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Correlation strategy for determining the parameters of the revised Helgeson-Kirkham-Flowers model for aqueous nonelectrolytes

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Abstract—The main goal of this study is to revise the correlation algorithm for estimating parameters of the revised Helgeson-Kirkham-Flowers (HKF) model for aqueous nonelectrolyte solutes. The basis for the revision is the analysis of a large body of experimental values of the standard partial molar heat capacities and volumes of aqueous nonelectrolytes published mainly during the last decade. Unlike earlier estimation methods, we show that one of the most useful properties for developing correlations for uncharged species is the standard Gibbs energy of hydration of a solute at 298.15 K and 0.1 MPa, $\Delta_h G^\circ$, which reflects the strength of water-solute interactions. Explicit correlations with $\Delta_h G^\circ$ seem to provide reliable means to estimate the “solvation” parameter ω and the “caloric” parameter c_2 in the revised HKF model. “Volumetric” parameters a_1 to a_4 depend on both the size of a solute and its standard Gibbs energy of hydration. It is expected that the revised estimation strategy will improve the reliability of predictions of thermodynamic properties of aqueous nonelectrolytes in the framework of the revised HKF model. A related problem is the temperature and density ranges of the applicability of the model for uncharged species. A comparison of experimental properties and those fitted in the framework of the revised HKF model made in this study or in articles published elsewhere shows that the model can be used along the saturation vapor-liquid curve of pure water in the density region sufficiently remote from the critical point of water, say up to 630 K. At densities above 500 to 600 $\text{kg} \cdot \text{m}^{-3}$ the range of applicability of the revised HKF model for uncharged species may extend up to higher temperatures. At temperatures up to 500 K at pressures up to 50 MPa, the revised HKF model is capable of excellent description of the standard thermodynamic properties of aqueous nonelectrolytes, except in the narrow temperature range below 280–290 K. Copyright © 2001 Elsevier Science Ltd

1. INTRODUCTION

Thermodynamic modeling is an integral part of modern geochemistry, and the thermodynamic modeling of geochemical processes involving hydrothermal solutions represents a particular challenge for two main reasons. First is the great diversity in speciation (ions, uncharged forms, and complex species) of chemical elements in aqueous solution as functions of composition (salt content, pH, reduction-oxidation potential) and the state parameters (temperature, pressure/density). Second is the particular nature of water as a solvent, resulting in the complicated shape of the temperature/density surface of standard chemical potentials and its temperature/pressure derivatives for aqueous solutes. As a result, until the end of the 1970s, the temperature range for sound thermodynamic modeling of geochemical processes was limited to 500 K, and most extrapolation methods were developed for correlating chemical potentials (equilibrium constants).

The publication of the Helgeson-Kirkham-Flowers Born-type model (HKF; Helgeson et al., 1981) as the last part of a notable series of articles (Helgeson and Kirkham, 1974a,b, 1976) represented a breakthrough in the formidable task of the application of thermodynamic methods to geochemical prob-

lems. Later, this model was revised by Tanger and Helgeson (1988), who incorporated analytical relations consistent with the existence of a singular temperature of supercooled water to correlate the temperature dependence of the standard (i.e., at infinite dilution) partial molar volumes, V_2° , and heat capacities, C_p° , and adopted the Tait-Tamman-Gibson equation for volumetric properties of a solute. In addition, the Born-type equation for the solvation contribution was modified (Tanger and Helgeson, 1988; Shock et al., 1992) by introducing the temperature/density dependence of the so-called electrostatic radii of ions in such a way as to provide an accurate match to high-temperature experimental values of V_2° and C_p° for 1:1 and 2:1 electrolytes. As a result, the revised HKF model accurately describes the temperature-pressure surfaces of the derivatives of the standard chemical potentials for ionic species, at least up to 700 K and densities of pure water above 500 $\text{kg} \cdot \text{m}^{-3}$. The analytical relations forming the basis of the revised HKF model are given in the Appendix with minimal comments (an extensive discussion is given in references mentioned above). A correlation algorithm for ionic species proposed by Shock and Helgeson (1988) allowed expansion of the revised HKF model to hundreds of ions and electrolytes. Parameters for many solutes are available in the computer package SUPCRT92 (Johnson et al., 1992), where data for new compounds can easily be added to the existing and already very extensive database.

The extension of the model to noncharged species, i.e., nonelectrolytes (Shock et al., 1989; Shock and Helgeson,

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1990), was done at the risk of a considerable erosion of the theoretical basis of the Born-type HKF approach. However, at that time, practically no set of accurate high-temperature V_2^0 or Cp_2^0 data existed to make a comprehensive analysis of the consequences feasible. During the last few years, a considerable amount of precise experimental data on thermodynamic properties of aqueous nonelectrolytes at elevated temperatures was published, and some conclusions can be drawn. As described below, the temperature and pressure/density range of applicability of the revised HKF model for aqueous nonelectrolytes is limited. In addition, the correlation algorithms employed to predict the model's parameters work well in some cases (Criss and Wood, 1996; Inglese et al., 1997) and fail in other cases (Hakin et al., 1998; Clarke and Tremaine, 1999; Clarke et al., 2000). For these reasons, the goals of this study are to discuss the temperature/density range of the applicability of the revised HKF model and, mainly, to revise the correlation algorithms for estimating parameters in the model. These discussions are based on a consideration of a large body of experimental data published mainly during the last decade and the analysis of the theoretical problems arising when the Born-type model is applied to neutral solutes.

2. CORRELATION OF THE THERMODYNAMIC PROPERTIES OF AQUEOUS SOLUTES OVER WIDE TEMPERATURE AND PRESSURE RANGES

2.1. Qualitative Outline of the Nature of Water–Solute Interactions

It is useful for the purposes of this work to begin with a short, qualitative, and simplified discussion of the specific features of water–solute interactions. The material for this discussion is taken mainly from the books of Hildebrand and Scott (1950); Mason and Spurling (1980); Prausnitz et al. (1986); and Fernandez-Prini et al. (1992). First, there are always universal interactions between species due to the existence of intermolecular forces. Even two molecules of inert gases will repel each other when they are brought close enough for their electronic charge clouds to overlap, and this repulsion rises very steeply as the separation distance decreases. Other universal forces, existing even between spherically symmetrical molecules, are the so-called London (or dispersion, or induced dipole-induced dipole) forces. These weak attractive forces exist because of correlations of the electron charge distribution in one molecule with that of another molecule. Because the London forces decrease with the interparticle distance much more slowly than the repulsive forces, the net effect at large separation distances is the attractive interactions between molecules.

Additional attractive forces of an electrostatic nature appear if at least one of the interacting neutral molecules has permanent electrical multipole moments.¹ This is exactly the case of

the water molecule, which has at least an appreciable dipole moment of 1.8 debye. There will be dipole–dipole, dipole–quadrupole, quadrupole–quadrupole, and other multipole–multipole interactions when water interacts with another polar molecule, with the average potential energy of these interactions depending on separation distance and the magnitude of the multipole moments involved. Additional effects are due to charge distortions in the second molecule caused by the electric field of the water molecule, and vice versa. Such distortions can be described in terms of induced dipole, quadrupole, etc., moments. There will be interactions between permanent multipole moments of one molecule with induced multipole moments in another molecule, and the energy of the corresponding interactions are proportional to the polarizability of the molecule, which describes the response of the electron charge cloud to an external electric field. In turn, the induced multipole moments in one molecule will additionally polarize another molecule, but these third-order forces are expected to be small. The main point is the fact that the permanent multipole-induced multipole interactions will exist between water and even nonpolar solutes (Ar, N₂, methane, cyclohexane, etc.), because polarization in the presence of an external field is a rather general phenomenon. Indeed, compounds with zero dipole moments (O₂, SF₆, hexane, cyclohexane, benzene, and even He) have nonzero values of average polarizability. So the relatively large permanent dipole moment of the water molecule is one major feature characterizing the peculiarities of water as a solvent.

It is commonly stated that water has anomalous values of many physical characteristics. For example, its normal boiling temperature, enthalpy of vaporization, and heat capacity are much higher than would be expected for a compound of such low molecular mass. Close to its melting point, water has an open structure, where H₂O molecules maintain tetrahedral coordination and thus have much smaller numbers of nearest neighbors (~4) than molecules of most liquids (~10). The magnitude of the dipole moment of the water molecule, although relatively high (1.8 debye), is comparable to that of SO₂ (1.6 debye) or CH₃F (1.8 debye), and alone cannot explain the anomalous physical characteristics of water, including the very high value of its dielectric constant. A universal explanation of these phenomena is given by the formation of the so-called hydrogen bond. This bond forms when the hydrogen atom linked to an electronegative atom (usually F, O, N) in a dipole molecule approaches another electronegative atom (again usually F, O, N). Because the size of the bare proton in the dipole is small, it can come very close to the second atom, and the corresponding atom–hydrogen–atom interactions are so strong that they can be considered either as exceptionally strong dipole–dipole interactions or as the formation of a relatively weak chemical bond. It is the extensive formation of “hydrogen bonds,” which hinders the molecular rotation of water, that is responsible for its open tetrahedral structure, its high dielectric constant, and other “abnormalities.”

In principle, all these qualitative reasonings can be put into an appropriate mathematical form and be used to “construct”

¹There are dipole, quadrupole, octupole, etc., moments. Higher moments are usually of lesser importance because of their smaller contributions to the potential energy of interactions compared with lower multipole moments. However, molecules that do not have a dipole moment because of symmetry may have higher moments (H₂, O₂, C₂H₂, benzene, etc.), the existence of which determines some characteristics of these compounds. One example is CO₂, which has no dipole moment but does have a strong quadrupole moment, and as a result, its

thermodynamic properties differ from those of other nonpolar molecules of similar size and molecular mass.

the potential-energy function for water–solute interactions. There are difficulties, both technical and theoretical, in doing this: for nonspherical molecules, the intermolecular forces depend not only on the separation distance but also on the relative orientation of molecules; there may be difficult-to-account-for specific (chemical interaction) forces, resulting, for example, in formation of small fractions of H_2CO_3 , HCO_3^- , and H^+ species in addition to H_2O and CO_2 as a result of water–carbon dioxide interactions. Because of these difficulties, at the present state of knowledge, rigorous calculations are possible only at the level of the second virial coefficient, where interactions of only two particles are to be accounted for. In the case of interactions involving more than two particles, it is already necessary to use the approximation of considering only pairwise contributions to represent the potential energy of multibody interactions, because the nature of nonadditive contributions to the energy of interparticle interactions is poorly understood and typically, by necessity, ignored. This is a major theoretical obstacle. Calculations for dense solutions, even assuming the pairwise nature of the potential energy of interactions between particles, require additional approximations for evaluating the radial distribution functions, which determine the probability of finding two particles at a given distance from each other. The analytical expressions for statistical mechanical approaches are possible only for some strongly simplified variants of theories. As a result, when relations following from theory are forced to reproduce experimental data, a match can often be achieved only by introduction of some correction factors (temperature dependence of “hard-sphere” diameters, for example), which account for all imperfections of both the basic theory and the approximations involved.

2.2. Correlation of Properties of Aqueous Solutes over Extended Temperature and Pressure/Density Ranges

In such a situation, the use of much more simple analytical semiempirical “equations of state” is a valuable alternative for calculating the thermodynamic properties of solutes in water at infinite dilution. By “equations of state,” we mean empirical and semiempirical relations between parameters of state (temperature, T ; pressure, P), macroscopic properties of pure water (density, dielectric constant, compressibility, etc.), and the chemical potential (or its derivatives) of an aqueous species at infinite dilution. Experience shows that properly formulated models can provide an excellent correlation of data over experimentally studied T - P ranges and can even be used for rather accurate calculation of thermodynamic properties at conditions where no data are available. Of course, expertise, based on the knowledge of the nature of water–solute interactions, is needed for both the development of such correlating models and sound discussions of their advantages/limitations.

Some notions used in our further discussions should be explained here; first among these is the near-critical divergence of the derivatives of the chemical potential of a solute. A particular region of T - P parameters, where the problems of correlating models are particularly transparent, is the near-critical region, which is close to the critical point of the solvent (approximately 647.1 K, 22.1 MPa, 322 $\text{kg} \cdot \text{m}^{-3}$ for water). The chemical potential of a solute at infinite dilution is finite at and around the critical point of the solvent, but the derivatives

of the chemical potential of a solute (the partial molar enthalpy, H_2° , entropy, S_2° , volume, V_2° , heat capacity, Cp_2° , isothermal compressibility, κ_2°) diverge—that is, go to infinite values, approaching the critical point of a pure solvent. There may be negative (all electrolytes, some strongly polar nonelectrolytes, such as boric acid and silica in water) and positive types of divergence (most nonelectrolytes in water), where diverging properties go to negative or positive infinite values, respectively. Accurate prediction and reproduction of the sign and magnitude of the near-critical divergence is one of the biggest challenges for models proposed to correlate the infinite dilution properties of solutes. The second problem is the definition of the process of hydration (or solvation in general), which follows from the standard state convention adopted here. The standard state adopted for gaseous compounds is unit fugacity of the ideal gas at any temperature and the ideal gas reference pressure $P^\ominus = 0.1$ MPa, and the standard state for aqueous species calls for unit activity in a hypothetical solution of unit molality referenced to infinite dilution at any temperature and pressure. Correspondingly, hydration is defined as the process of transfer of one mole of a solute from the ideal gas state at any T and $P^\ominus = 0.1$ MPa to the standard aqueous solution at any T and P . It was emphasized by Ben-Naim (1987) that this definition is not the optimal one from the point of view of statistical mechanics; however, it is convenient for practical applications. For example, the Gibbs energy, enthalpy, entropy, and heat capacity of hydration can be calculated directly from thermodynamic tabulations as the differences in the corresponding properties of a solute in the state of the ideal gas and in the state of the standard aqueous solution.

