^{hs} due to hard-core effects and an electrostatic contribution a_{es} from dipoles or quadrupoles.

$$a^{\mathrm{ref}}(T, v, x) = a^{\mathrm{hs}}(v, x) + a^{\mathrm{es}}(T, v, x) \tag{4}$$

2.1. Repulsive Contribution

Following Boublik [18] and Mansoori et al. [19], the molar Helmholtz energy of a hard sphere mixture is given by

$$\frac{a^{\mathrm{hs}}}{RT} = \frac{[(3DE/F)\eta - (E^3/F^2)]}{1-\eta} + \frac{(E^3/F^2)}{(1-\eta)^2} + \left(\frac{E^3}{F^2} - 1\right)\ln(1-\eta) \tag{5}$$

where

$$D = \sum_{i=1}^{n} x_i\sigma_i, \qquad E = \sum_{i=1}^{n} x_i\sigma_i^2, \qquad F = \sum_{i=1}^{n} x_i\sigma_i^3 \tag{6}$$

with x_i and σ_i the mole fraction and hard sphere diameter, respectively, of species i. The reduced density η is defined as

$$\eta = b/4v \tag{7}$$

where v is the molar volume and b is the van der Waals covolume parameter

$$b = \tfrac{2}{3}\pi N_A F \tag{8}$$

with N_A the Avogadro number.

2.2. Dipolar and Quadrupolar Contributions

Stell et al. [20] and Rushbrooke et al. [21] developed a perturbation theory for dipolar hard spheres. They expressed the dipolar contribution to the Helmholtz energy (i.e., the difference between the Helmholtz energy of dipolar hard spheres and that of simple hard spheres) as an expansion,

$$\frac{a^{\mathrm{es}}}{RT}=A_2+A_3+\cdots \tag{9}$$

which can be rearranged to yield a closed-form expression using the following Padé approximant:

$$\frac{a^{\mathrm{es}}}{RT}=\frac{A_2}{1-(A_3/A_2)} \tag{10}$$

The second- and third-order perturbation terms, A_2 and A_3, are expressions involving the dipole or quadrupole moments and the hard-core diameter of the pair or triplet interactions. They are too extensive to give in this brief paper but are given in Refs. 7–9, as well as by Gubbins and Twu [22] and Larsen et al. [23].

The electric moments appear in reduced form as follows:

$$(\mu^*)^2=\frac{\mu^2}{\sigma^3kT}, \qquad (Q^*)^2=\frac{Q^2}{\sigma^5kT} \tag{11}$$

where μ is the dipole moment and Q is the quadrupole moment.

The validity and accuracy of the Padé approximation for the present examples were checked by comparison with Monte Carlo calculations. For the dipole–dipole case, the work of Patey and Valleau [24] was available. For quadrupole–dipole systems, new Monte Carlo calculations were made: Jiang and Pitzer [25]. In each case the agreement was good. Figure 1 displays an example for the Helmholtz energy $\Delta A/NkT$ for a mixture of equal-sized spheres with varying reduced quadrupole moments of component B and constant reduced dipole moment $(\mu_A^*)^2=3.0$. Examples at two mole fractions, $x_B=0.25$ and 0.5, are shown. For each case, appropriate series expansions were developed for convenient numerical calculations of thermodynamic properties. For practical calculations, it is convenient to recast equations using the van der Waals covolume b rather than the hard sphere diameter σ.

2.3. Perturbation Contribution

Following Dohrn and Prausnitz [26] and Anderko and Pitzer [27], a generalized van der Waals attractive term using a truncated virial expansion is used for the perturbation contribution.

$$\frac{a^{\mathrm{per}}}{RT}=-\frac{1}{RT}\left(a\rho+\frac{acb\rho^2}{4}+\frac{adb^2\rho^3}{16}+\frac{aeb^3\rho^4}{64}\right) \tag{12}$$

