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## Infinite dilution partial molar properties of aqueous solutions of nonelectrolytes. II. Equations for the standard thermodynamic functions of hydration of volatile nonelectrolytes over wide ranges of conditions including subcritical temperatures

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**Abstract**—The volumetric equation proposed previously (Plyasunov et al., 2000), for estimating the infinite dilution Gibbs energy of hydration of volatile nonelectrolytes at temperatures exceeding the critical temperature of pure water,  $T_c$ , is extended to subcritical temperatures. The basis for the extension without inclusion of new fitting parameters besides the experimental values of the thermodynamic functions of hydration at 298.15 K, 0.1 MPa, is an auxiliary function,  $\Delta_h Cp^0(T, P_r)$ , for the variation of the infinite dilution partial molar heat capacity of hydration of a solute in liquid-like water between temperatures  $T = 273.15$  K and  $T = T_s = 658$  K along the isobar  $P_r = 28$  MPa. The analytical form of  $\Delta_h Cp^0(T, P_r)$  was found by globally fitting all available data for the seven best-studied solutes ( $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ , Ar, Xe, and  $\text{C}_2\text{H}_4$ ). Four constraints were used to determine the values of four terms of the  $\Delta_h Cp^0(T, P_r)$  function: the numerical values of the temperature increments between  $T = 298.15$  K and  $T = T_s = 658$  K for the Gibbs energy and the enthalpy of hydration, and numerical value of the heat capacity at  $T_s$  and at 298.15 K, all at the selected isobar  $P_r$ . This approach, in combination with the volumetric equation, may be used to describe and predict all the infinite dilution thermodynamic functions of hydration for nonelectrolytes over extremely wide ranges of temperature and pressure. The model allows calculation of the standard state partial molar properties, including the Gibbs energy of aqueous solutes in a single framework for conditions from high-temperature magmatic processes through hydrothermal phenomena to low-temperature conditions of hypergenesis. Copyright © 2000 Elsevier Science Ltd

### 1. INTRODUCTION

Supercritical aqueous solutions are present during most geologic processes involved in crustal development. Dehydration reactions in subducted slabs generate fluids which flux the melting of overlying mantle wedge material, leading to arc volcanism, and the transport of material from the slab and/or mantle to the crust (Selverstone et al., 1992; Philippot et al., 1995; Barnicoat and Cartwright, 1995; Nelson, 1995; Thirlwall et al., 1996; Eiler et al., 1998; Ayers, 1998). The presence of aqueous fluids lowers the temperatures at which continental rocks melt, resulting in melts of granitic composition that are also often cooled by supercritical hydrothermal circulation (Rose et al., 1994; McCulloch, 1995; Valley and Graham, 1996; Nabelek and Ternes, 1997). The presence of fluids in deep basins and during continental convergence events is revealed by the progress of regional metamorphic reactions (Ferry, 1994; Young, 1995; Vityk and Bodnar, 1995; Smith et al., 1998; Manning and Ingebritsen, 1999). The distribution of oxygen isotopes and heat flow anomalies require the deep circulation of fluids in young oceanic crust (Gregory and Taylor, 1981; Gillis et al., 1993; McCollom and Shock, 1998; Jupp and Schultz, 2000), where supercritical aqueous fluids leave

their traces as fluid inclusions in gabbros and other oceanic rocks (Kelley, 1996; Kelley and Frueh-Green, 1999). All of these processes challenge the abilities of geochemists to model accurately the thermodynamic and transport properties of supercritical aqueous solutions.

Neutral (uncharged) forms determine the speciation of many chemical elements in high-temperature aqueous solutions. However, thermodynamic properties of neutral aqueous species are far less understood than those of ionic solutes. Clearly, this is an obstacle for quantitative modeling of equilibria in high-temperature aqueous solutions, which is an integral part of efforts to understand the evolution of hydrothermal solutions and the nature of fluid–rock interactions. Description, and, particularly, prediction of the standard state thermodynamic properties of aqueous neutral species over a very wide range of state parameters is a challenging task.<sup>1</sup> Only for a very few dissolved compounds, such as  $\text{SiO}_2(\text{aq})$  and  $\text{CO}_2(\text{aq})$ , are there enough experimental data to construct a set of thermodynamically consistent equations to describe the available results up to very high temperatures and pressures. In most cases it is

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<sup>1</sup> In this study the standard state adopted for aqueous species is unit activity in a hypothetical one molal solution referenced to infinite dilution at any temperature and pressure. The standard state adopted for gaseous compounds is unit fugacity of the ideal gas at any temperature and pressure of 0.1 MPa.

necessary to rely on semiempirical models and correlating equations to predict the thermodynamic properties of species at  $T$ - $P$  conditions where no experimental results are available. This work develops a model that can correlate and predict standard state thermodynamic properties over wide ranges of temperature and pressures/densities of neutral, and especially volatile, aqueous compounds of geochemical interest. Of particular importance is that it accurately describes the region close to the critical point of water, which has traditionally been very challenging.