Many empirical and semiempirical models are proposed in the literature to correlate the thermodynamic properties at infinite dilution of ionic, neutral, or both ionic and neutral species in water over extended temperature and density ranges (although only for the revised HKF model there is an extensive database of parameters for hundreds of aqueous species). Most of them can be arbitrarily divided into the “electrostatic,” “density,” and the fluctuation solution theory (FST)-based models.

Most electrostatic approaches (including the revised HKF model) are based on “continuum” models, where water (or a solvent in general) is approximated by a polarizable structureless continuum characterized by its dielectric constant. There are simple but powerful “semicontinuum” modifications (Tremaine and Goldman, 1978; Pitzer, 1982; L’vov and Zarembo, 1982a,b, 1983; Tanger and Pitzer, 1989), where the molecular nature of water is recognized for the first hydration shell and the approximation of a continuum is used for the solvent outside the first hydration shell. The basic result of a continuum model as first derived by Born (1920) is that the Born charging energy represents the difference in the Gibbs energy of an ion in vacuum (a medium with dielectric constant equal to one) and in the structureless incompressible continuum dielectric of dielectric constant, ϵ . The Born charging energy, G_{Born} , is the difference between the energy of charging a sphere of radius r (the approximation for an ion) from zero charge to Ze in an incompressible continuum of dielectric constant ϵ and in a vacuum, and is equal to

$$G_{\text{Born}} = -\frac{(Ze)N_A}{2r} \left(\frac{1 - \varepsilon}{\varepsilon} \right), \quad (1)$$

where Z designates the ionic charge of a species, e stands for the charge of an electron, and N_A represents Avogadro's number.

It is recognized (Friedman and Krishnan, 1973; Ben-Naim, 1987) that the Born charging process corresponds to the isochoric transfer process, and the correct relation between the Born charging energy and the Gibbs energy of hydration, as defined above, is given by (Friedman and Krishnan, 1973):

$$\Delta_h G^\circ = G_{\text{Born}} + RT \ln \frac{RT}{V_1^\circ P^\ominus} - RT \ln \frac{1000}{M_w}, \quad (2)$$

where V_1° represents the molar volume of water at the temperature and pressure of interest, $P^\ominus = 0.1$ MPa designates the standard pressure of the ideal gas state, and $M_w = 18.0152$ g · mol⁻¹ stands for the molecular mass of water. In Eqn. 2, the second term is often called the "standard state conversion term," and the last term is needed to convert values from the mole fraction to the molality concentration scale. At near-critical conditions, the derivatives of the chemical potential of a solute for the Born model diverge as the corresponding derivatives of the reciprocal solvent dielectric constant, $1/\varepsilon$. From the point of view of the near-critical theory of dilute solutions (see below), this divergence path is correct if the reciprocal dielectric constant is directly proportional to the solvent density. The available experimental results on the values of dielectric constant of water suggest that this is a reasonable approximation for near-critical conditions (Archer and Wang, 1990). It is necessary to emphasize the approximations of the Born model: water is not a structureless incompressible continuum, and most ions are not unpolarizable spheres. An additional problem is that the Born model gives only the attractive (electrostatic) part of the potential energy of ion-water interactions. As a result, additional terms, representing the "intrinsic volume" or "hard core" and its temperature and pressure variations, and terms providing for the temperature and density dependence of the "radius" of a species, must always be added to assure the satisfactory performance of continuum models over appreciable temperature and pressure ranges.

The "density" approaches are based on the empirical observations (traced back to works of Franck, 1961, in Germany, Styrikovich, 1969, in the USSR, and Marshall, 1970, in the United States in 1950s–1960s) that the standard state (infinite dilution) chemical potential of a solute, μ_2 , is proportional to the logarithm of the density of pure water. Some rationalizations of this finding can be found in the works of Levelt Sengers and coworkers (Japas and Levelt Sengers, 1989; Levelt Sengers, 1991a), who showed theoretically that in the neighborhood of the critical point of a solvent the chemical potential of the infinite dilute solute is proportional to the solvent density, ρ_1 (consequently, the derivatives of μ_2 diverge as the corresponding derivatives of ρ_1). Harvey (1990) pointed out that this near-critical linearity in density of a solvent, ρ_1 , is asymptotically equivalent to linearity in the logarithm of density of the solvent, $\ln \rho_1$, at least around the critical point. This linear relation can be successfully extended into conditions far

removed from the critical point of water (Harvey and Levelt Sengers, 1990; Harvey et al., 1991); however, the actual slope of the μ_2 - ρ_1 dependence differs from that required by the near-critical theory (Harvey et al., 1991; Harvey, 1998). So there is not a satisfactory theoretical basis behind the "density" approaches, although successful models having few parameters can be formulated on this basis, at least for ionic species (Marshall, 1970; Anderson et al., 1991; Plyasunov, 1993; among others).

Some common drawbacks of both the electrostatic and density models may be found (at least by purists) in the fact that they do not provide a clear separation of solvent-solvent and solvent-solute interactions, both of which contribute to the chemical potential of a solute at infinite dilution. Indeed, such models are formulated as the sum of a number of terms. One of them (often called the "solvation" term), proportional to either the dielectric constant or to the density (or logarithm of density) of pure water, makes the largest contribution to the diverging properties of a solute at near-critical conditions. Other terms are often called "nonsolvation" or "structural." However, this division is arbitrary and these terms cannot be unambiguously identified as resulting from either solvent-solvent or solvent-solute interactions (besides, as discussed above, the general definition of "hydration/solvation" is incompatible with this separation of "solvation" and "nonsolvation" contributions to the process of solvation). On the other hand, an unambiguous separation of solvent-solvent or solvent-solute contributions can be made with the FST-based models.

The FST-based models, as suggested by O'Connell (1995), start with the "exact" relation from FST: $V_2^\circ = \kappa_T RT \cdot A_{12}(T, \rho)$. This relation clearly shows two contributions to the partial molar volume of a solute at infinite dilution, V_2° . One contribution arises from solvent-solvent interactions, the $\kappa_T RT$ term, where κ_T stands for the compressibility coefficient of the pure solvent. The second contribution is due to the interactions between the solvent and the infinite dilution solute, the $A_{12}(T, \rho)$ term, where $A_{12}(T, \rho) = 1 - C_{12}$, with C_{12} being the integral of the solute-solvent direct correlation function. Direct correlation functions are of short range, and their integral is a well-behaved property everywhere, even at the critical point of the solvent. The $A_{12}(T, \rho)$ term has to be considered as a semiempirical function of temperature and the density of pure water. At this stage, the model loses some theoretical rigor. However, qualitative arguments can be presented that allow sound constraints to be placed on the temperature and density variations of the $A_{12}(T, \rho)$ parameter in rather loose terms of "attractive" and "repulsive" interactions/correlations (Plyasunov et al., 2000a). Having the analytical equation for the infinite dilution partial molar volume, V_2° , as a function of temperature and density, one can calculate the chemical potential (the Gibbs energy) of a solute at infinite dilution, and then obtain analytical relations for the "caloric" properties (partial molar heat capacity, enthalpy) by the proper thermodynamic manipulations. On the basis of these arguments, it is expected that the FST-based models have a promising potential to serve as correlating approaches with a sound theoretical basis over extended temperature and density ranges (O'Connell et al., 1996; Plyasunov et al., 2000b; Sedlbauer et al., 2000).

2.3. Problems with the Application of the Revised HKF Model to Neutral Species

Solute–water interactions at short separations are always repulsive, irrespective of the type of solutes. Therefore, we would expect that the nonsolvation parameters of the revised HKF model are needed to correlate the properties of neutral species, particularly at high water densities. Because of the essentially empirical origin of these terms, selected to match accurately the low-temperature V_2^o and Cp_2^o data for electrolytes, it is difficult to judge their applicability for nonelectrolytes (indeed, some problems are known with the correlation of V_2^o and Cp_2^o data for nonelectrolytes at $T < 290$ K in the framework of the revised HKF model; see below).

Nevertheless, most problems arise when applying this model for nonelectrolytes at high temperatures, especially at near-critical conditions. The usual (and fair) critique of the revised HKF model in application to neutral species is the fact that the Born model is formulated only for ions and has nothing to do with neutral solutes. This is true; however, at least in principle, a formulation in terms of the dielectric constant of the bulk solvent can be obtained for the case of neutral solutes with permanent multipole (dipole, quadrupole, etc.) moments (Beveridge and Schnuelle, 1975). By applying a process analogous to the Born treatment of the energy of ion–dielectric interactions, a solute can be approximated as an electroneutral distribution of discrete charges in a continuum dielectric (the approximation for a solvent), and the Gibbs energy of hydration of a dipole (quadrupole, etc.) can be approximated as the difference in the work of charging this distribution in the dielectric and in a vacuum. Besides the principal drawback of the method, that it ignores the molecular nature of water, additional problems arise.

The first problem is that electrostatic contributions for dipoles, quadrupoles, etc., cannot be approximated by the Born-type term. Indeed, for dipoles, the charging energy is proportional to a $[(1 - \epsilon)/(2\epsilon + 1)]$ term, and for quadrupoles to the term $[(1 - \epsilon)/(3\epsilon + 2)]$ (Beveridge and Schnuelle, 1975), and these relations cannot be accurately represented by scaling the electrostatic term for an ion, which is proportional to the ratio $[(1 - \epsilon)/\epsilon]$.

Electrostatic terms uniformly provide a negative type of the near-critical divergence for ions, dipoles, quadrupoles, and so forth, when the derivatives of the chemical potential of a solute go to negative infinity approaching the critical point of pure water. However, an experimental study (Hnedkovsky, 1994; Hnedkovsky et al., 1996; Hnedkovsky and Wood, 1997) of the dilute aqueous solutions of ammonia (a solute with an appreciable dipole moment, 1.5 debye) revealed a positive type of near-critical divergence for this solute in water. What is going on? The answer is that it is precisely the effect of the “standard-state conversion term” (see Eqn. 2), that is missing in the revised HKF analytical formulation. This missing term is relatively unimportant for ionic solutes, where it is masked by the much bigger Born term, but it is significant for nonpolar and most polar neutral solutes close to the critical point of water, where it overwhelms the dipolar, quadrupolar, and other multipolar electrostatic contributions to the water–solute interactions and provides positive near-critical divergence for many dissolved compounds.

This discussion shows that the extension of the revised HKF model to neutral species is not straightforward and not justified from a theoretical point of view. Nevertheless, on a purely empirical basis, the revised HKF model can be used to correlate the properties of neutral species over temperature and density ranges, extensive enough for many practical applications. This is because the model is flexible enough: it contains a large number (seven) of fitting parameters, including one (the Born term) for which the temperature and pressure derivatives diverge approaching the critical point of water. As the Born term effectively approximates a number of contributions (the standard-state conversion term contribution universal for all solutes and electrostatic ones for dipoles, quadrupoles, etc.), it is difficult to expect this term to describe accurately the divergent properties for all types of neutral solutes.

3. EXPECTED RANGE OF APPLICABILITY OF THE REVISED HKF MODEL FOR AQUEOUS NONELECTROLYTES

Some limitations of the revised HKF model for aqueous nonelectrolytes are obvious. As an example, it does not exhibit a proper asymptotic behavior at the ideal gas limit. Indeed, at very low densities, where an aqueous solution may be considered as an ideal mixture of ideal gases, the following relation must hold for V_2^o of a solute: $V_2^o = \kappa_T RT = (RT/P)$. The equality $\kappa_T RT = (RT/P)$ is kept for the ideal gas, where $PV = RT$, and the following relation is valid: $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \frac{1}{P}$. For the revised HKF approach, it can be argued that the relations at the ideal gas limit, where all the Born functions are zero, are given by the nonsolvation contributions, and these equations do not reduce to the form $V_2^o = \kappa_T RT = (RT/P)$. Likewise, it can be shown that the revised HKF relations are incompatible with those derived from the virial equation of state, truncated at the second virial coefficient, which are valid up to densities corresponding to approximately half of the critical density of a pure solvent. So the revised HKF model is not expected to provide accurate results at pure water densities below 200 kg m^{-3} .

However, at supercritical temperatures, the range of applicability of the revised HKF model for nonelectrolytes is reduced even at relatively high densities. This was shown by comparison of experimental values of the chemical potentials of aqueous H_2 and those predicted in the framework of the revised HKF model (Plyasunov, 1991), as well as comparison between predicted chemical potentials for aqueous CH_4 and those generated by computer simulations (Lin and Wood, 1996). An analysis of the performance of the revised HKF equations for description of the variations of V_2^o and Cp_2^o at near-critical conditions for nonelectrolytes was performed by Hnedkovsky (1994), O’Connell et al. (1996), and Hnedkovsky and Wood (1997). These authors have concluded that the Born-type functions are not able to provide correct shapes of the T - ρ surfaces of the derivatives of the chemical potentials of aqueous nonelectrolytes close to the critical point of water.

A global fit of all the standard partial molar thermodynamic properties (Gibbs energy, enthalpy, volume, and heat capacity) in the framework of the revised HKF model for a few dissolved gases, including results at near- and supercritical conditions

(Plyasunov et al., 2000b), yielded standard weighted deviations as large as 3.0 to 8.8. The standard weighted deviation, SWD, is defined as

$$\text{SWD} = \left[\sum_i^{N_p} \frac{(\Delta_i/\delta_i)^2}{N_p - m} \right]^{1/2}, \quad (3)$$

where Δ stands for the difference between an experimental and a calculated data point, δ represents the uncertainty of this experimental point, N_p designates the number of experimental points, and m indicates the number of fitting parameters, equal to seven in the revised HKF model. Therefore, the SWD approximately shows by how many times the difference between experimental and calculated values exceeds the uncertainty of the experimental value, and SWD as large as 3 to 8 signals poor performance of the correlating model. However, if the data set was limited to temperatures below 630 K (i.e., to the high-density region remote from the critical point of pure water), then the goodness of the fit improves considerably, with standard weighted deviations in the range 1.3 to 2.6.