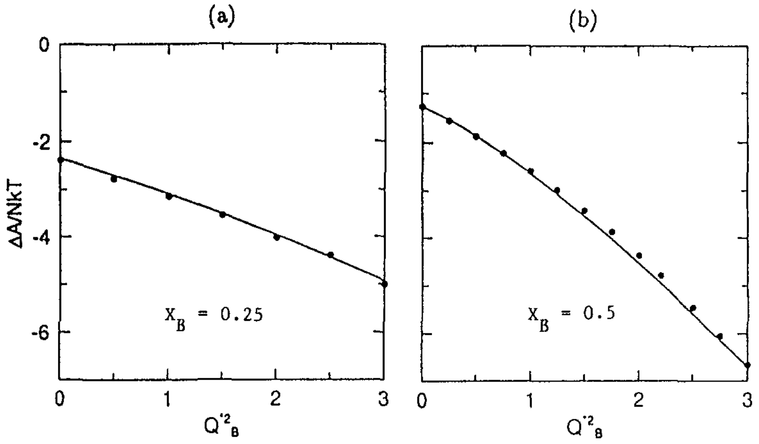

Fig. 1. Excess Helmholtz energy $\Delta A/NkT$ vs the square of the quadrupole moment of component $B(Q_B^{*2})$ for a mixture of dipolar ($\mu_A^{*2} = 3$) hard spheres and quadrupolar hard spheres of equal size at (a) $x_B = 0.25$ and (b) $x_B = 0.5$ calculated from simulations (●) and the Padé approximation (——).

Here b is the van der Waals covolume and the perturbation term parameters a, c, d, and e are required to represent the properties of pure water. For pure $CaCl_2$, only two parameters (a and b) are needed to describe vapor pressures and molar volumes of pure liquid $CaCl_2$.

For mixtures, we follow the technique developed by Anderko and Pitzer [27]. According to statistical mechanics, the second virial coefficient of a mixture should be a quadratic function of composition, the third virial coefficient a cubic, and so on. Therefore, the following mixing rules are adopted:

$$a = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j a_{ij} \tag{13}$$

$$acb = \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} x_i x_j x_k (ac)_{ijk}\, b_{ijk} \tag{14}$$

$$adb^2 = \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} \sum_{l=1}^{n} x_i x_j x_k x_l (ad)_{ijkl}\, b_{ijkl}^2 \tag{15}$$

$$aeb^3 = \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} \sum_{l=1}^{n} \sum_{m=1}^{n} x_i x_j x_k x_l x_m (ae)_{ijklm}\, b_{ijklm}^3 \tag{16}$$

Specific combining rules are needed to describe the cross terms from pure fluid parameters. For the van der Waals covolume parameters, the pair parameter b_{ij} is defined by Eq. (17) with the corresponding expressions for the higher terms.

$$b_{ij} = [(b_i^{1/3} + b_j^{1/3})/2]^3 \tag{17}$$

The parameter a_{ij} is related to pure fluid parameters according to the prescription of

$$a_{ij} = (a_i a_j)^{1/2} \alpha_{ij} \tag{18}$$

with corresponding expressions for the higher terms in γ_{ijk}, δ_{ijkl}, and ε_{ijklm}. These parameters correct for deviations from the combining rules for the cross terms.

Equations for the other thermodynamic properties (e.g., compressibility factor and fugacity coefficients) can be readily obtained by applying the usual thermodynamic identities to the Helmholtz energy presented in Sections 2.1–2.3. The compressibility factor is given by

$$Z = \rho \left[\frac{\partial(a^{\text{res}}/RT)}{\partial \rho} \right]_{T,\, n_i} + 1 \tag{19}$$

The fugacity coefficient is given by

$$\ln \phi_i = \left[\frac{\partial(na^{\text{res}}/RT)}{\partial n_i} \right]_{\rho,\, T,\, n_{j \neq i}} + (Z - 1) - \ln Z \tag{20}$$

Explicit expressions for hard sphere and perturbation contributions to the compressibility factor and fugacity coefficient (or chemical potential) are given in Refs. 7 and 9.

3. EXPERIMENTAL DATA FITTED AND EVALUATION OF PARAMETERS

For water the experimental value of the dipole moment 1.85 D [28] was adopted and other parameters adjusted to fit properties generated from the comprehensive equations of state of Hill [29]. The agreement was fully adequate for use for the electrolyte binaries. For pure NaCl and KCl no attempt was made to fit the vapor pressures or vapor densities. Both pure-salt and mixing parameters were adjusted to fit the experimental compositions and densities of equilibrium vapor and liquid phases and single-phase densities of the mixed fluids. For the coexisting phases of NaCl–H_2O

up to 773 K, the very extensive data had been evaluated by Bischoff [30] and his values were used. At higher temperatures there are only a few values at pressures from 500 bar upward from the synthetic fluid inclusion method. These and other sources yielding single phase data are discussed and cited in Refs. 7 and 8. Unfortunately, the vapor pressure of pure NaCl was not included.

