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Thermodynamic Properties of Aqueous Solutions at High Temperatures: Needs, Methods, and Challenges[1]

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Needs exist for thermophysical data on aqueous solutions at high temperatures and pressures in many different areas of science and engineering. These needs are reviewed and references are given to recent relevant conference proceedings, reviews, and papers. Aspects and drawbacks are discussed of current methods, which are most often extensions to high temperatures of methods developed for liquid water. The challenges posed by engineering needs and by new phenomena resulting from experimental breakthroughs are discussed. Some examples are given of alternative approaches more suitable for highly compressible media.

KEY WORDS: aqueous solutions; chemical industry; Debye-Hückel limiting law; excess properties; geology; Helmholtz free energy; high pressure; high temperature; power industry; standard states.

1. INTRODUCTION

Attempting to describe the present status of high-pressure high-temperature thermophysical properties research in aqueous solutions is somewhat comparable with, singlehandedly, trying to come to grips with an octopus. This field of research has an unwieldy appearance because the requirements for data and models come from very disparate groups, ranging from geologists and deep-ocean scientists, to the chemical industry and fossil- and nuclear-power engineers, to environmentalists of various colors. Fundamental work has lagged far behind that devoted to solutions in ordinary liquid water. The reason is that just those features that make ordinary liquid water such

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a fascinating substance, namely, its hydrogen bonding and ice-like local structure, high dielectric constant, and electrolytic properties, all tend to diminish or disappear when the temperature is raised. In this review, however, I argue that there are plenty of rewarding problems that scientists could address in high-temperature aqueous solutions. There is another factor, this one historical, that has made it hard to progress in the formulation of the properties of high-temperature aqueous solutions. For practical reasons, the thermodynamics of fluid mixtures and the physical chemistry and chemical thermodynamics of electrolyte solutions have taken different paths since early in this century. When methods that were quite succesful in aqueous solutions at ambient temperatures are extended to higher temperatures, numerous difficulties are encountered that point to reduced usefulness of the low-temperature methods.

I would not have accepted the task of preparing this paper if I felt negative about this field of research. On the contrary, positive signs abound. First, breakthroughs in experimental techniques have revealed new phenomena and accurate data that motivate construction of better models and that will serve as stringent tests. Second, a convergence of the various disciplines is going on, as is evident from the attendance and topics at a number of recent conferences to which I refer. The needs of geologists and power chemists begin to overlap: where the first usually deal with concentrated brines, and the latter with water parts per billion pure, the power chemists have discovered that in crevices in the plant where the flow is stagnant, high concentrations can build up, often with disastrous consequences. Scientists are beginning to realize that the high compressibilities associated with near-critical dilute mixtures give rise to huge anomalies in the thermodynamic properties of aqueous solutions in a wide range around the critical point of steam and that aqueous solutions share this feature with other fluid mixtures, but that there are additional challenging questions regarding the interplay of dielectric constant, degree of dissociation, and critical fluctuations that need to be addressed. Finally, there is a clamor for data, mostly by government and trade organizations and by the private companies that are developing computerized data bases.

In my view, the time is ripe for progress with high-temperature aqueous systems. I do not expect this progress to be revolutionary. Concepts and methods developed in other contexts will be adapted and applied as part of the ongoing process of convergence. Furthermore, the overlapping interests of geology, chemical, and power industry will be recognized and forces joined for the good of all. A number of recent conference proceedings that I refer to are witness that this new era has already begun.

In the overview that follows, I have not even tried to be complete. My own preferences and limitations of expertise have determined the topics to be emphasized. Thus, there will be scant attention to the brines, multiple solid–liquid phase equilibria, and manifold other subjects dear to the geologist. Examples are in the areas of dilute solutions, with a minimum of chemistry. The lack of breadth is, in part, compensated by citing references to relevant reviews. My hope is that this paper will be useful because it stresses the general and universal, rather than the particular.

2. THE NEEDS FOR PROPERTY DATA

The needs for thermophysical property data for high-temperature aqueous systems arise principally from geology, including mineralogy; mining of minerals, gas, coal, and oil; and chemical and power industry. Computer-based models being developed for applications in these various areas are relentless in their demand for more and better input data for thermophysical properties [1]. We discuss the needs of each constituency; a review of industrial interests by Wilhoit [2] has been very useful.

Geologists deal with complex solid–liquid phase equilibria and chemical reactions in concentrated brines at pressures that can exceed 400 MPa and at temperatures that far exceed the critical temperature of steam (374°C). Geological interests have indeed driven the early high-pressure research of aqueous systems in the United States, with Kennedy as one of the best-known examples. To this day, geologists such as Potter, Bischoff, and Rosenbauer have performed demanding phase-equilibrium experiments in near-critical aqueous solutions, while Helgeson and his group model complex multicomponent and chemically active high-temperature solutions. For examples, see Refs. 3–6.

Following loosely the classification of Wilhoit [2], we now discuss the needs of industry.