Schulte (1997) tested the performance of the revised HKF equations to describe V_2^o and Cp_2^o results for some aqueous nonelectrolytes at subcritical temperatures. He has shown that the revised HKF equations do a better job representing the Cp_2^o data than the V_2^o results and emphasized that at lower temperatures, both experimental V_2^o and Cp_2^o data show rather more linear temperature dependence than a strong curvature implied by the revised HKF equations for nonsolvation contributions. One of the immediate results of this finding is that the pressure dependence of Cp_2^o , given by one of the Maxwell relations as

$$\left(\frac{\partial Cp_2^o}{\partial P} \right)_T = -T \left(\frac{\partial^2 V_2^o}{\partial T^2} \right)_P, \quad (4)$$

cannot be accurately reproduced in the framework of the revised HKF approach at low temperatures. However, these deficiencies of the model on the level of the derivatives of the chemical potentials translate into relative small errors when integrated to calculate the temperature/pressure increments of the Gibbs energies of solutes.

Estimates of introduced errors in the Gibbs energies, δG , can be obtained with the relation

$$\begin{aligned} \delta G &= \delta H - T\delta S = \delta \left(\int_{T_r}^T Cp_2^o dT \right) - T\delta \left(\int_{T_r}^T \frac{Cp_2^o}{T} dT \right) \\ &\approx \delta Cp_2^o \left[T - T_r - T \ln \left(\frac{T}{T_r} \right) \right], \end{aligned} \quad (5)$$

where δCp_2^o is the average error of Cp_2^o at temperatures between $T_r = 298.15$ K and T . If δCp_2^o is $15 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ at 298 to 473 K and $30 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ at 298 to 573 K, then calculated values of δG are $<0.2 \text{ kJ} \cdot \text{mol}^{-1}$ at 373 K, $<0.7 \text{ kJ} \cdot \text{mol}^{-1}$ at 473 K, and $<3.0 \text{ kJ} \cdot \text{mol}^{-1}$ at 573 K. In terms of errors in the value of the equilibrium constant, $\delta \log K$, the following values are obtained: <0.03 at 373 K, <0.08 at 473 K, and <0.27 at

573 K. Errors in the V_2^o value of $5, 20, \text{ and } 40 \text{ cm}^3 \cdot \text{mol}^{-1}$ (typical estimates at 373, 573, and 623 K) result in δG values of 0.25, 1.0, and $2.0 \text{ kJ} \cdot \text{mol}^{-1}$ at 50 MPa.

These findings can be summarized as follows: (a) the window for the use of this model for nonelectrolytes along the saturation vapor–liquid curve of pure water exists up to 630 K (i.e., in the high-density region sufficiently remote from the critical point of water) and may extend up to higher temperatures (~ 800 K?) at densities above $500\text{--}600 \text{ kg} \cdot \text{m}^{-3}$; (b) at low temperatures, the revised HKF model is not as accurate for V_2^o and Cp_2^o of nonelectrolytes as for corresponding values of electrolytes for which it was originally proposed. Nevertheless, at the level of chemical potentials these low-temperature deficiencies are not of concern for most practical geochemical applications. Over the temperature range up to 500 K at pressures up to 50 MPa, the revised HKF model is capable of excellent description of the standard thermodynamic properties of aqueous nonelectrolytes, except in the narrow temperature range below 280–290 K.

4. NEW CORRELATION STRATEGY TO ESTIMATE PARAMETERS OF THE REVISED HKF MODEL FOR AQUEOUS NONELECTROLYTES

4.1. Motivation for Revision of the Correlation Algorithm

Parameters of the revised HKF model, given for many nonelectrolytes in a number of publications (Shock et al., 1989; Shock and Helgeson, 1990; Shock, 1992, 1995; Schulte and Shock, 1993; Amend and Helgeson, 1997a; Dale et al., 1997; Haas and Shock, 1999; and others), are based mainly on the correlation algorithms developed by Shock and Helgeson (1988) for ionic species and later extended to nonionic aqueous compounds (Shock et al., 1989). We would like to stress that at the time when these methods were developed, the experimental data were typically available over a small temperature range near 298.15 K. Since then, many new experimental determinations of V_2^o and Cp_2^o have been published for aqueous neutral species. In some of these articles, the authors compared their experimental data with the revised HKF predictions, with mixed results. In a number of cases, for example, for 1-propanol, acetic acid, propylamine, predictions are classified as satisfactory (Criss and Wood, 1996) or even excellent (Inglese et al., 1997). However, for amino acids, Shock and Helgeson (1990) and Amend and Helgeson (1997b) predicted an increase in the standard state volumes with increasing temperatures. On the other hand, experimental data are consistent with the reverse trend, as first suggested by Hakin et al. (1998), and then experimentally confirmed by Clarke and Tremaine (1999) and Clarke et al. (2000). Another example of the problems with the correlation algorithms is their failure to predict the negative values of V_2^o and Cp_2^o for boric acid at near-critical conditions (Hnedkovsky et al., 1995). With these results in hand, the challenge is to improve predictions of the revised HKF parameters. Therefore, we decided to test the proposed correlation algorithms against the new experimental data for aqueous nonelectrolytes and, if necessary, suggest new ones.

4.2. Determination of the Complete Set of the Revised HKF Parameters for a Representative Set of Aqueous Nonelectrolytes

We determined the optimal set of the revised HKF parameters for a number of aqueous nonelectrolytes for which experimental values of standard thermodynamic properties are available at high temperatures. The list of species used is given in Table 1. We believe that this set of solutes is representative for our purposes. It includes both nonpolar (methane, argon, cyclohexane) and polar (ammonia, alcohols, monocarboxylic acids, amide, boric acid, glycine) species with wide variations in sizes (from small argon and ammonia to large toluene, *n*-hexane, and proline). At ambient conditions, the compounds tested exist in their pure state as gases (methane, Xe), liquids (benzene, ethanol, acetic acid) or solids (boric acid, propionamide, glycine). Table 1 also gives the references to the main sources of various thermodynamic data (V_2^o , Cp_2^o , partial molar Gibbs energy of hydration, $\Delta_h G^o$, partial molar enthalpy of hydration, $\Delta_h H^o$, partial molar isothermal compressibilities, κ_2^o), the number of experimental data points for each property under consideration, and the temperature range covered by each type of data (the pressure range is not indicated because the overwhelming majority of data points refer to pressures <40 MPa, and only three sources (Høiland, 1973; Eastal and Woolf, 1985, 1988) give V_2^o at pressure in excess of 100 MPa). When necessary, the partial molar isothermal compressibilities,

$$\kappa_2^o = -\left(\frac{\partial V_2^o}{\partial P}\right)_T$$

were calculated from the partial adiabatic compressibilities, $\kappa_{2,s}^o$, reported in the literature, by use of the relation

$$\kappa_2^o - \kappa_{2,s}^o = \frac{TE_1^o}{Cp_1^o} \left\{ 2E_2^o - E_1^o \frac{Cp_2^o}{Cp_1^o} \right\}, \quad (6)$$

where

$$E_1^o = \left(\frac{\partial V_1^o}{\partial T}\right)_p$$

and

$$E_2^o = \left(\frac{\partial V_2^o}{\partial T}\right)_p;$$

V_1^o and Cp_1^o stand for the molar volume and heat capacity of pure water.

Determination of the revised HKF parameters was performed by means of a global fit of data using a weighted least-squares procedure. In principle, the weight of the experimental datum point is defined as $1/\delta^2$, where δ stands for the uncertainty of this experimental point. However, the most precise V_2^o and Cp_2^o data are obtained at low temperatures, where the functional forms of nonsolvation equations, accepted in the revised HKF model, appear to be not appropriate for nonelectrolytes (see above). To diminish detrimental effects in the fitting procedure, we employed δ values (0.5 – 2.0 $\text{cm}^3 \cdot \text{mol}^{-1}$) that are larger than experimental uncertainties of V_2^o at low temperatures. Only experimental results at temperatures below 630 K have been used in the fit.

Preliminary fits revealed some problems. In cases of solutes for which there are no experimental κ_2^o values, the parameters from the fit procedure predicted improbably high values of κ_2^o , up to $\pm 500 \cdot 10^{-4} \text{ cm}^3 \cdot \text{bar}^{-1} \cdot \text{mol}^{-1}$, which exceed by one to two orders of magnitude the experimental results available. Such high values of κ_2^o at low temperatures suggest changes in V_2^o of up to 10 to 20 $\text{cm}^3 \cdot \text{mol}^{-1}$ when pressure increases from 0.1 to 40 MPa. All experimental data available suggest changes of less than 1 to 3 $\text{cm}^3 \cdot \text{mol}^{-1}$ over this pressure range at ambient temperatures. To overcome such artifacts, we have added in the fit values of $\kappa_2^o = 0$ with uncertainties of $20 \cdot 10^{-4}$ to $40 \cdot 10^{-4} \text{ cm}^3 \cdot \text{bar}^{-1} \cdot \text{mol}^{-1}$ at a number of temperatures below 333 K just to exclude the appearance of improbably high values of κ_2^o . In addition, data for a number of solutes in our set are only available at temperatures below 525 K. Our experience shows that reliable determination of the ω parameter (which governs the magnitude of the solvation contribution to the thermodynamics of a solute) requires data above 550 K and that the value of ω is most accurate if high-temperature Cp_2^o data are available. To overcome this problem, we used a recently proposed correlating model (Piyasunov et al., 2000a,b), developed specifically for nonelectrolytes, to generate estimates of V_2^o and Cp_2^o values for some solutes at temperatures of 540 to 620 K and $P = 28$ MPa, the pressure of the vast majority of high-temperature V_2^o and Cp_2^o data. The generated data were included in the fit (with relatively large uncertainties) for 7 of the 21 solutes in our set: propylamine, methanol, ethanol, 1-propanol, acetic acid, propionic acid, and propionamide.

Results of the global fit are presented in Table 1, together with their uncertainties at the 0.95 confidence level, shown in parentheses as the number of significant figures; that is, 117 (13) means 117 ± 13 and -1.93 (16) means -1.93 ± 0.16 . For all species except the alcohols, monocarboxylic acids, and amino acids, uncertainties in the “volumetric” parameters a_1 to a_4 are very large. There are two reasons for this. First, there are insufficient experimental V_2^o and κ_2^o data covering wide ranges of temperatures and particularly pressures to allow accurate resolution of the contributions from the four volumetric parameters a_1 to a_4 to the properties of solutes. Second, the particular analytical form of the nonsolvation contribution, accepted in the revised HKF model, does not appear to match precisely the temperature-pressure surface of the standard partial molar volumes of aqueous nonelectrolytes (O’Connell et al., 1996; Schulte, 1997). A comparison of experimental data and values fitted in the framework of the revised HKF model for V_2^o and Cp_2^o is shown in Figures 1 and 2. The strong temperature variations of the standard thermodynamic properties at $T < 298$ K are artifacts introduced for nonelectrolytes by inappropriate functional forms in the revised HKF model for V_2^o and Cp_2^o , as discussed above (Section 3).

4.3. New Correlation to Estimate the Solvation Parameter ω

The high-temperature behavior of the standard thermodynamic properties of solutes in the framework of the revised HKF model is governed by the solvation parameter ω . Shock et al. (1989) suggested correlating this parameter with the value of the standard partial molar entropy, S_2^o , of a solute at 298.15 K

Table 1. Main sources of experimental data used for the global fit, some standard partial molar thermodynamic properties at 298.15 K and 0.1 MPa, and the revised HKF parameters for aqueous nonelectrolytes in the test set.