For $CaCl_2$ the quadrupole moment was estimated from the known Ca–Cl distance, 2.51 Å, and an approximate correction for polarization. The result was -22.84×10^{26} esu. Of the various densities and other properties cited [9], the most important are the compositions of the saturated liquids of Bischoff et al. [31] and Tkachenko and Shmulovich

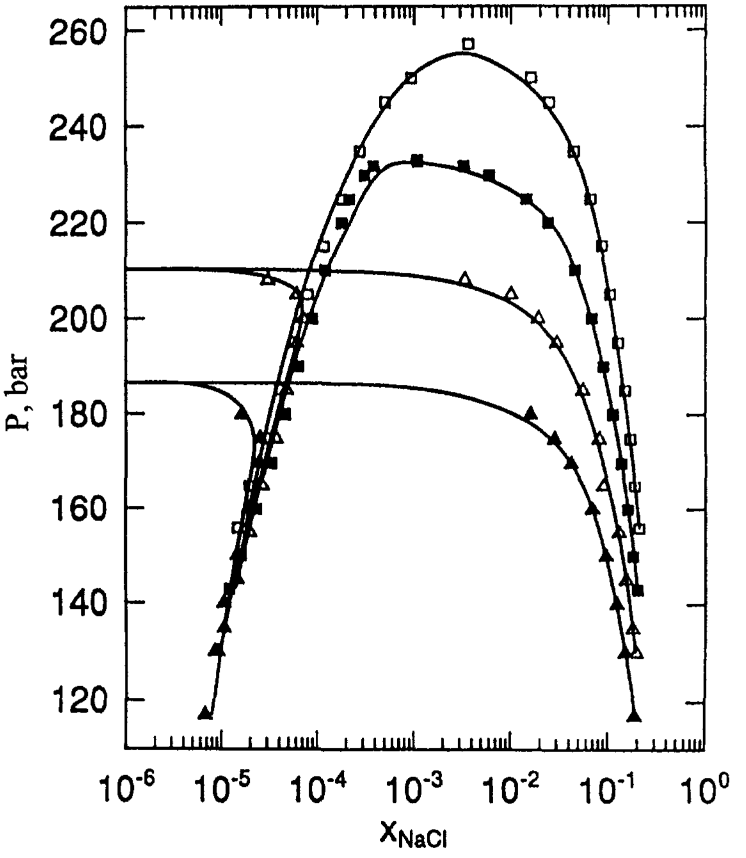

Fig. 2. Comparison of vapor–liquid equilibria calculated from the equation of state (lines) with the smoothed data reported by Bischoff [30] at $T = 633.15$ K (▲), 643.15 K (△), 653.15 K (■), and 663.15 K (□).

[32] at supercritical temperatures. In this case the vapor pressure of the pure liquid $CaCl_2$ was used and extrapolated to temperatures below the melting point.

Further details on the evaluation of parameters are given in Refs. 7–9, where the full sets of parameters are listed.

4. RESULTS AND DISCUSSION

For this rather brief review it is not possible to give detailed tables of calculated properties or full sets of all figures showing the results in comparison with experimental data. Figures 2–4 present examples for two-phase data for different ranges of temperature for the system NaCl–H_2O.

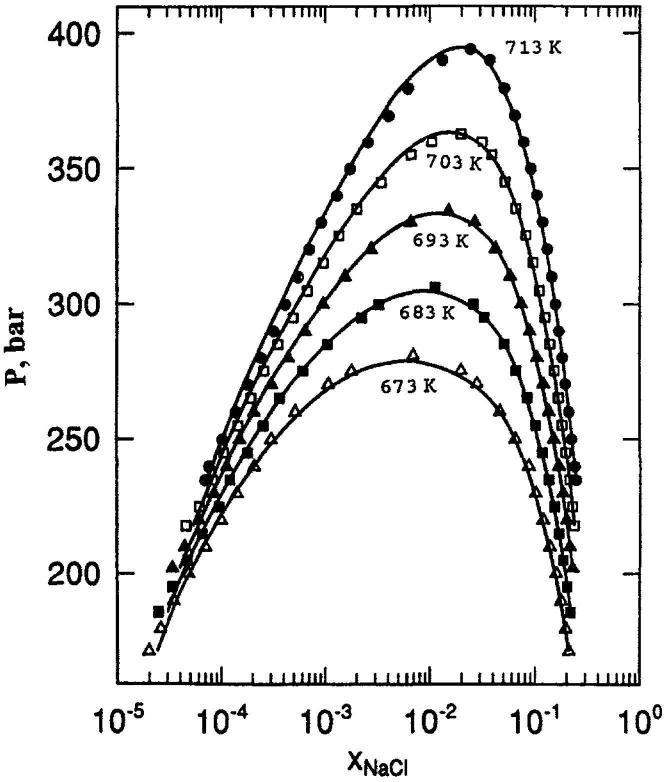

Fig. 3. Comparison of vapor–liquid equilibria calculated from the equation of state (lines) with the smoothed data reported by Bischoff [30] at $T = 673.15$ K (△), 683.15 K (■), 693.15 K (▲), 703.15 K (□), and 713.15 K (●).