(1) With the advent of powerful computers, process simulation in the chemical industry, for chemical synthesis and separations, for heat and mass balance calculations, is bypassing the construction of costly pilot plants. Process simulators need to be fed data or predictions for numerous property values at every point of the process stream calculations. International unions, such as IUPAC and CODATA, government, trade associations, universities, private companies, and individuals are engaged in providing the models, programs, and software needed to satisfy the hunger for data. Proceedings of recent conferences [7–9], as well as the software demonstrations at the 10th Symposium on Thermophysical Properties, testify to the increasing importance of computerized data bases.

(2) Pollution control, specifically of gaseous and wastewater effluents

in the chemical and power industry, is becoming of overriding concern in the industrialized world. More stringent regulations provide strong motivation for developing models for the thermodynamics of chemically reactive species in water and water vapor [7–9]. These temperatures are not high from the perspective of the present paper. Nevertheless, the chemical engineer is forced to extend his modeling to 100°C in liquid water and even higher in the vapor phase. The few cases where a fundamental approach has been attempted in order to describe the temperature-dependent chemical equilibria in systems such as water–carbon dioxide–ammonia [10] are humbling experiences: the complexity and the amount of effort required to solve a practical problem, with no new principles involved, make us aware of the lack of progress that can result because of gaps between fundamental understanding and practical application.

(3) Metallurgy, electrochemical processes, and corrosion are at the core of what keeps an industrialized world going; here we cannot even begin to cover them in any depth. The presence of water as a solvent or reaction agent at high temperatures and/or pressures is essential in all these cases, and the water chemistry involved keeps a large number of scientists and engineers extremely busy [1, 7–9].

(4) The power industry forms the basis of industrial activity throughout the world. Most power is generated in steam plants fueled by gas, oil, or coal. In order to improve efficiency, the maximum operating temperatures now approach 650°C in some of the newer plants. Even though the feed water for power plants is the cleanest water in the world, with impurity levels no higher than a few parts per billion, the strong solvent powers and reactivity of near- and supercritical steam and the need for additives in order to control the corrosion that might result make for the presence of a large number of species. Concentration of these species in cracks and crevices is a power engineer's nightmare. The quest for solubility and deposition predictions in mixed electrolyte solutions is strong [11]. It is a major concern of organizations such as the Electric Power Research Institute (EPRI) in the United States and the International Association for the Properties of Steam (IAPS). Nuclear power generation, although generally not carried out at extreme temperatures, requires worst-case scenario calculations in which the fate of both solids and gases released in an accident needs to be forecast. It therefore demands data for both solid and gas solubilities.

(5) The production of energy alternatives such as synthetic gas and fuel and the hydrolysis of heavy oils and tar require knowledge of properties of aqueous mixtures at high temperatures, in some cases at substantial pressures.

Tertiary oil recovery by injection of steam into deep wells will require prediction of the multiple phase equilibria to be expected at elevated temperatures and in the presence of brines and heavy and light hydrocarbons.

3. DATA SOURCES

Within the scope of this paper, it is obviously impossible to do justice to the wealth of data acquired for aqueous systems in more than a century of effort. Even the restriction to data above 100°C would still lead to a project that is out of bounds. The review by Helgeson et al. [12] gives a very large number of useful references. I confine myself to explicit mention of some of the most productive groups and of the most recent experiments in near- and supercritical steam.

Thermodynamic behavior of aqueous electrolytes is traditionally investigated in terms of excess or apparent molar properties, which are defined and discussed in Section 4. The important feature to mention here is that they involve comparing the properties of the solution with those of the pure solvent *at the same pressure and temperature.* This is very convenient choices of variables in incompressible liquid water. Although, as we discuss in Section 4, the advantage of the apparent molar properties diminishes as the solvent becomes compressible, electrolyte chemists have devised ingenious and accurate methods for measuring them even in supercritical aqueous solutions. Well-known examples are the calorimetric experiments of the Oak Ridge group, where heats of dilution of many electrolyte solutions have been measured with exemplary accuracy up to 300°C; see, for instance, Ref. 13. The recent calorimetric experiments of Wood and collaborators have drawn much attention. An experimental breakthrough, in which clever use was made of the new possibilities offered by high-pressure chromatography equipment, led to accurate measurements of apparent molar heat capacities of near- and supercritical electrolyte and nonelectrolyte aqueous solutions up to 720 K; see, for instance, Refs. 14–16.

Physical chemists who entered the field of high-temperature aqueous systems from experience with other fluid mixtures, on the other hand, tend to treat the aqueous system as a special type of fluid mixture and use the PVT, VLE, and caloric methods developed for that purpose. The best example of this approach is the school of E. U. Franck in Karlsruhe. The methods Franck and his collaborators have developed are those suitable for ordinary fluid mixtures but pushed to the extreme conditions of pressure, temperature, and corrosiveness typical of supercritical electrolyte solutions; for a review, see Ref. 17. Both groups, the Oak Ridge group and the Karlsruhe group, have at all times realized that aqueous solutions are special. Some of the finest and unique work on the conductivity of high-temperature aqueous solutions has sprouted from joint effort of these groups [18]; Franck's recognition of the extraordinary importance of the dielectric constant of water for understanding aqueous solutions led him to perform the high-pressure studies of this property [19] that are now basic to our description of high-temperature aqueous electrolytes.