Compound	No. of points, T range, references	$\Delta_f G^{\circ a,b}$ $S_2^{\circ c,b}$	$Cp_2^{\circ c,b}$ $V_2^{\circ d,b}$	$10 \cdot a_1^e$	c_1^c	$10^{-5} \cdot \omega^f$
				$10^{-2} \cdot a_2^f$	$10^{-4} \cdot c_2^h$	
				a_3^g		
				$10^{-4} \cdot a_4^h$		
Ar	Cp_2° : 30, 306–630 ⁱ	16.29 ⁱ	221	49 (31)	117 (13)	–1.93 (16)
	V_2° : 18, 298–627 ⁱ	59.8 ^j	32.6	–10 (87)	40 (14)	
	$\Delta_f H^{\circ}$: 2, 288–308 ⁱ			–188 (221)		
CH ₄	$\Delta_f G^{\circ}$: 62, 273–573 ⁱ			8 (61)		–1.66 (20)
	Cp_2° : 6, 304–623 ⁱ	16.29 ⁱ	252	74 (45)	171 (11)	
	V_2° : 22, 290–623 ⁱ	87.8 ^k	36	–64 (131)	27 (8)	
Xe	$\Delta_f H^{\circ}$: 13, 273–323 ⁱ			–284 (325)		–1.64 (15)
	$\Delta_f G^{\circ}$: 71, 273–623 ⁱ			48 (92)		
	Cp_2° : 12, 319–632 ⁱ	13.45 ⁱ	271	77 (27)	150 (15)	
C ₂ H ₄	V_2° : 11, 299–628 ⁱ	61.2 ^j	42.5	–10 (77)	58 (17)	–1.29 (21)
	$\Delta_f H^{\circ}$: 2, 288–308 ⁱ			–247 (193)		
	$\Delta_f G^{\circ}$: 55, 273–573 ⁱ			6 (54)		
CO ₂	Cp_2° : 22, 302–630 ⁱ	13.25 ⁱ	280	74 (54)	184 (28)	–1.31 (19)
	V_2° : 22, 298–627 ⁱ	119.7 ^k	46	–23 (155)	54 (31)	
	$\Delta_f H^{\circ}$: 2, 288–308 ⁱ			–225 (385)		
H ₂ S	$\Delta_f G^{\circ}$: 35, 273–573 ⁱ			15 (109)		–1.06 (14)
	Cp_2° : 7, 298–623 ⁱ	8.28 ⁱ	217	64 (47)	154 (16)	
	V_2° : 17, 298–623 ⁱ	117.6 ^j	33.5	–42 (133)	15 (17)	
NH ₃	$\Delta_f G^{\circ}$: 70, 273–623 ⁱ			–232 (335)		–0.65 (7)
	Cp_2° : 9, 283–623 ⁱ	5.66 ⁱ	178	31 (95)	109 (10)	
	V_2° : 19, 283–623 ⁱ	125.5 ^j	34.9	67 (35)	32 (11)	
<i>n</i> -Hexane	$\Delta_f H^{\circ}$: 2, 288–308 ⁱ			–251 (254)		–1.95 (48)
	$\Delta_f G^{\circ}$: 26, 273–573 ⁱ			42 (72)		
	Cp_2° : 9, 283–623 ⁱ	–10.05 ⁱ	75	31 (21)	87 (10)	
Cyclohexane	V_2° : 18, 278–623 ⁱ	107.8 ^j	24.0	0 (60)	–8 (6)	–1.63 (37)
	$\Delta_f H^{\circ}$: 26, 273–623 ^o			–66 (161)		
	$\Delta_f G^{\circ}$: 26, 273–623 ^o			5 (45)		
Benzene	Cp_2° : 5, 288–340 ^{l,m}	18.04	660	191 (67)	453 (39)	–1.05 (26)
	V_2° : 10, 298–623 ^{n,m,k}	222.5 ^k	114	–20 (178)	96 (32)	
	$\Delta_f H^{\circ}$: 6, 288–623 ^{l,m}			–519 (487)		
Toluene	$\Delta_f G^{\circ}$: 26, 273–623 ^o			12 (125)		–1.20 (33)
	Cp_2° : 5, 288–340 ^{l,m}	12.95 ^k	516	166 (63)	380 (36)	
	V_2° : 12, 298–623 ^{n,m,k}	143.9 ^k	87	–18 (164)	78 (33)	
Propylamine	$\Delta_f H^{\circ}$: 9, 288–623 ^{l,m}			–505 (466)		–1.01 (25)
	$\Delta_f G^{\circ}$: 26, 273–623 ^o			10 (115)		
	Cp_2° : 9, 278–413 ^{l,m}	4.29 ^k	370	151 (64)	280 (19)	
Methanol	V_2° : 27, 288–623 ^{n,p,q}	149.2 ^k	83.0	–66 (173)	41 (17)	–0.63 (9)
	$\Delta_f H^{\circ}$: 16, 288–623 ^{m,r,s}			–485 (453)		
	$\Delta_f G^{\circ}$: 26, 273–623 ^o			45 (122)		
Ethanol	Cp_2° : 8, 278–413 ^p	4.55 ^k	454	183 (71)	342 (32)	–0.52 (7)
	V_2° : 19, 278–623 ^{q,p,n,m}	184.1 ^k	97.5	–106 (189)	60 (31)	
	$\Delta_f H^{\circ}$: 10, 288–623 ^{l,m}			–586 (501)		
Methanol	$\Delta_f G^{\circ}$: 26, 273–623 ^o			70 (133)		–0.63 (9)
	Cp_2° : 4, 303–523 ^t	–10.4 ^y	332	117 (75)	313 (41)	
	V_2° : 6, 278–523 ^{u,v}	170.7 ^z	74.0	–64 (214)	–18 (34)	
Ethanol	$\Delta_f H^{\circ}$: 3, 277–303 ^{w,x}			–280 (493)		–0.52 (7)
	$\Delta_f G^{\circ}$: 73, 273–573 ^{kk-mm,xx-ccc}			39 (139)		
	κ_2° : 9, 278–318 ^{pp}			35 (2)	144 (6)	
Methanol	Cp_2° : 22, 273–398 ^{aa-cc}	–13.21 ^k	158	17 (2)	4 (4)	–0.63 (9)
	V_2° : 67, 273–573 ^{m,aa,dd-gg}	132.4 ^k	38.2	–1 (8)		
	$\Delta_f H^{\circ}$: 277–523 ^{m,w,hh-ij}			–6 (2)		
Ethanol	$\Delta_f G^{\circ}$: 51, 273–426 ^{kk-oo}					–0.52 (7)
	κ° : 9, 278–318 ^{pp}					
	Cp_2° : 22, 273–398 ^{bb,cc,qq}	–13.00 ^k	263	49 (2)	246 (5)	
Ethanol	V_2° : 39, 278–373 ^{bb,ee,ff,qq,rr}	146.6 ^k	55.1	26 (3)	7 (3)	–0.52 (7)
	$\Delta_f H^{\circ}$: 36, 277–523 ^{hh,ii,ss-ww}			25 (11)		
	$\Delta_f G^{\circ}$: 73, 273–573 ^{kk-mm,xx-ccc}			–14 (2)		
Ethanol	κ_2° : 9, 278–318 ^{pp}					–0.52 (7)

Table 1. (Continued)

Compound	No. of points, T range, references	$A_h G^{oa,b}$ $S_2^{oc,b}$	$Cp_2^{oc,b}$ $V_2^{od,b}$	$10 \cdot a_1^e$ $10^{-2} \cdot a_2^f$ a_3^g $10^{-4} \cdot a_4^h$	c_1^c $10^{-4} \cdot c_2^h$	$10^{-5} \cdot \omega^f$
1-Propanol	Cp_2^o : 26, 273–523 ^{bb,cc,qq,ddd}	–12.4 ^k	355	61 (3)	311 (10)	–0.85 (14)
	V_2^o : 33, 273–523 ^{u,bb,ee,ff,qq}	169.8 ^k	70.7	38 (5)	14 (5)	
	$\Delta_h H^o$: 17, 277–363 ^{w,hb,ij,ss}			51 (19)		
	$\Delta_h G^o$: 29, 273–373 ^{kk,ll}			–23 (3)		
Acetic acid	κ_2^o : 12, 278–318 ^{pp}					
	Cp_2^o : 41, 278–523 ^{fff–hhh}	–21.0 ^{ttt}	168	48 (6)	188 (6)	–0.32 (8)
	V_2^o : 33, 278–573 ^{ggg–kkk}	178.7 ^z	51.8	23 (17)	–11 (4)	
	$\Delta_h H^o$: 15, 274–373 ^{x,lll,mmm}			7 (46)		
Propionic acid	$\Delta_h G^o$: 60, 275–517 ^{ll,nnn–qqq}			–12 (12)		
	κ_2^o : 4, 298–328 ^{rrr,sss}					
	Cp_2^o : 13, 278–523 ^{aa,bb,fff}	–20.4 ^{ttt}	255	61 (9)	265 (7)	–0.38 (6)
	V_2^o : 22, 278–523 ^{u,bb,iii,kkk}	206.7 ^z	68.0	33 (23)	–6 (5)	
Propionamide	$\Delta_h G^o$: 15, 318–373 ^{ll}			29 (64)		
	κ_2^o : 4, 298–328 ^{rrr,sss}			–18 (17)		
	Cp_2^o : 13, 278–523 ^{t,aa,bb}	–31.5 ^{uuu}	256	93 (20)	265 (23)	–0.31 (18)
	V_2^o : 10, 278–523 ^{u,bb,kkk}	209.2 ^z	71.8	–31 (52)	–7 (14)	
H_3BO_3				–142 (129)		
				19 (34)		
	Cp_2^o : 6, 304–623 ^{vvv}	–36.9 ^{yyy}	120	54 (25)	170 (18)	0.25 (6)
	V_2^o : 16, 278–623 ^{vvv–xxx}	162.4 ^{zzz}	39.6	–16 (65)	–40 (19)	
Glycine				–100 (162)		
				11 (43)		
	Cp_2^o : 21, 278–499 ^{aaaa–dddd}	–73.5 ⁿⁿⁿⁿ	40.9	45.1 (21)	117.0 (54)	0.83 (22)
	V_2^o : 45, 273–473 ^{cccc,eeee–jjjj}	164.4 ^{oooo}	43.1	5.6 (53)	–34.1 (22)	
Proline	κ_2^o : 21, 278–343 ^{gggg,hhhh,kkkk,mmmm}			32 (15)		
				–14.8 (38)		
	Cp_2^o : 14, 288–499 ^{dddd,pppp}	–75.1 ⁿⁿⁿⁿ	82.7	80.0 (27)	262.5 (57)	0.40 (17)
	V_2^o : 25, 278–524 ^{ffff,hhhh,iiii,pppp,qqqq}	208.5 ^{oooo}	178.5	25.6 (69)	–39.7 (32)	
			57 (18)			
			–27.7 (46)			

^a kJ · mol^{–1}; ^b at 298.15 K and 0.1 MPa; ^c J · K^{–1} · mol^{–1}; ^d cm³ · mol^{–1}; ^e J · mol^{–1} · bar^{–1}; ^f J · mol^{–1}; ^g J · K · mol^{–1} · bar^{–1}; ^h J · K · mol^{–1}; ⁱ data set described in Plyasunov et al., 2000b; ^j Shock et al., 1989; ^k Plyasunov and Shock, 2000a; ^l Gill et al., 1976; ^m Degrange, 1998; ⁿ Majer et al., 1999; ^o Plyasunov and Shock, 2000b; ^p Makhatadze and Privalov, 1988; ^q Sakurai, 1990; ^r Hallén et al., 1989; ^s Gill et al., 1975; ^t Inglesse et al., 1997; ^u Criss and Wood, 1996; ^v Kaulgud et al., 1982; ^w Lucas, 1970; ^x Konicek and Wadsö, 1971; ^y Christie and Crisp, 1967; ^z Shock and Helgeson, 1990; ^{aa} Makhatadze and Privalov, 1990; ^{bb} Makhatadze et al., 1997; ^{cc} Westh and Hvidt, 1993; ^{dd} Xiao et al., 1997; ^{ee} Alexander, 1959; ^{ff} Sakurai et al., 1994; ^{gg} Eastal and Woolf, 1985; ^{hh} Alexander and Hill, 1969; ⁱⁱ Simonson et al., 1987; ^{jj} Pfeffer et al., 1995; ^{kk} Snider and Dawson, 1985; ^{ll} Gmehling and Onken, 1977; ^{mm} Christensen, 1998; ⁿⁿ Kurihara et al., 1995; ^{oo} McGlashan and Williamson, 1976; ^{pp} Amend and Helgeson, 1997a; ^{qq} Makhatadze and Privalov, 1989; ^{rr} Ott et al., 1993; ^{ss} Hallén et al., 1986; ^{tt} Ott et al., 1986; ^{uu} Mathonat et al., 1994; ^{vv} Ott et al., 1987; ^{ww} Wormald and Lloyd, 1996; ^{xx} Griswold et al., 1943; ^{yy} Kolbe and Gmehling, 1985; ^{zz} Kolbe et al., 1992; ^{aaa} Pemberton and Mash, 1978; ^{bbb} Niesen et al., 1986; ^{ccc} Barr-David and Dodge, 1959; ^{ddd} Inglesse and Wood, 1996; ^{eee} Gabaldon et al., 1996; ^{fff} Inglesse et al., 1996b; ^{ggg} Ballerat-Busserolles et al., 1999; ^{hhh} Allred and Woolley, 1981; ⁱⁱⁱ Majer et al., 2000; ^{jjj} Høiland, 1973; ^{kkk} Makhatadze et al., 1990; ^{lll} Olofsson, 1984; ^{mmm} Stern et al., 1972; ⁿⁿⁿ Othmer et al., 1952; ^{ooo} Freeman and Wilson, 1985; ^{ppp} Sebastian and Lacquaniti, 1967; ^{qqq} Rumpf et al., 1998; ^{rrr} Høiland and Vikingstad, 1976; ^{sss} Korpela, 1971; ^{ttt} Khan and Brimblecombe, 1992; ^{uuu} Wolfenden et al., 1981; ^{vvv} Hnedkovsky et al., 1995; ^{www} Ward and Millero, 1974; ^{xxx} Ganopolsky et al., 1996; ^{yyy} Plyasunov and Shock, 2001; ^{zzz} Cox et al., 1989; ^{aaa} Gucker et al., 1939; ^{bbb} Cabani et al., 1977; ^{ccc} Hakin et al., 1994; ^{ddd} Clarke et al., 2000; ^{eee} Cabani et al., 1981b; ^{fff} Kharakoz, 1989; ^{ggg} Chalikian et al., 1993; ^{hhh} Kikuchi et al., 1995; ⁱⁱⁱ Banipal and Kapoor, 1999; ^{jjj} Shen et al., 2000; ^{kkk} Kharakoz, 1991; ^{lll} Hedwig, 1995; ^{mmm} Wadi and Ramasami, 1997; ⁿⁿⁿ Kruijff et al., 1979 + Fasman, 1975; ^{ooo} Amend and Helgeson, 1997b; ^{ppp} Hakin et al., 1997; ^{qqq} Clarke et al., 2000.

and 0.1 MPa. Results of the present study do not support this correlation, as shown in Figure 3A. Given these new results, we are inclined to connect the failure of the old correlation algorithms to predict the high-temperature behavior of boric acid and amino acids with the use of S_2^o to estimate ω . A new way to get reliable values of the parameter ω is needed to improve the quality of predictions of the revised HKF parameters.