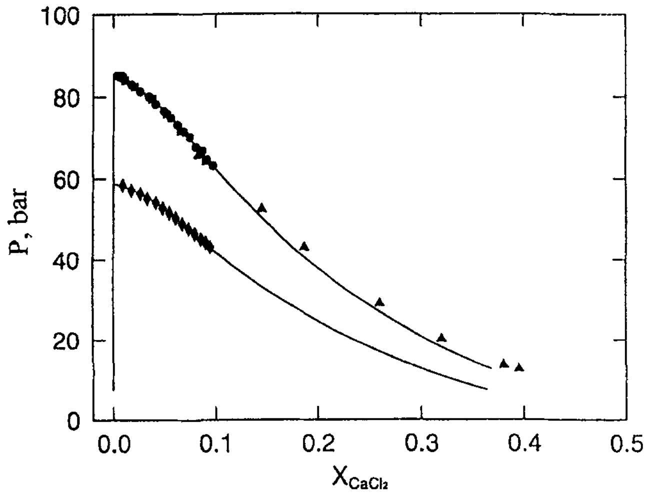

Fig. 4. Comparison of saturated vapor pressures of aqueous $CaCl_2$ solutions calculated from the equation of state (——) vs experimental data by Wood et al. [33] at 548.15 K (◆) and by Wood et al. (●), Zarembo et al. [34] (■), and Ketsko et al. [35] (▲) at 573.15 K.

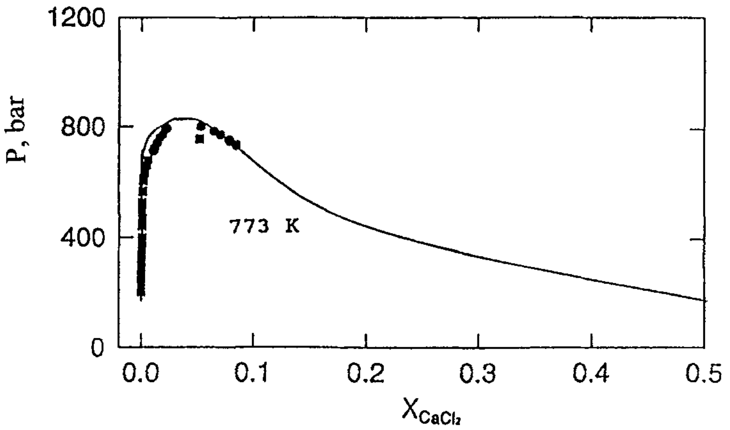

Fig. 5. Vapor–liquid equilibria of aqueous $CaCl_2$ solutions calculated from the equation of state (——) vs experimental data by Tkachenko and Shmulovich [32] (●) and by Bischoff et al. [31] (■) at 773.15 K.

Figure 2 is especially interesting since it includes both near-subcritical and near-supercritical isotherms. Figure 3 shows typical sets of higher temperature data. Above 773 K there are only data from the synthetic fluid inclusion method. Figures 4 and 5 show examples of two-phase data for $CaCl_2$–H_2O. Only at 773 K is the vapor phase composition shown in detail. At lower temperatures there is substantial hydrolysis in the vapor as discussed above, but this should not affect significantly the liquid values on Fig. 4. Extensive arrays of single-phase density data were also fitted satisfactorily.

The equation for $CaCl_2$–H_2O is important for consideration of the range of type I behavior since it is valid for the full composition range including pure $CaCl_2$. The critical temperature for $CaCl_2$ is undoubtedly higher than that of NaCl and the ratio to T_c of H_2O certainly exceeds 5. But the complexity of the numerous perturbation terms makes further interpretation difficult. It will be interesting to investigate the behavior patterns of equations with only the dipole and quadrupole terms. For such cases one can determine the limits, if any, on the ratio of T_c values for type I behavior.