Systematic studies of one particular system by a variety of methods are few. Rather than surveying fragmentary work on numerous systems, it seemed more instructive and worthwhile to concentrate on the one system that has been thoroughly studied: NaCl in H_2O. In at least one respect this system is unusual: as far as the experiments can tell, there appears to be complete miscibility of the two components, even though their critical temperatures are a factor of four or more apart. Experimental data have been reported by both geochemists and physical chemists, on properties as diverse as critical lines [3, 20], equation of state [3, 21], dew-bubble curves [5], conductivity [18], heat of dilution [13], and apparent molar heat capacity [14, 15], over large temperature and pressure ranges, up to 1000 K and 400 MPa. The challenges posed by the task of making sense of this body of data are the topic of Section 5.

The properties of nonelectrolytic aqueous systems are of interest in their own right. Here again, the work by Franck has spearheaded a flourish of subsequent experimental activity; for a recent account, see Ref. 22.

4. METHODS

4.1. Excess Properties

The formulation of the thermodynamics of liquid mixtures and of aqueous solutions are traditionally performed in terms of excess properties, which indicate the difference of the properties of the real mixture (solution) and that of an appropriately defined ideal mixture (solution) at the same temperature and pressure. The definitions used for mixtures and solutions are different and reflect the fact that in mixtures one is usually interested in the entire composition range, whereas aqueous elctrolyte solutions are mostly studied at low mole fractions and the pure-solute state is usually irrelevant. For the excess volume, the symmetric convention for the liquid mixture and the asymmetric convention for the solution are schematically indicated in Figs. 1 and 2. The symmetric convention, Fig. 1, uses the molar volumes of the pure components, at the same pressure and temperature, weighted with their respective mole fractions, as a basis for comparing with the molar volume of the mixture. In elctrolyte solutions, the excess volume is calculated for a solution of m mol of salt in 1 kg of solvent as the dif-

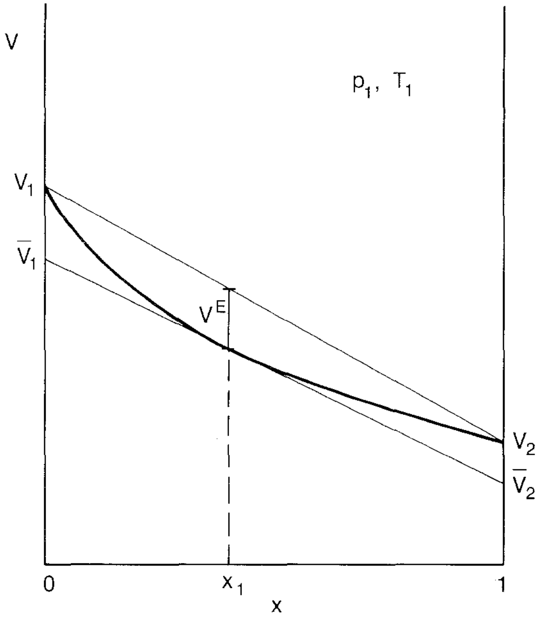

Fig. 1. Molar volume V of a mixture as a function of the mole fraction x, plotted at constant pressure p_1 and temperature T_1. For the composition x_1, the tangent construction defining the partial molar volumes $\bar{V}_1$ and $\bar{V}_2$ and the chord construction leading to the excess volume V^E are shown in the symmetric convention.

ference of the volume of the actual solution and the volume according to a straight line drawn tangent to the actual volume curve at the origin, $m=0$ (Fig. 2), all at the same pressure and temperature. The volume so obtained at $m=1$ is the hypothetical ideal solution volume $\bar{V}_2^{\infty}$, the infinite-dilution partial molal volume of the solute. For an m-molar solution, the partial molal volume of the solute, $\bar{V}_1$, that of the solute, $\bar{V}_2$, and the apparent molar volume of the solute, ${}^{\varphi}\bar{V}$, are defined as for the ordinary mixture, except that the $m=1$ state replaces the $x=1$ state; see Fig. 2. Therefore we have

$$m^{\varphi}V=(M_s m+1)v_{\text{soln}}-v_w \qquad (1)$$

where M_s is the molecular weight of the salt in kg, v_{soln} is the specific volume of the solution, and v that of water, both in $\text{dm}^3 \cdot \text{kg}^{-1}$, and m is the molality. Equation (1) uses the volume as an example of the definition of an apparent molar property. Apparent molar enthalpy and specific heat are defined analogously.

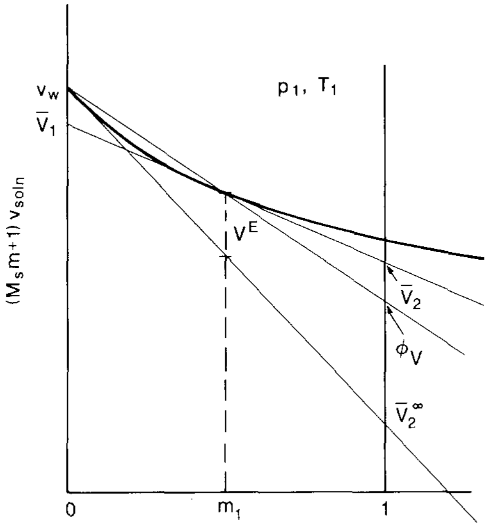

Fig. 2. The volume of a solution of $M_s m$ grams of salt in 1 kg of water is plotted, at constant temperature and pressure, as a function of the molality m. For the molality m_1, the tangent construction defining the partial molar volumes $\bar{V}_1$ and $\bar{V}_2$, the chord construction defining $^{\varphi}V$, the infinite-dilution partial molar volume of the solute, $\bar{V}_2^{\infty}$, and the excess volume V^E, are indicated in the asymmetric convention, with $m = 1$ as a reference composition.