The solvation contribution to the thermodynamic properties of solutes is dominant at conditions where the values of the dielectric constant of water and its derivatives are very different from ones at ambient conditions. As the dielectric constant rapidly decreases approaching the critical point of pure water,

the contribution of ω will maximize at near-critical conditions, where the Born functions (X , Y , Q , N ; see Appendix) go to infinite values. In the framework of the revised HKF model, the sign and the value of ω will determine the sign and magnitude of the near-critical divergence of V_2^o and Cp_2^o , when these properties go to either ∞ or $-\infty$ values approaching the critical point of water.

Insight about this divergent behavior can be gained from studies of the thermodynamics of infinite dilution critical solutions, where it was shown that the properties of such systems are governed by the value of the Krichevskii parameter (Levelt Sengers, 1991b), A_{Kr} :

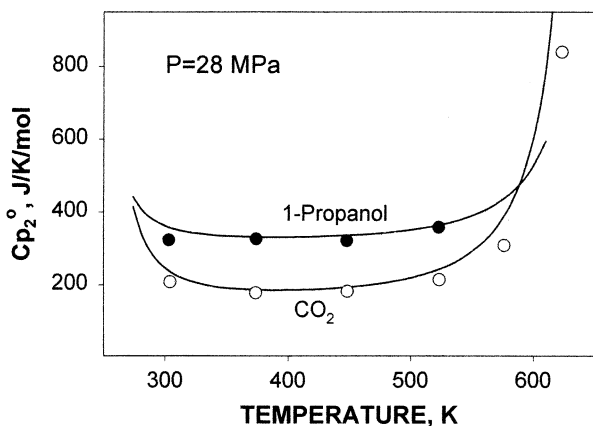


Fig. 1. Fitted (lines) and experimental (symbols) values of Cp_2^0 for aqueous CO_2 and 1-propanol. Experimental data are from Hnedkovsky and Wood (1997) and Inglesse and Wood (1996).

$$A_{Kr} = \left(\frac{\partial P}{\partial X_2} \right)_{T,V,X_2=0}^c, \quad (7)$$

where P designates pressure, X_2 represents the mole fraction of a solute, V stands for volume, and the superscript c indicates that the evaluation is done at the critical point of the pure solvent. This remarkable quantity determines the initial slopes of the critical line of a binary mixture, the density/temperature dependence of the Henry constant, and the gas-liquid distribution factor along the water saturation curve, as well as the magnitude and the sign of the derivatives of the chemical potential of an infinitely dilute solute close to the critical point of water. Solutes with positive values of the Krichevskii parameter will show a positive sign of divergence of the derivatives of the chemical potentials, and solutes with negative values of A_{Kr} will exhibit a negative sign of the divergence approaching the critical point of pure water. The scope of this article does not allow us to go into further details. However, if the near-critical values of V_2^0 and Cp_2^0 , governed by the Krichevskii parameter, are to be reproduced in the framework

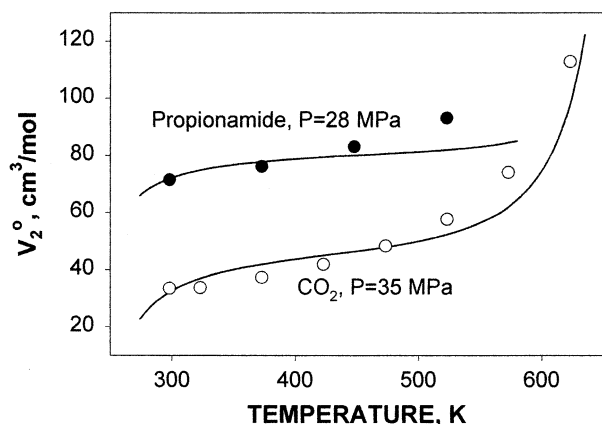


Fig. 2. Fitted (lines) and experimental (symbols) values of V_2^0 for aqueous CO_2 and propionamide. Experimental data are from Hnedkovsky et al. (1996) and Inglesse et al. (1997).

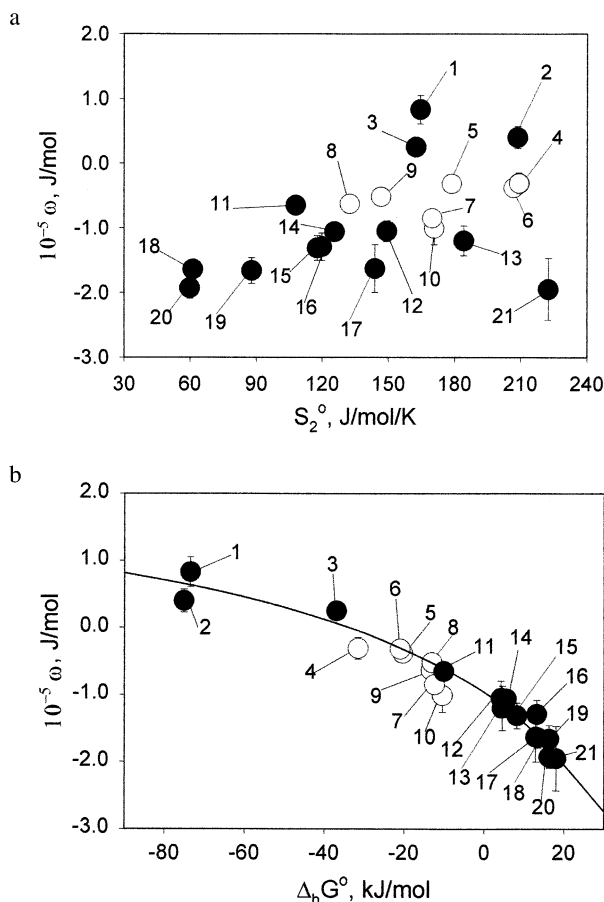


Fig. 3. Values of ω plotted vs. the standard partial molar entropy, S_2^0 (A) and standard partial molar Gibbs energy of hydration, $\Delta_h G^0$ (B), both at 298.15 K and 0.1 MPa. The open circles represent solutes for which estimated values of V_2^0 and Cp_2^0 at high temperatures were added to the fit (see text). The line is given by Eqn. 9. Numbers designate the following solutes: 1, glycine; 2, proline; 3, boric acid; 4, propionamide; 5, acetic acid; 6, propionic acid; 7, propanol; 8, ethanol; 9, methanol; 10, propylamine; 11, ammonia; 12, benzene; 13, toluene; 14, hydrogen sulfide; 15, carbon dioxide; 16, ethene; 17, cyclohexane; 18, xenon; 19, methane; 20, argon; 21, *n*-hexane. The brackets show the uncertainties of ω values.

of the HKF model by the product of ω and the Born functions, then one would expect a correlation involving the Krichevskii parameter and ω . Experimental values of the Krichevskii parameter are available for only a few aqueous nonelectrolytes, so this suggestion is of limited practical importance. However, earlier we found an empirical correlation between the Krichevskii parameter and the value of the Gibbs energy of hydration of a solute at 298.15 K and 0.1 MPa (Plyasunov and Shock, 2001) as a measure of polarity of a neutral species and the strength of water-solute interactions.

This line of argument suggests an empirical correlation between the Born coefficient ω and the Gibbs energy of hydration of a solute at 298.15 K and 0.1 MPa, $\Delta_h G^0$. The corresponding plot is given in Figure 3B. As expected, there is a definite correlation given by

$$\omega \cdot 10^{-5} = 2.61 + \frac{324.1}{\Delta_h G^0 - 90.6}, \quad (8)$$

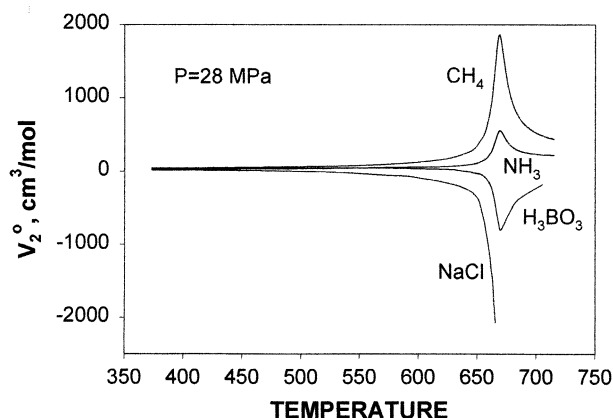


Fig. 4. The temperature dependence of V_2^0 for some aqueous solutes at 28 MPa, showing the sign and magnitude of near-critical divergence. Data for NaCl are from Archer (1992) and Sedlbauer et al. (1998); data for CH_4 and NH_3 are from Hnedkovsky et al. (1996); and data for H_3BO_3 are from Hnedkovsky et al. (1995).

where ω is in $\text{J} \cdot \text{mol}^{-1}$ and $\Delta_{\text{h}}G^\circ$ is in $\text{kJ} \cdot \text{mol}^{-1}$. The correlating equation is empirical, and its analytical form reflects an apparent trend of change in the slope, $\partial\omega/(\partial\Delta_{\text{h}}G^\circ)$, together with the assumption that the Born coefficient ω will not pass through a maximum at some value of $\Delta_{\text{h}}G^\circ$. Of course, Eqn. 8 predicts infinity for ω at $\Delta_{\text{h}}G^\circ = 90.6 \text{ kJ} \cdot \text{mol}^{-1}$; however, at 298.15 K, values of the Gibbs energy of hydration exceeding 25 to 26 $\text{kJ} \cdot \text{mol}^{-1}$ have never been detected for any solute, so this concern seems unimportant. For strongly polar compounds, having $\Delta_{\text{h}}G^\circ < -40 \text{ kJ} \cdot \text{mol}^{-1}$, the situation with the prediction of ω is rather uncertain. Available data refer only to amino acids and the upper temperature limit for experimental data is $\sim 500 \text{ K}$, which may be not sufficiently high to determine unambiguously the ω value.

One may speculate why the correlation of ω with S_2^0 , which works well for electrolytes, does not apply to aqueous nonelectrolytes. We note that nonelectrolytes demonstrate more diverse behavior at near-critical conditions than electrolytes do (see Fig. 4). All electrolytes show negative divergence of the standard thermodynamic properties when approaching the critical point of water, with both V_2^0 and Cp_2^0 going to large negative values (see example for NaCl in Fig. 4). However, nonelectrolytes may demonstrate either positive (CH_4 , NH_3) or negative divergence (H_3BO_3), with the magnitude and sign of divergence correlating with the polarity of the solute. For nonelectrolytes, the standard partial molar Gibbs energy of hydration is a better characteristic of polarity than entropy, which strongly depends on solute size (note the large increase of S_2^0 with increasing carbon number in homologous series of organic solutes). On the other hand, for ions, the known interrelation between the size and entropy justifies the use of S_2^0 to estimate ω .

4.4. Correlations to Estimate the Volumetric Parameters a_1 to a_4

For most solutes in Table 1 the uncertainties of the volumetric parameters a_1 to a_4 are too large to allow a test of the correlations. Therefore, we selected an additional set of com-

pounds, for which experimental values of both standard partial molar volumes, V_2^0 , and isothermal compressibilities, κ_2^0 , are available over a temperature range of more than 35 K. Because of the particular analytical forms of the revised HKF equations for volumetric properties, which contain terms proportional to $1/(T - \Theta)$, experimental data at $T < 298 \text{ K}$ are of particular value for the proper parameterization of the model. Furthermore, values of κ_2^0 are needed for accurate determination of the contribution of the a_2 and a_4 terms. In expanding the number and variety of compounds, we tried to include solutes of different sizes (from relatively small acetonitrile to bigger butyl acetate and phenylalanine) and different strengths of water-solute interactions. The standard Gibbs energy of hydration provides a convenient, even if not quite direct, measure of water-solute interactions (Pierotti, 1976), prompting us to include solutes with great variations in the Gibbs energy of hydration, from alkyl acetates to amino acids and carbohydrates. Table 2 gives the list of species, references to sources of volumetric data, some thermodynamic information, and the set of the revised HKF parameters a_1 to a_4 determined by means of the least-squares fit of experimental values. During the least-squares treatment, the solvation parameter ω was fixed at the value predicted by Eqn. 8. Note that the results of the fit are not particularly sensitive to the value of ω if temperatures do not exceed 450–500 K. Values of the a_1 to a_4 parameters in Table 1 are given, together with their uncertainties at the 0.95 confidence level, shown in parentheses as the number of significant figures.

Earlier correlations proposed by Shock and Helgeson (1988) and Shock et al. (1989) suggested nearly constant values of the ratios σ/V_2^0 and a_1/V_2^0 , where V_2^0 refers to 298.15 K and 0.1 MPa (actually these authors discuss the ratios given for non-solvation volumes, V_n^0 [see Appendix]; however, at this temperature, the difference between V_2^0 and V_n^0 , equal to $-\omega Q$, does not exceed $2 \text{ cm}^3 \cdot \text{mol}^{-1}$ and can be neglected). In Figure 5, we plot these ratios against the Gibbs energy of hydration, $\Delta_{\text{h}}G^\circ$, at 298.15 K and 0.1 MPa. In addition to solutes given in Table 2, we also include data for some solutes from Table 1 (acetic and propionic acids, methanol, ethanol, 1-propanol, glycine, and proline). The ratio σ/V_2^0 (solid squares) seems to not depend on $\Delta_{\text{h}}G^\circ$ even over the range of 100 $\text{kJ} \cdot \text{mol}^{-1}$ shown in the Fig. 5. Therefore, the ratio can be approximated by

$$\sigma = 1.069V_2^0, \quad (9)$$

if both σ and V_2^0 are given in $\text{cm}^3 \cdot \text{mol}^{-1}$. Ratios of a_1/V_2^0 (open circles) are about constant at fixed $\Delta_{\text{h}}G^\circ$ values but show a linear increase as values of the Gibbs energy of hydration become more negative. This behavior can be described by

$$\frac{10 \cdot a_1}{V_2^0} = 0.820 - 1.85 \cdot 10^{-3} \cdot \Delta_{\text{h}}G^\circ, \quad (10)$$

Because σ and a_1 are in a linear dependence with the revised HKF parameter a_2 (see Appendix), then after some elementary algebra, one obtains

$$\frac{10^{-2} \cdot a_2}{V_2^0} = 0.648 + 4.81 \cdot 10^{-3} \Delta_{\text{h}}G^\circ \quad (11)$$

Table 2. Data sources and the revised-HKF parameters a_1 – a_4 for aqueous nonelectrolytes in the expanded set.