This paper is organized as follows: first we give a short review of methods proposed in the literature to describe the infinite dilution thermodynamic functions of aqueous nonelectrolytes over very wide ranges of temperatures and pressures/densities. Then we outline the method to extend to subcritical temperatures a recently proposed model (Plyasunov et al., 2000), which allows predictions of the Gibbs energy for many nonelectrolytes at supercritical temperatures. This is followed by a discussion of the performance of this model in correlating different properties at ambient, near-critical, and supercritical temperatures.

## 2. MODELS PROPOSED IN THE LITERATURE TO CORRELATE THE STANDARD STATE PROPERTIES OF AQUEOUS NONELECTROLYTES OVER A WIDE TEMPERATURE RANGE

Notable progress in predicting the thermodynamic properties of neutral species for numerous geochemical applications was accomplished within the framework of the Born-type HKF model (Shock et al., 1989; Shock and Helgeson, 1990; Amend and Helgeson, 1997). The strategy employed in these studies is to predict the infinite dilution partial molar volumes and heat capacities of neutral species at elevated temperatures and pressures, and then integrate the corresponding thermodynamic relations to calculate the infinite dilution partial molar Gibbs energy. Estimated HKF parameters are available for hundreds of inorganic and organic neutral compounds in aqueous solutions, which makes it the most practical method available. Experimental studies of densities and heat capacities of organic solutes performed after publication of these predictions confirmed that in many cases the predictions are reasonable up to 500 K (Criss and Wood, 1996; Inglese and Wood, 1996). This means that the calculated Gibbs energy is accurate up to somewhat higher temperatures, probably 550 K. However, recent experimental and computer simulation results show that the HKF model is much less accurate at near-critical and supercritical conditions, i.e., at temperatures above 600 K and densities below 400–500 kg m<sup>-3</sup> (Hnedkovsky, 1994; Lin and Wood, 1996; O'Connell et al., 1996).

The literature has a few other approaches to correlate the thermodynamic properties of neutral species over a very wide temperature range, including both subcritical and supercritical temperatures. Harvey et al. (1991) pointed out that the Henry's law constant,  $K_H$ , is the equilibrium constant for the process of the transfer of a species from the state of an ideal gas to the state of a standard aqueous solution, and in this formulation can be applied at both subcritical and supercritical temperatures of pure water. These authors extended the correlating equation for  $K_H$  from Harvey and Levelt Sengers (1990) to the temperature range 273–1173 K and the pressure range up to 500 MPa. The

formulation by Harvey et al. (1991) results in the following equation for the Gibbs energy of hydration  $\Delta_h G^0$  (this is by definition the difference between the chemical potential of a solute in the state of the standard aqueous solution at any temperature and pressure and the chemical potential of this species in the ideal gas state at any temperature and the ideal-gas reference pressure  $P^\infty = 0.1$  MPa):

$$\Delta_h G^0 = R \left\{ A + B(\rho - \rho_c) + CT\rho \exp \left[ \frac{273.15 - T}{50} \right] \right\} + RT \ln f_1^0, \quad (1)$$

where  $A$ ,  $B$ , and  $C$  are three fitting parameters,  $\rho$  and  $\rho_c$  stand for the density and the critical density of pure water,  $f_1^0$  represents the pure water fugacity, and  $R$  stands for the gas constant. Note that Eqn. 1 is valid for the mole fraction concentration scale. However, it was later pointed out (Harvey, 1998) that the ideal gas limit is not preserved in this formulation because at  $\rho = 0$  Eqn. 1 does not predict  $\Delta_h G^0 = 0$ .

Akinfiev (1997) used the Redlich–Kwong equation of state (EoS) to calculate the infinite dilution partial molar Gibbs energies of hydration for a few dissolved gases and made comparisons with available experimental results at different  $T$  and  $P$ . For pure compounds the numerical values of the parameters in the EoS were taken from the literature; for water the values of the “attractive” parameter  $a$  were calculated for every  $T$ - $P$  point using an accurate EoS for pure water (Kestin et al., 1984). Simple mixing rules were employed. Akinfiev pointed out that in such a formulation this approach cannot be used for very strongly polar neutral solutes like HCl(aq) and NaCl(aq) and proposed ways to extend the approach to get a quantitative description of the standard chemical potential of such strongly polar species.