4.2. Modeling of Electrolyte Solutions

This is obviously not the place to review all models that have been designed for aqueous solutions during the past centry. For an extensive review with numerous references, see Helgeson et al. [12]. Recent reviews by Pitzer [23] and by Friedman [24] are also very useful. Here, I restrict my comments to the general structure of models that are widely used for data-fitting and predictions and indicate, in Section 4.3, where one can expect difficulties when applications are made at temperatures near to or exceeding the critical temperature of steam. Usually, a formulation is given of the excess Gibbs free energy and derived excess properties, especially osmotic and activity coefficients. The interaction of the charged species in the solution is expressed along isotherm-isobars by means of the Debye-Hückel limiting law and empirical correction terms that are polynomials in m:

$$G^E_{DH}/n_w RT = -A_\varphi(4I/b)\ln(1+bI^{1/2}) + O(m^2) \qquad (2)$$

Here n_w is the number of moles in 1 kg of water, b an ion size parameter, and I is the ionic strength, defined as

$$I = \sum_i m_i z_i^2/2 \tag{3}$$

where the sum is over species i of ions present, z_i the ionic valency, and m_i its molality. The product $I \ln(1 + bI^{1/2})$ is proportional to $m^{3/2}$ for small m. The Debye-Hückel coefficient A_φ is defined in terms of properties of pure water at the same pressure and temperature, as

$$A_\varphi = \frac{1}{3}\left(\frac{2\pi N_A \rho_w}{1000}\right)^{1/2} (e^2/\varepsilon_w kT)^{3/2} \tag{4}$$

with ρ_w the density of pure water, in $kg \cdot m^{-3}$, at the given pressure and temperature, ε_w the dielectric constant of pure water, N_A Avogadro's number, R the gas constant, and e the electron charge. This representation, introduced by Pitzer and applied by him to NaCl in water at elevated temperatures (see, for instance, Ref. 25), has received wide acceptance and is incorporated in many of the computer software packages that are being marketed [1].

The contribution to ${}^{\varphi}G$ due to interaction of ions with the solute is often expressed by means of the Born model and variants thereof [12, 14]:

$${}^{\varphi}G_{el} = -(N_A e^2/8\pi\varepsilon_0)(R_+^{-1} + R_-^{-1})(1 - 1/\varepsilon_w) \tag{5}$$

where R_+ and R_- are the radii of cation and anion, respectively, and ε_0 is the permittivity of vacuum. ${}^{\varphi}G_{el}$ represents the free energy of charging a mole of hard-sphere ions in a continuous dielectric with dielectric constant ε_w [14].

4.3. Problems Caused by High Compressibility of the Pure Solvent

The extension of the methods referred to above runs into a number of difficulties at pressures and temperatures where pure steam is highly compressible. To make this point, we first examine what happens to excess properties, again using the excess volume as an example. Then, we investigate problems associated with particular terms occurring in the models referred to.

One problem one encounters is that, at a given pressure and temperature, it is possible for the solvent to be in a gaseous state while the solute is in the liquid state. This leads to unusual behavior of the excess volume (or enthalpy). A perusal of Fig. 3 will make it obvious why the excess volume curve is discontinuous in slope as a phase boundary is crossed [26]. A much more subtle problem arises, however, in the case

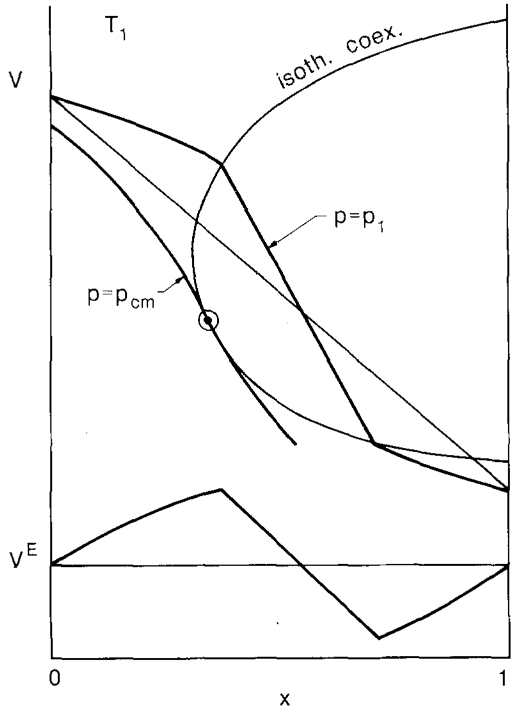

Fig. 3. When, on an isotherm isobar p_1, T_1, a two-phase region is traversed at a temperature exceeding the critical temperature of the solvent, the excess volume as a function of composition displays two discontinuities in slope.