Compound	No. of points, T range, references			$10 \cdot a_1^a$	$10^{-2} \cdot a_2^b$	a_3^c	$10^{-4} \cdot a_4^d$	$\Delta_h G^{\circ e}$	$10^{-5} \cdot \omega^b$	$V_2^{\circ f}$
	V_2°	k_2°								
Methyl acetate	5, 278–318 ^g	5, 278–318 ^h	58.0 (34)	52.1 (81)	82 (22)	–32.3 (53)	–5.1 ⁱ	–0.78	72.3	
Ethyl acetate	8, 278–318 ^{g,j}	5, 278–318 ^h	71.3 (35)	64.5 (86)	103 (23)	–39.9 (57)	–4.4 ⁱ	–0.80	89.0	
Propyl acetate	5, 278–318 ^g	5, 278–318 ^h	84.8 (30)	75.6 (35)	121 (19)	–47.4 (23)	–3.8 ⁱ	–0.82	105.2	
Butyl acetate	5, 278–318 ^g	5, 278–318 ^h	97.9 (37)	87.7 (44)	142 (24)	–56.0 (29)	–3.1 ⁱ	–0.85	121.1	
1-Butanol	14, 278–373 ^{k,l,m}	11, 278–318 ⁿ	76.2 (23)	45.9 (40)	68 (16)	–30.0 (26)	–11.9 ^o	–0.55	86.6	
1-Pentanol	14, 278–403 ^{l,m,p}	8, 278–318 ⁿ	91.4 (50)	58 (10)	79 (33)	–38.7 (70)	–11.1 ^o	–0.58	102.6	
1-Hexanol	9, 278–318 ^q	5, 278–318 ^l	96.3 (21)	73.4 (31)	148 (14)	–49.4 (20)	–10.2 ^o	–0.61	118.5	
2-Propanol	16, 278–521 ^{q,l,r}	5, 278–318 ^s	63.2 (60)	34.0 (96)	52 (36)	–20.7 (60)	–12.0 ^o	–0.55	71.8	
2-Butanol	9, 278–318 ^q	5, 278–318 ^s	71.6 (16)	44.6 (19)	98 (10)	–29.7 (12)	–11.2 ^o	–0.57	86.6	
<i>iso</i> -Butanol	5, 278–318 ^l	5, 278–318 ^s	71.4 (17)	46.5 (20)	94 (11)	–29.7 (14)	–11.2 ^o	–0.57	86.5	
<i>tert</i> -Butanol	11, 278–338 ^{l,t}	5, 278–318 ^s	74.1 (18)	42.2 (31)	93 (12)	–28.5 (21)	–11.1 ^o	–0.58	87.8	
Neopentanol	5, 278–318 ^l	5, 278–318 ^s	87.1 (29)	50.9 (35)	103 (20)	–34.9 (23)	–10.3 ^o	–0.60	102.3	
Acetonitrile	15, 273–323 ^{u,v,w}	6, 278–323 ^{u,x}	42.1 (20)	29.6 (46)	19 (14)	–16.8 (32)	–8.7 ^y	–0.65	47.3	
2-Methoxyethanol	11, 278–323 ^{z,aa,bb}	3, 278–318 ^z	64.5 (29)	36.4 (74)	61 (19)	–22.1 (48)	–20.3 ^{cc}	–0.31	75.2	
2-Ethoxyethanol	8, 278–323 ^{z,aa}	3, 278–318 ^z	77.8 (49)	45 (12)	84 (31)	–29.1 (79)	–19.7 ^{cc}	–0.33	91.2	
1,2-Ethandiol	9, 278–328 ^{dd,ee}	3, 278–318 ^{ff}	50.1 (18)	19.6 (44)	23 (11)	–11.1 (28)	–33.3 ^{gg}	–0.01	54.6	
1,3-Propanediol	8, 278–333 ^{q,hh}	3, 278–318 ^q	63.9 (12)	26.6 (21)	39 (7)	–13.7 (13)	–35.6 ⁱⁱ	0.04	72.1	
Glycerol	8, 273–333 ^{jj}	2, 298–333 ^{kk,ll}	65.6 (40)	25 (10)	33 (32)	–16.2 (84)	–50.0 ^{mm}	0.30	70.6	
α -Alanine	24, 278–523 ^{nn-qq}	17, 278–343 ^{pp,rr,ss}	57.0 (18)	11.1 (31)	67 (13)	–18.4 (27)	–70.6 ^{tt}	0.60	60.4	
Phenylalanine	14, 278–328 ^{nn,pp,uu}	9, 278–328 ^{rr,pp}	113.4 (24)	47.0 (61)	114 (17)	–46.5 (42)	–75.3 ^{cc}	0.66	121.7	
Xylose	16, 291–328 ^{ww-yy}	5, 291–318 ^{yy,zz}	94.2 (71)	21 (11)	32 (53)	–19.6 (82)	–77.3 ^{aaa}	0.68	95.7	
Glucose	34, 278–368 ^{ww-zz,bbb-fff}	10, 278–328 ^{yy,eee,fff}	111.0 (76)	29 (19)	36 (53)	–26 (13)	–98.3 ^{aaa}	0.89	112.2	

^a J · mol^{–1} · bar^{–1}; ^b J · mol^{–1}; ^c J · K · mol^{–1} · bar^{–1}; ^d J · K · mol^{–1}; ^e kJ · mol^{–1} at 298.15 K, 0.1 MPa; ^f cm³ · mol^{–1} at 298.15 K, 0.1 MPa; ^g Sakurai et al., 1996; ^h Sakurai et al., 1998; ⁱ Kieckbush and King, 1979; ^j Roux et al., 1978; ^k Makhatadze and Privalov, 1989; ^l Sakurai et al., 1994; ^m Makhatadze et al., 1997; ⁿ Amend and Helgeson, 1997a; ^o Plyasunov and Shock, 2000a; ^p Inglese et al., 1996a; ^q Høiland, 1980; ^r Schulte et al., 1999; ^s Sakurai et al., 1995; ^t Visser et al., 1977; ^u Eastal and Woolf, 1988; ^v Sakurai, 1992; ^w Meurs and Somsen, 1993; ^x Benson et al., 1981; ^y Welke et al., 1998; ^z Harada et al., 1978; ^{aa} Sikora, 1985; ^{bb} Page et al., 1993; ^{cc} Cabani et al., 1978; ^{dd} Müller and Rasmussen, 1991; ^{ee} Sakurai, 1991; ^{ff} Huot et al., 1988; ^{gg} Villamanan et al., 1984; ^{hh} Alexander, 1959; ⁱⁱ Suleiman and Eckert, 1994 + Knauth and Sabbah, 1988; ^{jj} Neal and Goring, 1970; ^{kk} Whalley and Heath, 1976; ^{ll} Miyamoto et al., 1990; ^{mm} To et al., 1990 + Stephenson and Malanowski, 1987; ⁿⁿ Kharakoz, 1989; ^{oo} Hakin et al., 1994; ^{pp} Kikuchi et al., 1995; ^{qq} Clarke and Tremain, 1999; ^{rr} Kharakoz, 1991; ^{ss} Chalikian et al., 1993; ^{tt} Kruif et al., 1979 + Fasman, 1975; ^{uu} Marriott et al., 1998; ^{vv} Svec and Clyde, 1965 + Fasman, 1975; ^{ww} Paljk et al., 1990; ^{xx} Banipal et al., 1997; ^{yy} Chalikian, 1998; ^{zz} Høiland and Holvik, 1978; ^{aaa} Oja and Suuberg, 1999 + Goldberg and Tewari, 1989; ^{bbb} Miyajima et al., 1983; ^{ccc} Bernal and Hook, 1986; ^{ddd} Kishore et al., 1993; ^{eee} Origlia et al., 2000; ^{fff} Franks et al., 1972.

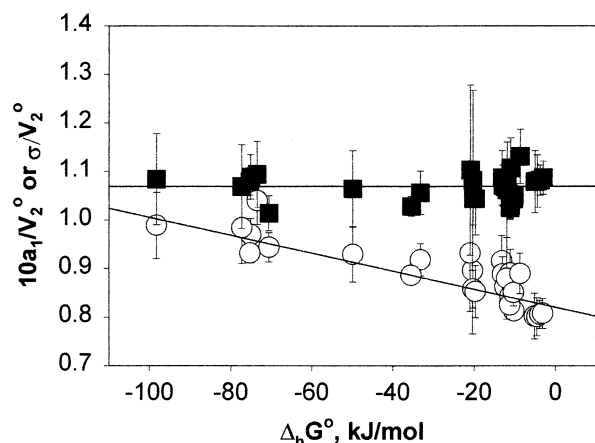


Fig. 5. The dependence of the ratios σ/V_2^0 (filled squares) and $10a_1/V_2^0$ (open circles) on values of the standard Gibbs energy of hydration, $\Delta_h G^0$, at 298.15 K and 0.1 MPa. The lines are given by Eqns. 9 and 10, respectively. The brackets show the uncertainties of the corresponding ratios.

Fitted vs. correlated values of the a_2 parameters are shown in Figure 6.

Earlier, Shock and Helgeson (1988) and Shock et al. (1989) suggested a linear correlation between parameters a_2 and a_4 . Our results support this conclusion but show the necessity of including the Gibbs energy of hydration into the correlation. In Figure 7, we plot values of a_4 vs. a_2 as circles or squares. Circles represent moderately polar compounds with values of $\Delta_h G^0$ within the range -3 to -20 $\text{kJ} \cdot \text{mol}^{-1}$ (all alcohols, all acetates, acetonitrile, 2-ethoxyethanol), and squares represent extremely polar compounds (amino acids: α -alanine, proline, glycine, phenylalanine; carbohydrates: glucose, xylose), for

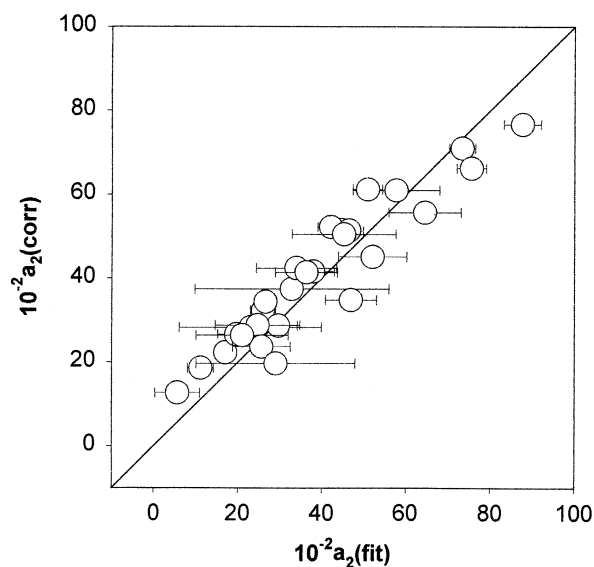


Fig. 6. Values of the revised HKF parameter a_2 from the fit of experimental data and those estimated with Eqn. 11. The brackets show the uncertainties of the fitted a_2 values.

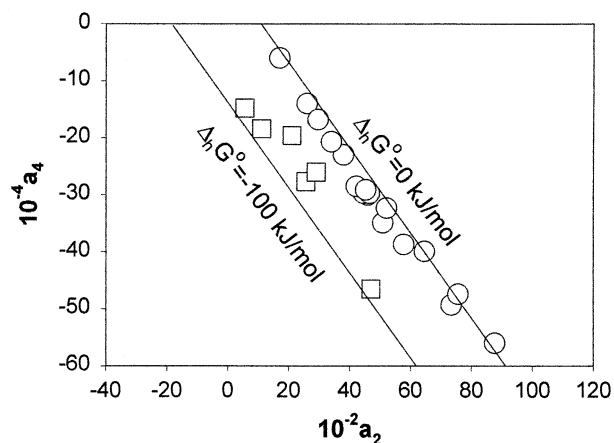


Fig. 7. Values of the revised HKF parameters a_2 and a_4 plotted vs. each other for two groups of aqueous compounds: one for which $-20 < \Delta_h G^0$, $\text{kJ/mol} < -3$ (circles), and another for which $-100 < \Delta_h G^0$, $\text{kJ/mol} < -70$ (squares) (see text). Contours shown for two values of $\Delta_h G^0$ are consistent with Eqn. 12.

which $-100 < \Delta_h G^0$ ($\text{kJ} \cdot \text{mol}^{-1}$) < -70 . Apparently, squares and circles fall into two separate groups having about the same slopes, and intercepts that depend on the Gibbs energy of hydration. This is indicated by the two $\Delta_h G^0$ contours shown in Figure 7. Thus, this correlation can be represented as

$$10^{-4}a_4 = 8.10 - 0.746 \cdot 10^{-2}a_2 + 0.219 \cdot \Delta_h G^0. \quad (12)$$

The parameter a_3 typically has the biggest uncertainties of all volumetric revised HKF parameters. It was found to correlate linearly with the a_4 parameter, as shown in Figure 8, where the relation between the two parameters is given as

$$a_3 = -11.9 - 3.09 \cdot 10^{-4}a_4. \quad (13)$$

However, from a practical point of view, it may be more convenient to evaluate a_3 in such a way to provide formal consistency between the calculated and accepted value of V_2^0 at

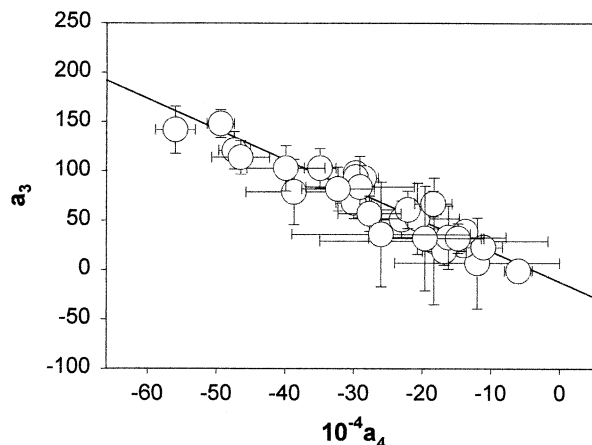


Fig. 8. The correlation between the revised HKF parameters a_3 and a_4 . The line is given by Eqn. 13. The brackets show the uncertainties of both a_3 and a_4 values.