ACKNOWLEDGMENTS

The excellent research of Andrzej Anderko and Shaoyi Jiang forms the basis for this review. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division and Division of Engineering and Geosciences, of the U.S. Department of Energy under Contract DE-AC03-76SF00098.

REFERENCES

1. K. S. Pitzer, *J. Chem. Thermodyn.* **25**:7 (1993).
2. D. G. Archer, *J. Phys. Chem. Ref. Data* **21**:793 (1992).
3. R. T. Pabalan and K. S. Pitzer, *J. Chem. Eng. Data* **33**:354 (1988).
4. H. F. Holmes, R. H. Busey, J. M. Simonson, and R. E. Mesmer, *J. Chem. Thermodyn.* **26**:271 (1994).
5. H. F. Holmes and R. E. Mesmer, *J. Chem. Thermodyn.* **28**:1325 (1996).
6. K. S. Pitzer and R. T. Pabalan, *Geochim. Cosmochim. Acta* **50**:1445 (1986).
7. A. Anderko and K. S. Pitzer, *Geochim. Cosmochim. Acta* **57**:1657 (1993).
8. A. Anderko and K. S. Pitzer, *Geochim. Cosmochim. Acta* **57**:4885 (1993).
9. S. Jiang and K. S. Pitzer, *AIChE J.* **42**:585 (1996).
10. F. J. Armellini and J. W. Tester, *Fluid Phase Equil.* **84**:123 (1993).
11. J. L. Bischoff, R. J. Rosenbauer, and R. O. Fournier, *Geochim. Cosmochim. Acta* **60**:7 (1996).
12. P. H. van Konynenburg and R. L. Scott, *Phil. Trans. Roy. Soc.* **A298**:495 (1980).
13. A. H. Harvey, *J. Chem. Phys.* **95**:479 (1991).

14. G. Orkoulas and A. Z. Panagiotopoulos, *J. Chem. Phys.* **101**:1452 (1994).
15. Y. Guissani and B. Guillot, *J. Chem. Phys.* **101**:490 (1994).
16. K. S. Pitzer, *J. Phys. Chem.* **99**:13070 (1995).
17. K. S. Pitzer, *J. Chem. Phys.* **104**:6724 (1996).
18. T. Boublik, *J. Chem. Phys.* **53**:471 (1970).
19. G. A. Mansoori, N. F. Carnahan, K. E. Starling, and T. W. Leland, *J. Chem. Phys.* **54**:1523 (1971).
20. G. Stell, J. C. Rasaiah, and H. Narang, *Mol. Phys.* **23**:393 (1972); **27**:1393 (1974).
21. G. S. Rushbrooke, G. Stell, and J. S. Hoye, *Mol. Phys.* **26**:1199 (1973).
22. K. E. Gubbins and C. H. Twu, *Chem. Eng. Sci.* **33**:863 (1978).
23. B. Larsen, J. C. Rasaiah, and G. Stell, *Mol. Phys.* **33**:987 (1977).
24. G. N. Patey and J. P. Valleau, *J. Chem. Phys.* **61**:534 (1974).
25. S. Jiang and K. S. Pitzer, *J. Chem. Phys.* **102**:7632 (1995).
26. R. Dohrn and J. M. Prausnitz, *Fluid Phase Equil.* **61**:53 (1990).
27. A. Anderko and K. S. Pitzer, *AIChE J.* **37**:1379 (1991).
28. A. L. McClellan, *Tables of Dipole Moments* (Freeman, San Francisco, 1963–1989).
29. P. G. Hill, *J. Phys. Chem. Ref. Data* **19**:1223 (1990).
30. J. L. Bischoff, *Am. J. Sci.* **291**:309 (1991).
31. J. L. Bischoff, R. J. Rosenbauer, and R. O. Fournier, *Geochim. Cosmochim. Acta* **60**:7 (1996).
32. S. T. Tkachenko and K. I. Shmulovich, *Dokl. Akad. Nauk.* **326**:1055 (1992).
33. S. A. Wood, D. A. Crear, S. L. Brantley, and M. Borcsik, *Am. J. Sci.* **284**:668 (1984).
34. V. I. Zarembo, S. N. Lvov, and M. Yu. Matuzenko, *Geochem. Int.* **17**:159 (1980).
35. V. A. Ketsko, M. A. Urusova, and V. M. Valyashko, *Russ. J. Inorg. Chem.* **29**:1398 (1984).
36. Y. G. Zhang and J. D. Franz, *Chem. Geol.* **74**:289 (1989).