sketched in Fig. 4, when the solvent is at its critical point. For fluid mixtures the volume and therefore, also, the excess volume on the critical isotherm-isobar have vertical tangents at the solvent's critical point [27]. This implies that the infinite-dilution partial and apparent molar volumes of an involatile solute diverge to minus infinity. The resulting infinity in the initial slope of the excess volume may not be a serious problem once one is aware of it, but it precludes the formulation of V^E in terms of a virial-type expression. The infinity of the partial molar volume of the solute, however, has dire consequences for the excess volume as defined for aqueous electrolytes (Fig. 2) because the hypothetical 1 M standard state disappears to minus infinity. Since the actual volume is finite, this implies that the excess volume is infinite everywhere on the critical isotherm-isobar.

One can take the position that this is an accident happening at an isolated point. This, however, is not true. $\bar{V}_2$ is proportional to the compressibility of the pure solvent [27]. This compressibility is strongly

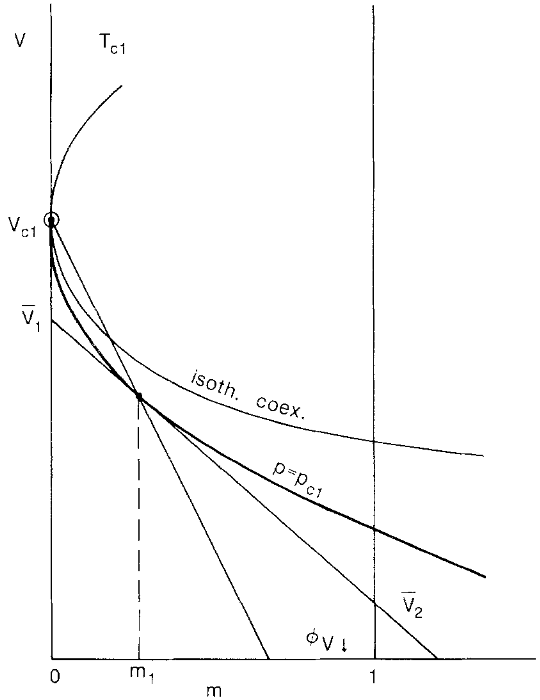

Fig. 4. At the solvent's critical point, the critical isotherm-isobar, at p_{c1}, T_{c1}, has a vertical tangent. This leads to a divergence of the infinite-dilution partial and apparent molar properties of the solute.

divergent and assumes large values in a substantial range around the critical point of steam, thus driving up the values of V^E (Fig. 2). The constant-pressure specific heat of steam, a quantity which diverges as the compressibility, can be used to predict in which range of pressure and temperature anomalous excess properties have to be expected due to the large compressibility of the pure solvent. Contour plots in the $p-T$ plane for c_p equal 10 and 20 $\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$, respectively, are shown in Fig. 5. At these temperatures, the ideal-gas specific heat of steam c_p^0 equals only about 2 $\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$. Thus, the hypothetical 1 M standard state is not a useful convention for aqueous solutions at conditions of p and T when pure steam is near-critical. Pitzer and co-workers, on various occasions, have used alternative standard states.

Everything we have said about the excess volume and apparent and partial molar volumes applies to the excess enthalpy or heat of dilution, since volume and enthalpy have similar critical anomalies [27]. For higher

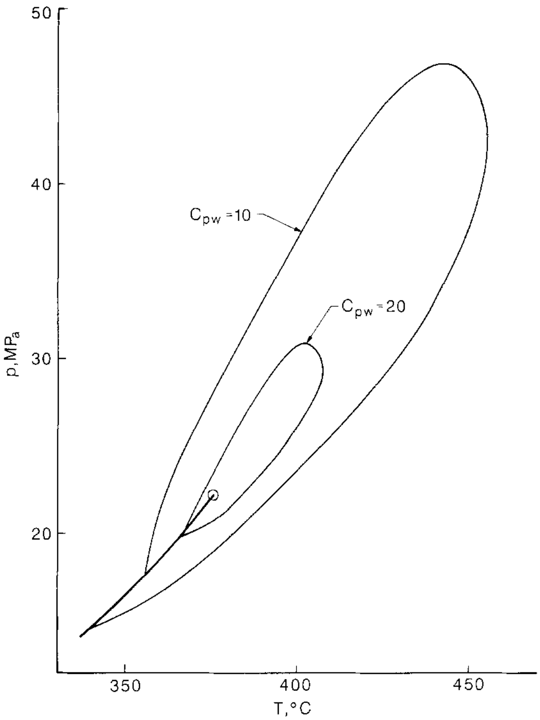

Fig. 5. Contours of constant c_p, in J · kg^{-1} · K^{-1} for pure water in the $p-T$ plane. In the same units, the ideal-gas value is about 2. These high values reflect the large compressibility of near- and supercritical steam.

derivatives, such as the excess specific heat, the reference state for the pure solvent diverges, thus adding to the complications.