We checked the performance of the Harvey et al. (1991) and Akinfiev (1997) equations at high temperatures over a wide range of pressures/densities. Both equations were used with parameters given by the authors to calculate the values of the standard chemical potential of either CH<sub>4</sub> (for Harvey et al., 1991) or CO<sub>2</sub> (for Akinfiev's model). We have chosen to present the results as values of the function  $\Delta_h^V G^0$ , the Gibbs energy of transfer of a solute from the gas phase to an equal volume of solution (see Lin and Wood, 1996):

$$\Delta_h^V G^0 = RT \ln \left[ \Phi_2^0 \frac{PV_1^0}{RT} \right], \quad (2)$$

where  $\Phi_2^0$  and  $V_1^0$  stand for a fugacity coefficient of the infinitely dilute solute (subscript 2) and molar volume of water (subscript 1), respectively. The zero-density value of this function is zero, the initial departure is linear in density, with its value at low densities determined by the second cross virial coefficient between water and the solute. As a consequence, it is a sensitive check of the accuracy of any EoS for mixtures at low densities. Akinfiev (1997) gave an analytical equation for calculating the fugacity coefficient of a solute in the framework of the Redlich–Kwong model. For the case of the Harvey et al. model we used the following relation (Lin and Wood, 1996):  $\Delta_h^V G^0 = \Delta_h G^0 + RT \ln[P^\infty V_1^0/RT]$ , where  $\Delta_h G^0$  is given by Eq. (1), and  $P^\infty = 0.1$  MPa is the ideal-gas reference pressure. Predictions can be compared with the molecular dynamic sim-

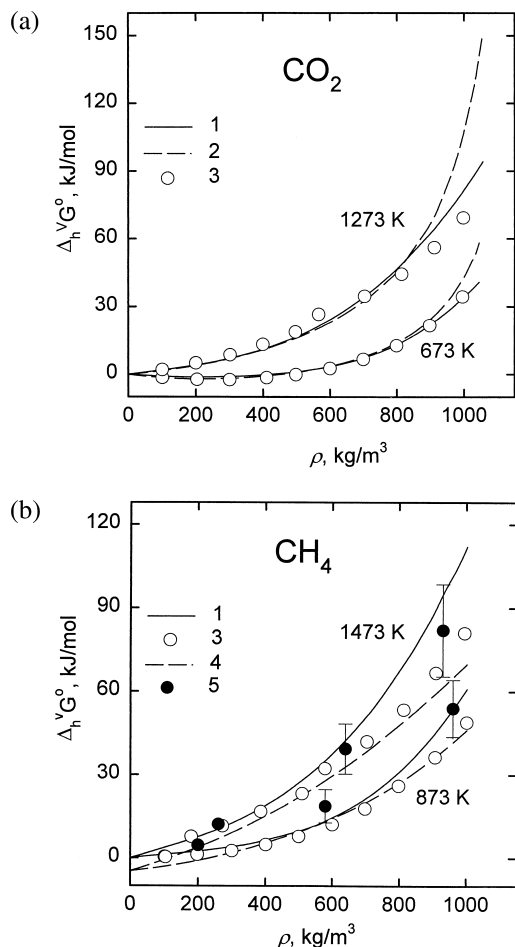


Fig. 1. Values of  $\Delta_h^V G^0$  at supercritical temperatures as a function of water density for (a)  $\text{CO}_2$  and (b)  $\text{CH}_4$ . (1) predictions of the Plyasunov et al. (2000) model; (2) predictions of the Akinfiev (1997) model; (3) results from "SUPERFLUID" (Belonoshko et al., 1992); (4) predictions of the Harvey et al. (1991) model; (5) computer simulation results from Lin and Wood (1996).

ulation results from Lin and Wood (1996) for aqueous  $\text{CH}_4$ , which are supported by a number of other EoS results for the system  $\text{H}_2\text{O}-\text{CH}_4$ . For aqueous  $\text{CO}_2$  we compared the predictions with calculations from the computer program "SUPERFLUID" (Belonoshko et al., 1992), which describe well the PVT properties of the  $\text{H}_2\text{O}-\text{CO}_2$  system at high  $T$  and  $P$ .

Comparisons are shown in Figs. 1a,b. Both the Akinfiev and Harvey et al. (dashed curves) equations predict the density dependence of the standard chemical potential of solutes well up to very high temperatures, 1273–1473 K. Only at densities above  $900 \text{ kg m}^{-3}$  does the Akinfiev model begin to predict values of  $\Delta_h^V G^0$  that are too large. The Harvey et al. model also performs well up to 1473 K. However, the predicted zero-density value  $\Delta_h^V G^0(\rho = 0) = R(A - B\rho_c)$  is equal to  $-4.7 \text{ kJ mol}^{-1}$  for aqueous methane.

Regarding the potential applicability of these approaches to a large variety of neutral solutes we should mention that cubic equations of state with simple mixing rules are not expected to be successful for describing the compositions of water-rich phases in water–hydrocarbon and other water–organic systems

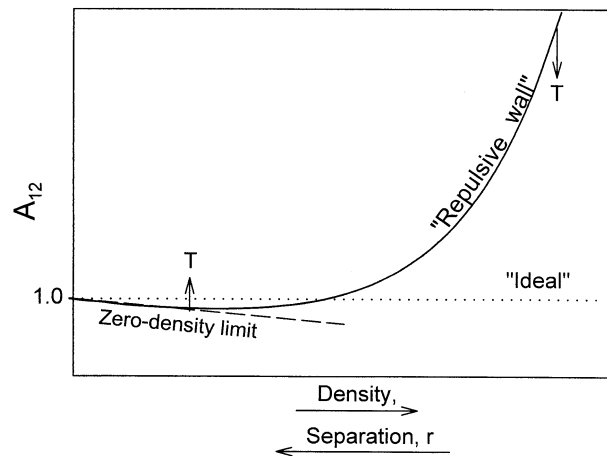


Fig. 2. The principal dependence of the  $A_{12}$  parameter on the density of pure water (or interparticle separation distance), see text.