Table 3. Data sources and the revised HKF parameters c_1 and c_2 for aqueous nonelectrolytes in the expanded set.

Compound	No. of points, T range, references	c_1^a	$10^{-4} \cdot c_2^b$	$\Delta_h G^\circ e$	$10^{-5} \cdot \omega^c$	$Cp_2^{oa,d}$
Ethyl acetate	6, 283–328 ^{e,f}	340 (48)	21 (23)	-4.4 ^g	-0.80	397
<i>n</i> -Butylamine	6, 278–398 ^h	390 (9)	5.2 (47)	-10.0 ⁱ	-0.61	411
Dimethylamine	4, 283–328 ^j	229 (43)	12 (21)	-10.0 ⁱ	-0.61	260
Diethylamine	4, 293–333 ^k	419 (17)	31 (10)	-9.1 ⁱ	-0.64	486
Triethylamine	7, 278–348 ^{l,m}	557 (21)	17.1 (71)	-4.7 ⁱ	-0.79	600
1-Butanol	11, 278–298 ^{n,o}	400 (10)	17.1 (49)	-11.9 ^p	-0.55	447
1-Pentanol	11, 278–298 ^{n,o}	470 (25)	32 (12)	-11.1 ^p	-0.58	544
<i>tert</i> -Butanol	6, 279–338 ^q	417.6 (45)	19.7 (18)	-11.1 ^p	-0.58	464
Butanoic acid	6, 278–373 ^{o,r}	337.2 (73)	-2.0 (35)	-20.9 ^s	-0.30	335
Pentanoic acid	5, 278–373 ^o	412.9 (52)	1.0 (25)	-18.4 ^s	-0.36	417
<i>N,N</i> -Dimethyl-2-ethanolamine	4, 283–328 ^t	374 (22)	-1 (10)	-23.6 ^u	-0.23	373
<i>N</i> -Methylformamide	4, 278–373 ^o	201 (18)	-15 (9)	-29.1 ^v	-0.10	163
Acetamide	6, 278–393 ^w	203 (14)	-14 (7)	-32.7 ^x	-0.02	167
<i>N</i> -Methylacetamide	5, 278–373 ^o	284 (15)	-10 (7)	-34.2 ^x	0.01	258
Diethanolamine	4, 283–328 ^t	362 (11)	-15.3 (50)	-47.9 ^y	0.27	327
Urea	7, 275–313 ^z	128.3 (17)	-18.5 (6)	-51.3 ^{aa}	0.33	89
α -Alanine	17, 278–473 ^{bb,dd}	202.5 (34)	-26.4 (23)	-70.6 ^{cc}	0.60	141
Xylose	6, 298–318 ^{ee-hh}	451 (68)	-83 (37)	-77.3 ⁱⁱ	0.68	276
Glucose	31, 278–393 ^{gg,ii-kk}	492.1 (64)	-60.1 (43)	-98.3 ⁱⁱ	0.89	363

^a $J \cdot K^{-1} \cdot mol^{-1}$; ^b $J \cdot K \cdot mol^{-1}$; ^c $J \cdot mol^{-1}$; ^d at 298.15 K, 0.1 MPa; ^e Cabani et al., 1977; ^f Roux et al., 1978; ^g Kieckbush and King, 1979; ^h Makhatadze and Privalov, 1990; ⁱ Christie and Crisp, 1967; ^j Shvedov and Tremaine, 1997; ^k Cabani et al., 1973; ^l Bergström and Olofsson, 1975; ^m Roux et al., 1980; ⁿ Makhatadze and Privalov, 1989; ^o Makhatadze et al., 1997; ^p Plyasunov and Shock, 2000a; ^q Visser et al., 1977; ^r Konicek and Wadsö, 1971; ^s Khan and Brimblecombe, 1992; ^t Collins et al., 2000; ^u Touhara et al., 1982; ^v value from Zielkiewicz, 1998, at 303.15 K recalculated to 298.15 K using the standard enthalpy of solution and vaporization from Carthy et al., 1991, and Majer and Svoboda, 1985, respectively; ^w Makhatadze and Privalov, 1990; ^x Wolfenden, 1978; ^y Chang et al., 1993; ^z Stokes, 1967; ^{aa} Jakli and Hook, 1981 + Wit et al., 1983; ^{bb} Hakin et al., 1994 + Clarke et al., 2000; ^{cc} Kruijff et al., 1979 + Fasman, 1975; ^{dd} Gucker and Allen, 1942; ^{ee} Kawaizumi et al., 1981; ^{ff} Jasra and Ahluwalia, 1982; ^{gg} Galema et al., 1993; ^{hh} Banipal et al., 1997; ⁱⁱ Oja and Suuberg, 1999 + Goldberg and Tewari, 1989; ^{jj} Kishore et al., 1993; ^{kk} Origlia et al., 2000.

298.15 K and 0.1 MPa, as suggested by Shock and Helgeson (1988).

It is not easy to provide explanations or justifications for these proposed correlations except very general ones: the volumetric a_1 to a_4 HKF parameters depend on both the intrinsic properties of solutes (size, first of all) and the strengths and types of water-solute interactions, one of the measures of which is the Gibbs energy of hydration at 298.15 K and 0.1 MPa, $\Delta_h G^\circ$. However, available results (see Figures 5–8), show that there are strong constraints on the mutual variations of the numerical values of the a_1 to a_4 HKF parameters, when both size (as the V_2° value at 298.15 K and 0.1 MPa) and $\Delta_h G^\circ$ are explicitly taken into account.

4.5. Correlation to Estimate the Revised HKF

Parameter c_2

To get a more representative set of the “caloric” c_1 and c_2 parameters of the revised HKF model, we selected an additional set of compounds for which experimental values of the standard partial molar heat capacity, Cp_2° , are available over a temperature range at atmospheric pressure. Table 3 gives the list of species, references to the sources of the Cp_2° data, some thermodynamic information and the set of the revised HKF parameters c_1 to c_2 determined by means of the least-squares fit of experimental values (together with the uncertainties in the parameters at the 0.95 confidence level, shown in parentheses as the number of significant figures). Again, in the least-squares treatment, the solvation parameter ω was fixed for each solute at the value predicted by Eqn. 8.

Our efforts were directed to the search for a correlation to estimate c_2 (if c_2 is available, then the parameter c_1 can be calculated from an experimental Cp_2° value). The parameter c_2 determines the sign and magnitude of change of the standard partial molar heat capacity of a solute, Cp_2° , at near-ambient temperatures, say up to 350 to 400 K. If $c_2 > 0$, then Cp_2° decreases with temperature in this temperature range; if $c_2 < 0$, then Cp_2° increases. So first it is necessary to have at least a

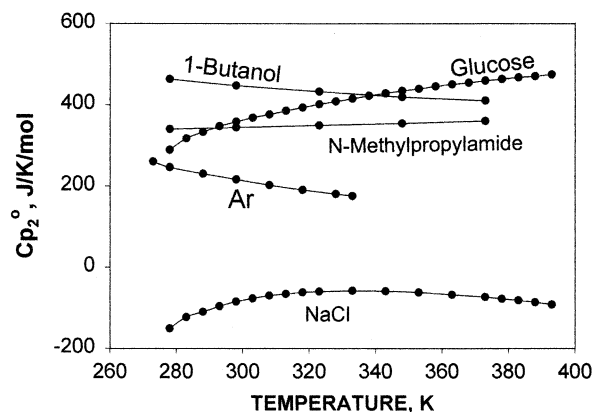


Fig. 9. The temperature dependence of the standard partial molar heat capacity at moderate temperatures for a number of aqueous compounds: NaCl (Archer, 1992), Ar (Krause and Benson, 1989), 1-butanol and *N*-methylpropylamide (Makhatadze et al., 1997), and glucose (Origlia et al., 2000). Lines are drawn through data points to aid the eye.

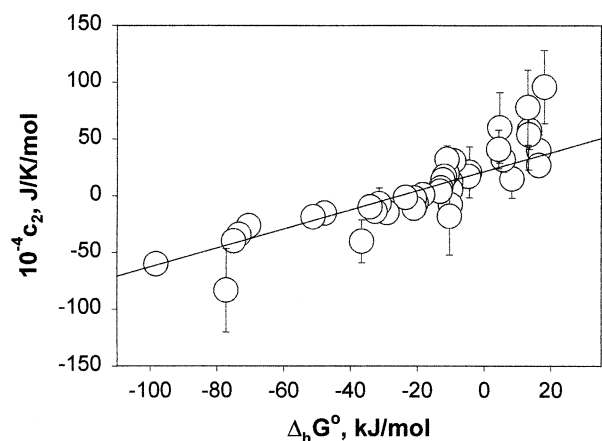


Fig. 10. Correlation between the revised HKF parameter c_2 and the standard Gibbs energy of hydration, $\Delta_h G^\circ$, at 298.15 K and 0.1 MPa. The brackets show the uncertainties of c_2 values. The line is given by Eqn. 14.

qualitative answer to the question of what governs the temperature course of Cp_2° at moderate temperatures. In Figure 9, we plot the values of Cp_2° vs. temperature for NaCl and for a number of nonelectrolytes. The temperature dependence of the standard partial molar heat capacity for NaCl is typical for all electrolytes: Cp_2° first increases, then passes through a flat maximum at 320 to 350 K, and finally starts decreasing. In contrast, nonelectrolytes demonstrate a wider range of behavior. Aqueous argon and 1-butanol exhibit decreasing values of Cp_2° with increasing temperature. Solutions of *N*-methylpropylamide in water show practically no temperature dependence of the heat capacity between 278 and 373 K. Values of Cp_2° for aqueous glucose increase sharply with temperature and exhibit low-temperature behavior that rivals that of electrolytes. The obvious difference between these solutes lies in the strength of their water–solute interactions. Argon is a nonpolar solute, 1-butanol is a moderately polar species, and *N*-methylpropylamide and the polyhydroxy compound glucose are examples of strongly polar and exceptionally strongly polar solutes, respectively. If this interpretation is reasonable, then one would expect a correlation between the revised HKF parameter c_2 and the Gibbs energy of hydration at 298.15 K and 0.1 MPa, $\Delta_h G^\circ$, as a measure of the strength of water–solute interactions. In Figure 10, we plot the values of c_2 vs. $\Delta_h G^\circ$ (data for solutes from Table 1 are also included). The correlation, although not perfect, is apparent, and is given by

$$10^{-4} c_2 = 21.4 + 0.849 \Delta_h G^\circ. \quad (14)$$

Attempts to include Cp_2° or V_2° (at 298.15 K and 0.1 MPa) into the correlation did not improve it significantly.

4.6. Suggested Strategy to Evaluate/Estimate the Revised HKF Parameters for Aqueous Nonelectrolytes

Determining the solvation ω parameter of the revised HKF model for aqueous nonelectrolytes by a global fit of experimental data can only be recommended for those solutes for which the derivatives of the chemical potential (Cp_2° , V_2°) have been extensively studied in the temperature range up to 550 to 600 K. In the overwhelming majority of cases, the ω parameter has to be estimated by means of Eqn. 8. Volumetric a_1 to a_4 parameters can all be determined by the fit of experimental data only if values of both V_2° and κ_2° are available at different temperatures. Otherwise, Eqns. 10 through 13 should be used to estimate some (or all) of the revised HKF volumetric parameters. If Cp_2° results are reported at various temperatures, then both c_1 and c_2 can be evaluated from experimental information; otherwise, the parameter c_2 has to be estimated by means of Eqn. 14. The necessary values of the Gibbs energy of hydration at 298.15 K and 0.1 MPa, $\Delta_h G^\circ$, are either available or can be evaluated from various sets of experimental information (see Plyasunov and Shock, 2000b).