Let us now discuss what happens with the formulations of the excess or apparent molar Gibbs free energies, Eqs. (2), (4), and (5). These expressions, at constant pressure and temperature, are of the form

$$\Delta G = A\{\rho_w, T, \varepsilon_w(\rho_w, T)\} m^p \tag{6}$$

with the prefactor a function of the dielectric constant of pure water at the same pressure and temperature and of the density and temperature of pure water; $\Delta G = {}^{\varphi}G_{\mathrm{el}}$ and $p=1$ for the Born equation; $\Delta G = G^{\mathrm{E}}_{\mathrm{DH}}$ and $p=3/2$ for the Debye-Hückel limiting law. In taking the temperature and pressure derivatives of Eq. (6) for calculating the Debye-Hückel contribution to the heat of dilution and excess volume, one needs to differentiate the prefactor. The dielectric constant being a smooth function of density [19], the derivative of the prefactor is proportional to the compressibility or expansion coefficient of the pure solvent. Both properties diverge strongly, so that an infinity results in, respectively, apparent or excess volumes and enthalpies on the critical isotherm-isobar. This infinity cannot cancel the infinity introduced by the hypothetical standard state, because the latter is independent of the presence of ions whereas the former is not. The infinities introduced by using relations of the form of Eq. (6) at the solvent's critical point are therefore not the consequence of infinities in the values or slopes of the reference states. Rather, they are due to the perturbative character of these expressions, where prefactors involving pure-solvent properties are multiplying powers of the molality. Because the pure-solvent Gibbs free energy is a nonanalytic function of its independent variables at the solvent's critical point, with strongly diverging second derivatives, such perturbative schemes must fail. The Helmholtz free energy, however, has finite or at most weakly diverging second derivatives, and therefore does not give rise to the problems noted above [28]. It is interesting to note that Debye and Hückel, in their original paper, introduced the limiting law into the *Helmholtz* free energy [29].

4.4. Modeling of Nonelectrolyte Solutions

Although the presentation, so far, has focused on aqueous electrolyte solutions, it seems fair to add at least a few words about nonelectrolyte

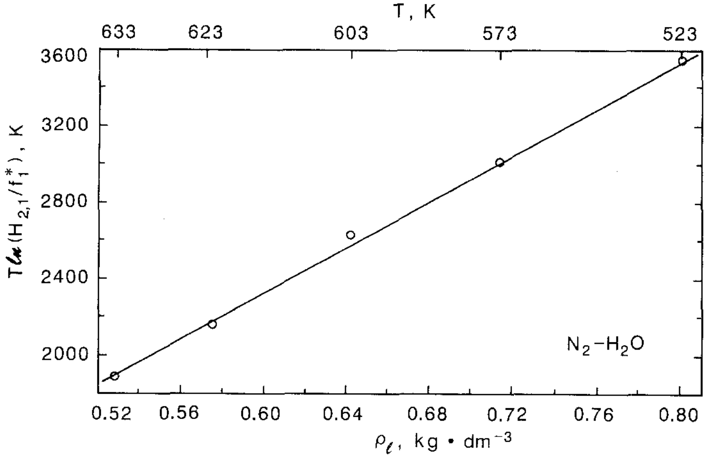

Fig. 6. For the system nitrogen in water, the quantity $T\ln(H_{2,1}/f_1^*)$ is a linear function of the pure-water liquid density ρ_ℓ over a large temperature range. At the top, the corresponding temperatures are indicated. The linear relation permits extrapolation to the critical point. This linear relation has been tested for several other gases, and, in addition, appears to hold quite well for the partition coefficient [31].

gaseous solutions. For a recent review, we refer to Crovetto and Fernandez-Prini [30]. The Argentinian group is a leading one in both experiment and theory. A particularly interesting topic is that of the behavior of the solubility, partition coefficient, and Henry's constant as the critical point of water is approached. For all solute gases, it is found that at increasing temperatures, Henry's constant $H_{2,1}$ passes through a maximum in the vicinity of the boiling point of water and then declines with increasing slope. The infinite-dilution partition coefficient $\mathrm{Lim}[y/x]_{y=0}$, with y the mole fraction in the vapor and x in the liquid, decreases rapidly to the value 1 at the critical point. The solubility passes through a minimum and then increases to a finite limit. Very recently Japas and Levelt Sengers have demonstrated that, near the solvent's critical point, thermodynamics requires both $T\ln(H_{2,1}/f_1^*)$, with f_1^* the fugacity of pure water, and the infinite-dilution partition coefficient to correlate linearly with the pure-solvent liquid density [31]; see Fig. 6. It was found that, for water as a solvent, the linear range is well over 100°C in extent for several gaseous solutes, which implies considerable predictive power for gas solubilities in high-temperature water.