(Peng and Robinson, 1976; Tsonopoulos and Wilson, 1983). In addition, the correct zero-density limit needs to be introduced in the Harvey et al. model. As a result, we use the alternative developed previously which does not appear to have such limitations.

An alternate method, based on neither the Born-type models, nor the cubic EoS, has been developed to evaluate the standard state Gibbs energy of hydration of aqueous nonelectrolytes at temperatures above the critical temperature of pure water (Plyasunov et al., 2000). After O'Connell et al. (1996) we considered the quantity

$$A_{12} = \frac{V_2^0}{\kappa_T RT} \equiv \lim_{N_2 \rightarrow 0} \frac{V}{RT} \left( \frac{\partial P}{\partial N_2} \right)_{T,V,N_1}, \quad (3)$$

as the property to be correlated [the subscript 12 indicates that this parameter reflects the interactions between the solvent (1, water) and a solute (2)]. Here,  $V_2^0$  is the infinite dilution partial molar volume of the solute, and  $\kappa_T$  stands for the isothermal compressibility of pure solvent. The origin of this collection of properties is from statistical mechanical fluctuation solution theory where  $A_{12} = 1 - C_{12}^0$  with  $C_{12}^0$  being the integral of the solute–solvent direct correlation function (O'Connell, 1971; 1994; 1995).

The connection with microscopic correlation functions and interparticle potential energies allows a qualitative understanding of the behavior of  $A_{12}$  as a function of density and temperature (see Fig. 2). For an ideal gas (no interactions), the value of  $A_{12}$  is equal to unity (dotted "ideal" line in Fig. 2). If one derives  $A_{12}$  from a rigorous PVT equation of state, such as the virial density series, the term linear in density ("zero-density limit" in Fig. 2) is related to the second cross virial coefficient,  $B_{12}$  between water and a solute (O'Connell et al., 1996; Plyasunov et al., 2000). Measured or estimated values of  $B_{12}$  provide important constraints on the  $A_{12}$  parameter at low densities. At high densities, the interaction functions are determined by repulsive excluded volume effects ("repulsive wall" in Fig. 2), which are strongly density dependent. The quantity  $A_{12}$  has the temperature and strong density dependencies qual-

itatively similar to the reduced bulk modulus of pure water given by  $A_{11} = V_1^0/\kappa_T RT$ . Since  $A_{12}$  is equal to  $A_{11}$  if particles 1 and 2 are identical and the PVT properties of pure water are well known,  $A_{11}$  can serve as a reference basis for many aqueous solutes.

All of these considerations led Plyasunov et al. (2000) to an equation to for  $A_{12}$  as a function of temperature and density:

$$A_{12} = NA_{11} + (1 - N) + 2\Omega\rho\{B_{12}(T) - NB_{11}(T)\}\exp[-c_1\rho] + \rho\left(\frac{a}{T^5} + b\right)(\exp[c_2\rho] - 1), \quad (4)$$

where  $N$ ,  $a$ , and  $b$  represent three fitting parameters;  $B_{11}(T)$  and  $B_{12}(T)$  stand for the temperature-dependent second virial coefficient for pure water, and the temperature-dependent second cross (water–solute) virial coefficient, respectively;  $c_1 = 0.0033 \text{ m}^3 \text{ kg}^{-1}$  and  $c_2 = 0.002 \text{ m}^3 \text{ kg}^{-1}$  are universal constants;  $\Omega = 10^{-3}/M_w \approx 55.51 \times 10^{-6} \text{ mol kg}^{-1}$  is the conversion needed if the values of the second virial coefficients are given in units of  $\text{cm}^3 \text{ mol}^{-1}$  and values of  $\rho$  in  $\text{kg m}^3$ ;  $M_w$  stands for the molar mass of pure water in  $\text{g mol}^{-1}$ . The size parameter,  $N$ , is expected to reflect the size of a solute relative to water. The low-temperature compensating parameter,  $a$ , mainly compensates for unrealistic low-temperature and high-density contributions to  $V_2^0$  from the term containing  $B_{12}(T)$  and  $B_{11}(T)$ . The correcting parameter,  $b$ , is expected to reflect the fact that solutes differ from  $\text{H}_2\text{O}$  not only in relative size, but also in polarity, shape, etc. In the limit of low densities Eqn. 4 has the correct limiting form for the EoS truncated at the second virial coefficient. The temperature dependencies of  $B_{11}(T)$  and  $B_{12}(T)$  are described by a simple analytical relation from the square-well potential:

$$B_{ij}(T) = \frac{2\pi N_A \sigma_{ij}^3}{3} \left\{ 1 - (\lambda^3 - 1) \left[ \exp\left(\frac{\varepsilon_{ij}}{k_B T}\right) - 1 \right] \right\}, \quad (5)$$

where  $N_A$  represents Avogadro's number;  $\sigma_{ij}$ ,  $\varepsilon_{ij}/k_B$ , and  $\lambda$  stand for the parameters of the square-well potential:  $\sigma_{ij}$  designates the collision diameter, in  $\text{\AA}$ ;  $\varepsilon_{ij}/k_B$  corresponds to the depth of the potential well ( $\varepsilon_{ij}$  stands for the minimum of the potential energy between particles  $i$  and  $j$ ;  $k_B$  represents the Boltzmann factor; and  $\lambda$  indicates the width of the potential well in molecular diameters, which is assumed to be a universal constant equal to 1.22). The  $N$ ,  $a$ , and  $b$  parameters in Eqn. 4 were determined for a few solutes using  $V_2^0$  data over the temperature range 298–700 K and pressures up to 35 MPa.

Equation (4) can be integrated in density starting with  $\rho = 0$  at temperatures equal to or greater than the critical temperature of water to yield the infinite dilution partial thermodynamic functions of hydration of solutes (i.e., the difference between partial molar properties of a solute in the standard aqueous solution and the same properties in the state of the ideal gas, see Appendix A). At supercritical conditions, calculation of the Gibbs energy of hydration from Eqns. A1–A6 is accurate up to 1300–1500 K and 10–15 kbar, see solid lines in Figs. 1a,b (Plyasunov et al., 2000). Several correlations were proposed to estimate the required parameters for many aqueous solutes. It is expected that this approach can be used for nonelectrolytes where  $A_{12}$  is positive and experimental values or reliable

estimates of the second cross virial coefficient  $B_{12}$  are possible. Thus the predictions we can make are for solutes that are nonpolar or only weakly polar. While the integration of Eqn. 4 in density to calculate the standard state thermodynamic functions of hydration is accurate at temperatures above the critical temperature of pure water,  $T_c$ , it fails for  $T < T_c$ , where the two-phase region exists for the solvent. Therefore, the main goal of this paper is to complete the description of the standard thermodynamic properties of neutral species (and most importantly the Gibbs energy of hydration), at temperatures below the critical temperature of water.

### 3. AN EXTENSION OF THE MODEL TO SUBCRITICAL TEMPERATURES

There are different ways to accomplish this task. For instance, the simplest approach is to use one of the successful equations proposed in the literature (Harvey and Levelt Sengers, 1990; Harvey, 1996) to correlate the temperature dependence of Henry's constant along the saturation curve of water, together with Eqns. 3 and 4 to calculate the values of the thermodynamic functions of hydration at pressures equal to or above the saturation vapor pressure of water up to  $T_c$ . However, at the critical temperature of water there will be, in general, differences between the numerical values of all the standard state caloric functions of hydration (the Gibbs energy of hydration  $\Delta_h G^0$ , the enthalpy of hydration  $\Delta_h H^0$ , the heat capacity of hydration  $\Delta_h C_p^0$ ) calculated in this way and those obtained by means of thermodynamic transformations of Eqn. 4. Besides, for only about a dozen solutes are there literature recommendations of Henry's law constants valid up to near-critical temperatures.

With all of this in mind, we decided to take advantage of the fact that the thermodynamic transformations of Eqn. 4 provide information about the numerical values of the standard thermodynamic functions of hydration at temperatures above or equal to  $T_c$ . This means that for all volatile nonelectrolytes, for which the parameters of the volumetric equation (Eqn. 4) are known or can be reliably estimated, one has numerical values of  $\Delta_h G^0$ ,  $\Delta_h H^0$ ,  $\Delta_h C_p^0$  at different densities/pressures along the supercritical isotherms. In addition, there are, as a rule, experimental determinations of the standard Gibbs energy of hydration,  $\Delta_h G^0$ , and the standard enthalpy of hydration,  $\Delta_h H^0$ , at ambient conditions such as 298.15 K, 0.1 MPa. For many organic nonelectrolytes in aqueous solution there are experimental determinations of the infinite dilution isobaric heat capacity. This combination provides a wealth of information about the thermodynamics of hydration of nonelectrolytes over the range of conditions of interest.