As a test of the proposed correlation algorithms, we determined the parameters of the revised HKF model for a number of nonelectrolytes for which experimental determinations of V_2° , Cp_2° , or both at elevated temperatures are available. This set of selected compounds consists of SO_2 , pyridine, 1,4-butanediol, and β -alanine. These solutes differ in size and strength of water–solute interactions, which can be inferred by comparing V_2° and $\Delta_h G^\circ$ values at 298 K in Table 4. To perform the most stringent test, all the revised HKF parameters are estimated from values of the thermodynamic functions of each solute at 298.15 K and 0.1 MPa by use of Eqns. 8, 10 through 12, and 14. The volumetric parameter a_3 and “caloric” parameter c_1 were calculated by means of estimated values of other HKF parameters and experimental values of V_2° and Cp_2° at 298.15 K and 0.1 MPa to provide formal consistency between the calculated and accepted values of the partial molar volume and heat capacity at the reference temperature and pressure. The predicted values of the revised HKF parameters for these solutes are given in Table 4. Note that these are estimated values and they may be not the optimal ones. A comparison of predicted and experimental values of V_2° and Cp_2° for the selected solutes

Table 4. Some standard-state thermodynamic properties of aqueous compounds selected to test the correlation algorithms and resulting estimated values of the revised HKF model parameters.

Compound	$\Delta_h G^{\circ a,b}$	$Cp_2^{\circ a,b}$	$V_2^{\circ a,d}$	$10^{-5} \cdot \omega^e$	$10 \cdot a_1^f$	$10^{-2} \cdot a_2^e$	a_3^g	$10^{-4} \cdot a_4^h$	c_1^c	$10^{-4} \cdot c_2^h$
SO_2	-0.51 ⁱ	146 ^j	39.0 ^k	-0.95	32.02	25.17	18.71	-10.79	93.2	20.97
Pyridine	-11.7 ^l	306 ^m	77.1 ⁿ	-0.56	64.89	45.62	69.94	-28.50	278.1	11.47
1,4-Butanediol	-37.7 ^o	347 ^p	88.23 ^p	0.08	78.50	41.17	76.32	-30.87	369.2	-10.61
β -Alanine	-74 ^q	76 ^r	58.7 ^s	0.64	56.17	17.14	54.55	-20.90	165.5	-41.43

^a 298.15 K, 0.1 MPa; ^b $kJ \cdot mol^{-1}$; ^c $J \cdot K^{-1} \cdot mol^{-1}$; ^d $cm^3 \cdot mol^{-1}$; ^e $J \cdot mol^{-1}$; ^f $J \cdot mol^{-1} \cdot bar^{-1}$; ^g $J \cdot K \cdot mol^{-1} \cdot bar^{-1}$; ^h $J \cdot K \cdot mol^{-1}$; ⁱ Goldberg and Parker, 1985; ^j Sharygin et al., 1997; the datum refers to 303 K, 28 MPa; ^k Sharygin et al., 1997; Barbero et al., 1983; ^l Cabani et al., 1981a; ^m Enea et al., 1977; ⁿ Criss and Wood, 1996; ^o Suleiman and Eckert, 1994 + Stephenson and Malanowski, 1987; ^p Jolicœur and Lacroix, 1976; ^q by analogy with other amino acids; ^r Gucker and Allen, 1942; ^s Wadi and Goyal, 1992.

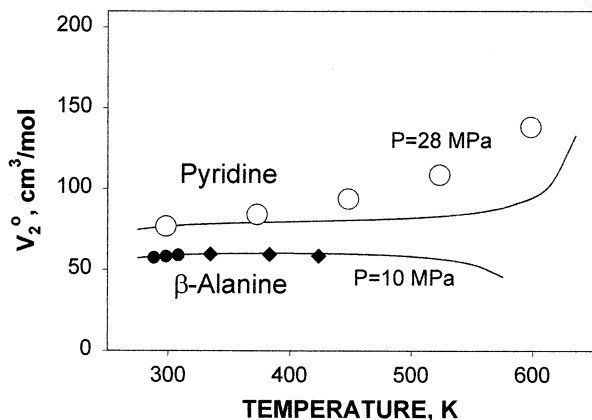


Fig. 11. The comparison of predicted (lines) and experimental values of V_2^0 for pyridine and β -alanine at elevated temperatures. Experimental data for pyridine are from Criss and Wood (1996), $P = 28$ MPa; for β -alanine from Clarke and Tremaine (1999), diamonds, $P = 10$ MPa; and from Wadi and Goyal (1992), circles, $P = 0.1$ MPa.

at elevated temperatures is presented in Figures 11 through 13. In our opinion, these comparisons reveal a satisfactory performance of the correlations proposed in this work. The worst case seems to be the prediction of V_2^0 for pyridine at 450 to 600 K (see Fig. 11). However, it is difficult to judge whether this deviation of experimental and calculated data is primarily due to a failure of the correlation algorithms or if it is an additional example of the known problems of the revised HKF model to represent accurately V_2^0 for aqueous nonelectrolytes (O'Connell et al., 1996; Schulte, 1997). Nevertheless, the positive sign of the near-critical divergence is correctly predicted for aqueous pyridine. The predictions of Cp_2^0 for aqueous 1,4-butanediol and β -alanine are better than expected (maybe fortuitously), and those for aqueous SO_2 are satisfactory up to 550 to 600 K.

5. CONCLUSIONS

The goals of this article are a discussion of the temperature/density range of applicability of the revised HKF model for

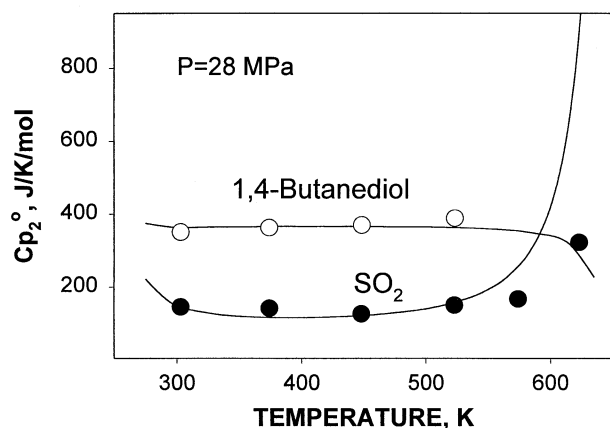


Fig. 12. The comparison of predicted (lines) and experimental values of Cp_2^0 for SO_2 and 1,4-butanediol at elevated temperatures and $P = 28$ MPa. Experimental data for SO_2 are from Sharygin et al. (1997) and for 1,4-butanediol are from Ingles and Wood (1996).

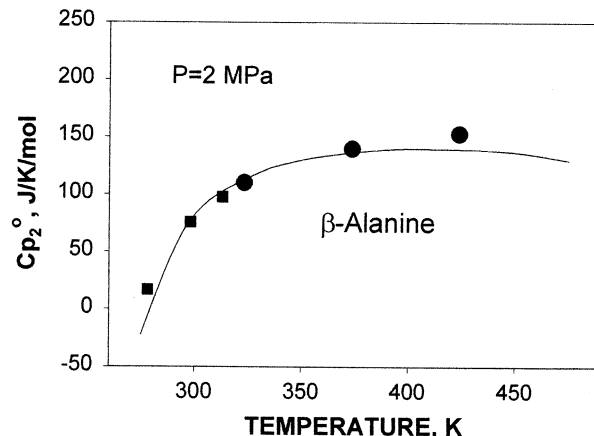


Fig. 13. The comparison of predicted (line) and experimental values of Cp_2^0 for β -alanine at elevated temperatures. Experimental data are from Clarke et al. (2000), circles, $P = 2$ MPa; and from Gucker and Allen (1942), squares, $P = 0.1$ MPa.

aqueous nonelectrolytes and, mainly, revision of the correlation algorithms for estimating parameters of this model. The basis of the revisions/corrections is the analysis of a large body of experimental data published mainly during the last decade. The temperature/density range of the applicability of the revised HKF model for aqueous nonelectrolytes seems to be not as extensive as originally thought. A comparison of experimental data with values fitted in the framework of the revised HKF model suggests that the window for the use of this model along the saturation vapor–liquid curve of pure water exists up to 630 K (i.e., in the high-density region sufficiently remote from the critical point of water) and may extend up to higher temperatures (800 K?) at densities above $500\text{--}600\text{ kg}\cdot\text{m}^{-3}$. Over the temperature range up to 500 K at pressures up to 50 MPa, the revised HKF model is capable of excellent description of the standard thermodynamic properties of aqueous nonelectrolytes, except in the narrow temperature range below 280–290 K. Through analysis of methods to estimate the revised HKF parameters, we have established that the Gibbs energy of hydration of a solute at 298.15 K and 0.1 MPa, $\Delta_h G^0$, which reflects the strength of water–solute interactions, is a particularly useful correlating parameter. Explicit correlations with $\Delta_h G^0$ seem to provide reliable means to estimate the solvation parameter ω and the “caloric” parameter c_2 (Eqn. 8 and 14), as well as to improve estimations of the volumetric parameters a_1 , a_2 , and a_4 (Eqns. 10–12).

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APPENDIX. SUMMARY OF THE REVISED HKF EQUATIONS

In the revised HKF model, all thermodynamic properties are considered as a sum of solvation and nonsolvation contributions, denoted by subscripts “s” and “n,” respectively. Analytical statements for Cp_2^o , V_2^o , and κ_2^o are expressed as

$$Cp_2^o = \Delta Cp_n^o + \Delta Cp_s^o = c_1 + \frac{c_2}{(T - \Theta)^2} - \frac{2T}{(T - \Theta)^3} \cdot \left[a_3(P - P_r) + a_4 \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) \right] + \omega TX, \quad (A1)$$

$$V_2^o = \Delta V_n^o + \Delta V_s^o = \sigma + \xi \left(\frac{1}{T - \Theta} \right) - \omega Q = a_1 + \frac{a_2}{\Psi + P} + \left(a_3 + \frac{a_4}{\Psi + P} \right) \left(\frac{1}{T - \Theta} \right) - \omega Q, \quad (A2)$$

and

$$\kappa_2^o = \Delta \kappa_n^o + \Delta \kappa_s^o = \left(a_2 + \frac{a_4}{T - \Theta} \right) \left(\frac{1}{\Psi + P} \right)^2 + \omega N, \quad (A3)$$

where

$$\sigma = a_1 + \frac{a_2}{\Psi + P}, \quad (A4)$$

$$\xi = a_3 + \frac{a_4}{\Psi + P}, \quad (5)$$

a_1 to a_4 , c_1 , c_2 , and ω represent solute-dependent parameters, and $\Theta = 228$ K and $\Psi = 2600$ bar represent the constants of the revised HKF model; P and T stand for pressure and temperature, respectively; P_r refers to the reference pressure of 0.1 MPa. X , Q , N , and Y represent Born functions defined by

$$X \equiv \left(\frac{\partial Y}{\partial T} \right)_P, \quad (A6)$$

$$Q \equiv - \left[\frac{\partial(l/\varepsilon)}{\partial P} \right]_T, \quad (A7)$$

$$N \equiv \left(\frac{\partial Q}{\partial P} \right)_T, \quad (A8)$$

and

$$Y \equiv - \left[\frac{\partial(l/\varepsilon)}{\partial T} \right]_P. \quad (A9)$$

In this study, the values of X , Q , N , and Y are calculated by means of the Archer and Wang (1990) equation for the dielectric constant of pure water, ε .

The standard molar entropy, S^o , and the apparent standard molar enthalpy and Gibbs energy of formation (ΔH^o and ΔG^o , respectively) of an aqueous species are given by

$$S^o = S_{P_r, T_r} + c_1 \ln \left(\frac{T}{T_r} \right) - \frac{c_2}{\Theta} \left[\left(\frac{1}{T - \Theta} \right) - \left(\frac{1}{T_r - \Theta} \right) + \frac{1}{\Theta} \ln \left(\frac{T_r(T - \Theta)}{T(T_r - \Theta)} \right) \right] + \left(\frac{1}{T - \Theta} \right)^2 \left[a_3(P - P_r) + a_4 \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) \right] + \omega(Y - Y_{P_r, T_r}), \quad (A10)$$

$$\Delta H^o \equiv \Delta_r H^o + (H^o - H_{P_r, T_r}^o) = \Delta_r H^o + c_1(T - T_r) - c_2 \left[\left(\frac{1}{(T - \Theta)} \right) - \left(\frac{1}{(T_r - \Theta)} \right) + a_1(P - P_r) + a_2 \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) \left(\frac{1}{T - \Theta} \right)^2 + \left[\frac{2T - \Theta}{(T - \Theta)^2} \right] \left[a_3(P - P_r) + a_4 \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) \right] + \omega \left(TY - T_r Y_{P_r, T_r} + \frac{1}{\varepsilon} - \frac{1}{\varepsilon_{P_r, T_r}} \right), \quad (A11)$$

and

$$\Delta G^o \equiv \Delta_r G^o + (G^o - G_{P_r, T_r}^o) = \Delta_r G^o - S_{P_r, T_r}^o(T - T_r) - c_1 \left[T \ln \left(\frac{T}{T_r} - T + T_r \right) \right] - c_2 \left\{ \left[\left(\frac{1}{(T - \Theta)} \right) - \left(\frac{1}{(T_r - \Theta)} \right) \right] \cdot \left(\frac{\Theta - T}{\Theta} \right) - \frac{T}{\Theta^2} \ln \left[\frac{T_r(T - \Theta)}{T(T_r - \Theta)} \right] + a_1(P - P_r) + a_2 \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) + \left(\frac{1}{T - \Theta} \right) \left[a_3(P - P_r) + a_4 \ln \left(\frac{\Psi + P}{\Psi + P_r} \right) \right] + \omega \left(Y_{P_r, T_r}(T - T_r) + \frac{1}{\varepsilon} - \frac{1}{\varepsilon_{P_r, T_r}} \right) \right\}, \quad (A12)$$

where T_r denotes the reference temperature of 298.15 K and $\Delta_r H^o$ and $\Delta_r G^o$ refer to the standard molar enthalpy and Gibbs energy of formation of the species from its elements in their stable form at 298.15 K and 0.1 MPa, respectively.