5. CHALLENGES

In formulating the properties of high-temperature aqueous electrolytes, we face a large number of tasks, only one of which is relatively easy to fulfill. The easy task is to remedy the problem discussed in the preceding section. We need to wean ourselves from excess properties defined at constant pressure and temperature. The simplest way to do this is by means of the techniques that have been succesfully used in nonelectrolyte mixtures, where the Helmholtz free energy $A(V, T, x)$ and the equation of state $P(V, T, x)$ are the natural framework from which all other properties are derived. Franck (private communication) suggested to extend his Helmholtz free energy description for aqueous nonelectrolyte systems [22] to high-temperature NaOH–H_2O. Tanger and Pitzer [34], and Gallagher and Levelt Sengers [35] developed Helmholtz free energies for high-temperature NaCl–H_2O. There is a difference in philosophy between the first approach and the other two that is worth pointing out. Franck and co-workers use a mixture equation of state with a modest number of adjustable parameters. The requirement that this equation represent pure water accurately is a hard one to fulfill. If pure water is not represented closely, neither will be the relatively dilute mixtures that are of most practical interest. The other two groups use as a reference the Helmholtz free energy of pure water, which is accurately known and formulated [33]. Few additional parameters are then required to get an adequate representation of even an effective third derivative such as the apparent molar heat capacity [34, 35]. This seems the preferable way to model dilute aqueous solutions. All approaches mentioned are equally applicable to nonelectrolyte solutions, see [35], where the apparent molar heat capacity of argon in steam is modeled quantitatively. The fact that close fits are obtained to a variety of experimental data with models that ignore the presence of charges completely illustrates an important point made before, namely, that the near-criticality of the solvent is the principal source of the reported large anomalies [27, 28]. These first attempts at modeling aqueous systems with a Helmholtz free energy, however, leave a number of problems unsolved, one of them being that of the ideal-gas properties of the pure solute at the temperatures of interest, a question that the authors have sidestepped or ignored. In a sequel to their work, Tanger and Pitzer have begun to incorporate dissociation into their model [36].

A challenge is certainly posed by the chemistry. Although the degree of dissociation of salt such as NaCl presumably is low at the critical point of steam, the salt must dissociate in very dilute states, and also at densities of about twice the critical or higher, when the dielectric constant rises. So far, thermodynamic models for compressible reactive mixtures have been mostly confined to dilute gases. Attempts at dealing with reactive dense mixtures, of which Ref. 10 is an example, show what immense complexity results. The chemical equilibria in supercritical steam will be even harder to describe because the reaction constants must depend on density as well as on temperature. The density dependence is complicated by the strong variation of the dielectric constant. Furthermore, it will not be possible to deal adequately with the chemical reactions if attention is not paid to the ion–ion and ion–solvent interactions, for which, as we have shown, the existing models are inadequate. Here is room for fundamental rethinking of the Debye-Hückel theory in the case where the dielectric constant is low and the ionic interactions strong enough to bring about substantial ion pairing [23].

Finally, a most interesting and challenging task lies ahead with respect to the reconciliation of the critical behavior of the pure solvent, the solution, and the effect of charges on the character of the critical behavior. Three crossover problems arise: the pure solvent, steam, crosses over from van der Waals-like behavior far from the critical point to nonclassical behavior nearby; the solution crosses over from pure-fluid critical behavior to mixture behavior as the concentration increases; and the ion–solvent and ion–ion interactions cease to dominate when the range of the critical fluctuations become large. At present, only the pure-solvent crossover problem has been solved [37]. For the mixture, it has been surmised that the long-range character of charge interactions will lead to suppression of critical fluctuations [38]. Although there is no evidence for this hypothesis in aqueous conducting binary liquids near consolute points [39], there are at present no estimates for the range where nonclassical behavior would prevail in an electrolyte solution near a vapor–liquid critical point.

6. CONCLUSION

The elements that will be part of an adequate understanding and formulation of near- and supercritical aqueous electrolyte solutions thus appear to be a changeover from Gibbs free energy to Helmholtz free energy formulations, incorporation of dissociation equilibria, description of solute–solvent and solute–solute interactions in a medium of low but strongly varying dielectric constant and solution of the crossover problem for a mixture with ions present. In first concentrating on dilute solutions, the use of the pure solvent as a reference in the Helmholtz free energy leads to simplification, generality, and accuracy of the resulting formulation.

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REFERENCES

1. Papers by S. L. Phillips et al., J. A. Rard, S. J. Sanders, and M. Rafal, C. C. Chen et al., J. S. Dweck et al., A. L. Smith, J. R. Morrey et al., and T. J. Wolery, in *Proceedings of the International Conference on Thermodynamics of Aqueous Systems with Industrial Applications*, Airlie House, VA, 1987. N. C. Scrivner, ed. (Hemisphere, Washington, D. C., 1990).
2. R. C. Wilhoit, in *Thermodynamics of Aqueous Systems with Industrial Applications*, ACS Symposium Series 133, S. A. Newman, ed. (ACS, Washington, D.C., 1980), p. 451.
3. S. Sourirajan and G. C. Kennedy, *Am. J. Sci.* **260**:115 (1962).
4. R. W. Potter and M. A. Clynne, *J. Soln. Chem.* 7:837 (1978).
5. J. L. Bischoff, R. J. Rosenbauer, and K. S. Pitzer, *Geochim. Cosmochim. Acta* **50**:1437 (1986).
6. J. C. Tanger, IV, and H. C. Helgeson, *Am. J. Svi.* **288**:19 (1986).
7. H. Renon, ed., *Fluid Properties and Phase Equilibria for Process Design*, Proc. 4th Int. Conf., Helsingor, Denmark, May 1986, Fluid Phase Equil. 29 and 30. (Elsevier, Amsterdam, 1986).
8. N. C. Scrivner, ed., *Proceedings of the International Conference on Thermodynamics of Aqueous Systems with Industrial Applications*, Airlie House, VA, 1987. (Hemisphere, Washington, D.C., 1990).