We formulated the task as follows: find an optimal analytical form of the equation for the temperature dependence of the infinite dilution partial molar heat capacity of hydration along a selected isobar ( $P_r$ ) for the temperature range between 273 K and  $T_s$  ( $T_s$  designates the switching temperature. Above the switching temperature all the thermodynamic functions of hydration are calculated by means of Eqn. 4 and its integrated forms, Eqns. A1–A19. Below  $T_s$  all the caloric thermodynamic functions of hydration are calculated as described below. The natural requirement for the switching temperature is  $T_s \geq T_c$ , where  $T_c = 647.14 \text{ K}$  stands for the critical temperature of

pure water). This  $\Delta_h C_p^0(T, P_r)$  function must provide a close description of the full variety of experimental data in the temperature range between 273.15 K and  $T_s$ :  $\Delta_h G^0$ , or Henry's law constants ( $K_H$ ), and related information such as solubility, etc., enthalpy of hydration or solution; and the heat capacity measurements where available. If experimental data refer to pressures other than  $P_r$ , then proper use of Eqn. 4 can yield the corresponding pressure increment for any thermodynamic property (see Appendix B). The requirement for  $P_r$  is that its value must exceed the critical pressure to ensure continuity and avoid infinite values of the derivative of the standard chemical potential of a solute at  $T_c$ . A natural choice is  $P_r = 28$  MPa, because many high-temperature experimental  $C_p^0$  results are obtained at this pressure (Inglese and Wood, 1996; Inglese et al., 1996; Hnedkovsky and Wood, 1997). Finally, if we require that the values of the Gibbs energy of hydration, the enthalpy of hydration, and the heat capacity of hydration for a solute calculated by means of the  $\Delta_h C_p^0(T, P_r)$  function coincide at  $T = T_s$  with ones predicted by means of Eqn. 4, then we have at least four constraints for the  $\Delta_h C_p^0(T, P_r)$  function. These are

- (1) the known numerical values of  $\Delta_h C_p^0(T_s, P_r)$  estimated from Eqn. 4;
- (2) the temperature increment of the enthalpy of hydration between  $T_r = 298.15$  K and  $T = T_s$  at our selected reference pressure  $P = P_r$ ,  $\Delta_h H^0(T_s, P_r) - \Delta_h H^0(T_r, P_r) = \int_{T_r}^{T_s} \Delta_h C_p^0(T, P_r) dT$ ;
- (3) the temperature increment of the Gibbs energy of hydration between  $T_r = 298.15$  K and  $T = T_s$  at our selected reference pressure  $P = P_r$ ,

$$\begin{aligned} \Delta_h G^0(T_s, P_r) - \Delta_h G^0(T_r, P_r) &= [\Delta_h H^0(T_s, P_r) - T_s \Delta_h S^0(T_s, P_r)] \\ &\quad - [\Delta_h H^0(T_r, P_r) - T_r \Delta_h S^0(T_r, P_r)] = -(T_s - T_r) \Delta_h S^0(T_r, P_r) \\ &\quad + \int_{T_r}^{T_s} \Delta_h C_p^0(T, P_r) dT - T_s \int_{T_r}^{T_s} \frac{\Delta_h C_p^0(T, P_r)}{T} dT; \end{aligned}$$

- (4) and, finally, the known numerical values of  $\Delta_h C_p^0(T_r, P_r)$  based on experimental determinations of the infinite dilution partial molar heat capacity of a solute at 298.15 K. It was found useful to include this constraint to secure the good performance of the model at ambient conditions.

If we employ a four-coefficient equation to describe the temperature dependence of  $\Delta_h C_p^0(T, P_r)$  then the existence of four constraints means that there will be no extra fitting parameters in addition to the parameters of the volumetric equation (Eqn. 4). As shown elsewhere (Plyasunov et al., 2000), the parameters of Eqn. 4 can be estimated for many solutes even from scarce experimental information. So, the potential exists for describing the whole  $T$ - $\rho$  surface of the thermodynamic functions of hydration of many volatile nonelectrolytes, even if experimental determinations of these properties are available for solutes only at 298.15 K and 0.1 MPa.

### 3.1. The Selection of the Four-Term $\Delta_h C_p^0(T, P_r)$ Equation at $273 < T < T_s$

The search for a four-parameter analytical form of the  $\Delta_h C_p^0(T, P_r)$  function at  $273 < T \leq T_s$  was accomplished by

a global fit of a variety of experimental data. First, we selected a basic set of the seven best-studied dissolved gases: CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub>, Ar, C<sub>2</sub>H<sub>4</sub>, Xe. For these solutes there is diverse experimental information available over a wide temperature and density range. There are experimental determinations of  $V_2^0$  and  $C_p^0$  up to 700–720 K and pressures up to 35 MPa (Allred and Woolley, 1981; Moore et al., 1982; Barbero et al., 1982; 1983; Biggerstaff et al., 1985; Biggerstaff and Wood, 1988a; 1988b; Hnedkovsky et al., 1996; Hnedkovsky and Wood, 1997; and others); as well as calorimetric values of the enthalpies of solution at ambient temperatures (Alexander, 1959; Vanderzee and King, 1972; Berg and Vanderzee, 1978; Krestov et al., 1982; Dec and Gill, 1984, 1985a,b; Olofsson et al., 1984; Naghibi et al., 1986; Prorokov et al., 1986). For all of these gases there are experimental determinations of the Henry's law constant in water up to 573–635 K. For the low-temperature range (below 348 K) we employed recommendations of Wilhelm et al. (1977) and added only experimental results published after the appearance of that review (Edwards et al., 1978; Cosgrove and Walkley, 1981; Rettich et al., 1981; Kawazuishi and Prausnitz, 1987; Carroll and Mather, 1989; Krause and Benson, 1989; Carroll et al., 1991; Bieling et al., 1995). Fernandez-Prini and Crovetto (1989) compiled a large set of high-temperature gas–water solubility data and consistently treated them taking into account the non-ideality of gas phases and the temperature and pressure dependence of the partial molar volumes of dissolved gases. This set of Henry's law constants at high temperatures was used to parametrize a number of equations for the temperature dependence of  $K_H$  (Fernandez-Prini and Crovetto, 1989; Harvey and Levelt Sengers, 1990; Harvey, 1996). For H<sub>2</sub>S there are recent experimental determinations of the Gibbs energy of hydration at saturation vapor pressure up to 590 K (Suleimenov and Krupp, 1994) and at elevated pressures at 573–773 K (Kishima, 1989). In addition, there are estimates of the standard Gibbs energy of hydration of CH<sub>4</sub> (Lin and Wood, 1996), CO<sub>2</sub>, Ar, H<sub>2</sub>S, and NH<sub>3</sub> (Belonoshko et al., 1992) at supercritical temperatures based on molecular dynamics simulations. In all there are 844 data points: 197 for  $V_2^0$ , 171 for  $\Delta_h C_p^0$ , 19 for  $\Delta_h H^0$ , and 457 for  $\Delta_h G^0$ .

First, there is the issue of what switching temperature,  $T_s$ , to use (above  $T_s$  all the thermodynamic functions of hydration are calculated by means of the volumetric equation and its integrated forms). Rigorously, that should be the critical temperature of water,  $T_c$ . However, because we are employing model equations for which considerable thermodynamic manipulation is involved, results for other properties besides  $V_2^0$  can be quite sensitive to inadequacies of the chosen mathematical form. Rather than make adjustments by adding other terms and parameters, we chose to optimize the value of  $T_s$ . We found that there was a significant decrease in the objective function values when  $T_s$  was somewhat higher than  $T_c$ , especially for the  $\Delta_h H^0$  values for larger solutes (benzene, *n*-hexane) from Degrange (1998). While this selection of  $T_s$  makes little difference in results for our basic set, and calculations in the region between 640 and 660 K are not affected significantly for all substances, descriptions over the entire range of conditions and substances have been found to be best with  $T_s = 658$  K.

Experimental determinations of the heat capacities of vola-

tile nonelectrolytes over a wide temperature range (Biggerstaff and Wood, 1988b; Inglese and Wood, 1996; Inglese et al., 1996; Hnedkovsky and Wood, 1997) show that  $\Delta_h Cp^0(T, P_r)$  passes through a flat minimum at 300–500 K and then steeply increases, with the magnitude of this increase correlating with the polarity of the solute (Hnedkovsky and Wood, 1997). Testing available experimental results on heat capacities of aqueous nonelectrolytes at  $T > 570$  K, we found that the high-temperature rising branch of the  $\Delta_h Cp^0(T, P_r)$  function is well described by a term proportional to  $n(n-1)T(T_0 - T)^{n-2}$ , where  $T_0 = 669$  K (approximate temperature of extrema for the temperature and pressure derivatives of the molar volume of pure water at  $P_r = 28$  MPa) and the optimal value of  $n$  falls between 0.5 and 0.7 ( $n = 0.6$  was finally adopted). This particular analytical form was suggested by the work of Harvey (1996), who showed that at near-critical conditions the leading term for the Gibbs energy of hydration along the vapor–liquid curve is proportional to  $(T_c - T)^m$ , where  $m$  designates the critical exponent characterizing the  $T$ - $\rho$  coexistence curve. Different combinations of other terms, which allow analytical statements for the integrals  $\int \Delta_h Cp^0 dT$  and  $\int (\Delta_h Cp^0/T) dT$ , were tested for the temperature dependence of  $\Delta_h Cp^0(T, P_r)$ . Tests were performed as follows: using different four-term analytical forms for  $\Delta_h Cp^0(T, P_r)$  we determined by a nonlinear fit the parameters  $N$ ,  $a$ , and  $b$  of the volumetric equation (Eqn. 4), together with the parameters for  $\Delta_h Cp^0(T, P_r)$  determined by the constraints discussed above, as well as the goodness of the fit for each model tested. The best model is one which gives the lowest value of the objective function  $F = \sum_i (\Delta_i/\delta_i)^2$ , where  $\Delta_i$  stands for the difference between experimental and calculated values of a property; and  $\delta_i$  indicates the total uncertainty of the experimental data point. The infinite dilution partial molar volumes, heat capacities, and Gibbs energies and enthalpies of hydration at both subcritical and supercritical temperatures were included in the fit. The best variant (the smallest sum of squared errors of the overall fit) was found to be