9. *Symposium on Chemistry in High Temperature Aqueous Solutions*, Provo, Utah, Aug. 1987, R. Izatt, ed., (EPRI, 1990).
10. G. Maurer, in *Fluid Properties and Phase Equilibria for Chemical Process Design*, H. Renon, ed., *Fluid Phase Equil.* **30**:337 (1986).
11. D. J. Turner, in *Thermodynamics of Aqueous Systems with Industrial Applications*, ACS Symposium Series 133, S. A. Newman, ed. (ACS, Washington, D. C., 1980), p. 653.
12. H. C. Helgeson, D. H. Kirkham, and G. C. Flowers, *Am. J. Sci.* **281**:1294 (1981).
13. R. H. Busey, H. F. Holmes, and R. E. Mesmer, *J. Chem. Thermodyn.* **19**:343 (1984).
14. D. Smith-Magowan and R. H. Wood, *J. Chem. Thermodyn.* **13**:1047 (1981).
15. D. E. White, R. H. Wood, and D. R. Biggerstaff, *J. Chem. Thermodyn.* **20**:159 (1988).
16. D. R. Biggerstaff and R. H. Wood, *J. Phys. Chem.* **92**:1994 (1988).
17. E. U. Franck, in *Phase Equilibria and Fluid Properties in the Chemical Industry*, ACS Symposium Series 60, T. S. Storvick and S. I. Sandler, eds. (ACS, Washington, D.C., 1977), p. 99.
18. E. U. Franck, J. E. Savoleian, and W. L. Marshall, *Rev. Sci. Instr.* **33**:115 (1962); A. S. Quist and W. L. Marshall, *J. Phys. Chem.* **72**:684 (1968).
19. K. Heger, Ph.D. thesis (Karlsruhe, 1969); M. Uematsu and E. U. Franck, *J. Phys. Chem. Ref. Data* **9**:1291 (1980).
20. W. M. Marshall and E. V. Jones, *J. Inorg. Nucl. Chem.* **36**:2313 (1974).
21. I. Kh. Khaibullin and N. M. Borisov, *Teplofiz. Vysok. Temp.* **4**:518 (1966).
22. M. Heilig and E. U. Franck, *Ber. Bunsenges. Phys. Chem.* **93**:898 (1989).
23. K. S. Pitzer, *J. Phys. Chem.* **88**:2689 (1984); *Rev. Mineral.* **17**:97 (1987).
24. H. L. Friedman, in *Water and Aqueous Solutions*, G. W. Neilson and J. E. Enderby, eds. (Hilger, Boston, 1986), p. 117.
25. K. S. Pitzer, J. C. Peiper, and R. H. Busey, *J. Phys. Chem. Ref. Data* **13**:1 (1984).
26. G. Morrison, J. M. H. Levelt Sengers, R. F. Chang, and J. J. Christensen, in *Supercritical Fluid Technology*, J. M. L. Penninger et al., eds. (Elsevier, Amsterdam, 1985), p. 25.
27. R. F. Chang, G. Morrison, and J. M. H. Levelt Sengers, *J. Phys. Chem.* **88**:3389 (1984).
28. J. M. H. Levelt Sengers, C. M. Everhart, G. Morrison, and K. S. Pitzer, *Chem. Eng. Comm.* **47**:315 (1986).
29. P. Debye and E. Hückel, *Phys. Z.* **24**:1426 (1923).
30. R. Crovetto and R. Fernandez-Prini, *J. Phys. Chem. Ref. Data* (in press).
31. M. L. Japas and J. M. H. Levelt Sengers, *AIChE J.* March (1989).
32. M. L. Japas and E. U. Franck, *Ber. Bunsenges. Phys. Chem.* **89**:793 (1985).
33. L. Haar, J. S. Gallagher, and G. S. Kell, *NBS-NRC Steam Tables* (Hemisphere, Washington, D.C., 1984).
34. K. S. Pitzer and J. C. Tanger, IV, *Proc. 10th Symp. Thermophys. Prop.*, A. Cezairliyan and J. V. Sengers, eds., *Int. J. Thermophys.* **9**: 635 (1988).
35. J. S. Gallagher and J. M. H. Levelt Sengers, *Proc. 10th Symp. Thermophys. Prop.*, A. Cezairliyan and J. V. Sengers, eds., *Int. J. Thermophys.* **9**:649 (1988).
36. J. C. Tanger, IV, and K. S. Pitzer, *Geochim. Cosmochim. Acta* **53**:973 (1989).
37. Z. Y. Chen, A. Abbaci, and J. V. Sengers, *Proc. 11th Int. Conf. Prop. Steam*, Prague 1989, O. Sifner, ed., (Hemisphere, Washington, D.C., 1990).
38. K. S. Pitzer, *J. Phys. Chem.* **90**:1502 (1986).
39. M. L. Japas and J. M. H. Levelt Sengers, *J. Phys. Chem.* (submitted).