$$\Delta_h Cp^0(T, P_r) = d_0 + d_1 T + d_2 T \exp\left(\frac{T}{\theta}\right) - d_3 n(n-1)T(T_0 - T)^{n-2}, \quad (6)$$

where  $T_0 = 669$  K;  $\theta = 40$  K,  $n = 0.6$ . It should be emphasized that the major contribution (more than 50–70%) to the value of the objective function  $F$  comes from errors in reproducing  $V_2^0$  and  $\Delta_h G^0$ . So, in this sense, Eqn. 6 is not the most accurate equation for describing the temperature dependence of  $\Delta_h Cp^0$  at 28 MPa, but rather the best compromise in combining the volumetric equation (Eqn. 4) with the measured caloric properties of aqueous nonelectrolytes at subcritical temperatures.

The analytical statements for the temperature dependence (at  $T \leq T_s$ ) of other infinite dilution thermodynamic functions of hydration for volatile nonelectrolytes at  $P_r = 28$  MPa consistent with Eqn. 6 are given by

$$\begin{aligned} \Delta_h H^0(T, P_r) - \Delta_h H^0(T_r, P_r) &= \int_{T_r}^T \Delta_h Cp^0(T, P_r) dT \\ &= d_0(T - T_r) + \frac{d_1}{2}(T^2 - T_r^2) + d_2 \theta \left\{ \exp\left(\frac{T}{\theta}\right)(T - \theta) \right. \\ &\quad \left. - \exp\left(\frac{T_r}{\theta}\right)(T_r - \theta) \right\} + d_3 \{ (T_0 - T)^{n-1} [T_0 + T(n-1)] \} \\ &\quad - d_3 \{ (T_0 - T_r)^{n-1} [T_0 + T_r(n-1)] \}, \quad (7) \end{aligned}$$

$$\begin{aligned} \Delta_h S^0(T, P_r) - \Delta_h S^0(T_r, P_r) &= \int_{T_r}^T \frac{\Delta_h Cp^0(T, P_r)}{T} dT \\ &= d_0 \ln \left[ \frac{T}{T_r} \right] + d_1(T - T_r) + d_2 \theta \left\{ \exp\left(\frac{T}{\theta}\right) - \exp\left(\frac{T_r}{\theta}\right) \right\} \\ &\quad + d_3 n [ (T_0 - T)^{n-1} - (T_0 - T_r)^{n-1} ], \quad (8) \end{aligned}$$

and

$$\begin{aligned} \Delta_h G^0(T, P_r) - \Delta_h G^0(T_r, P_r) &= -(T - T_r) \Delta_h S^0(T_r, P_r) \\ &\quad + \int_{T_r}^T \Delta_h Cp^0(T, P_r) dT - T \int_{T_r}^T \frac{\Delta_h Cp^0(T, P_r)}{T} dT = \\ &\quad - (T - T_r) \Delta_h S^0(T_r, P_r) + d_0 \left\{ T - T_r - T \ln \left[ \frac{T}{T_r} \right] \right\} \\ &\quad - \frac{d_1}{2} (T - T_r)^2 - d_2 \theta \left\{ \exp\left(\frac{T}{\theta}\right) \theta + \exp\left(\frac{T_r}{\theta}\right) (T_r - T - \theta) \right\} \\ &\quad + d_3 \{ (T_0 - T)^n - (T_0 - T_r)^n + n(T_0 - T_r)^{n-1} (T - T_r) \}. \quad (9) \end{aligned}$$

#### 4. RESULTS OF CORRELATION

The goal of this section is to discuss the quality of reproduction of the experimental data for the solutes tested in the framework of the proposed approach, which requires only three fitting parameters:  $N$ ,  $a$ , and  $b$ . The values of the fitting parameters are given in Table 1 together with the values we accepted for  $\Delta_h G^0$ ,  $\Delta_h H^0$ , and  $\Delta_h Cp^0$  at 298.15 K and 0.1 MPa. Tabulated values of the coefficients  $d_0$ ,  $d_1$ ,  $d_2$ , and  $d_3$  of Eqn. 6 are not independent (they can be calculated from the other parameters), but for convenience are given in Table 1. Previous estimates of the  $N$ ,  $a$ , and  $b$  parameters, obtained only from  $V_2^0$  data sets (Plyasunov et al., 2000) are given in *italics*. Note that both “new” (based on the fit of both volumetric and caloric properties) and “old” values are in good agreement, especially for  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , and  $\text{NH}_3$ , where  $V_2^0$  and  $\Delta_h Cp^0$  are most accurate. Only for Xe does the difference between the old and new values of the  $N$  parameter significantly exceed their combined error. However, for Xe the old values were not obtained by fit, but were predicted using proposed correlation algorithms (Plyasunov et al., 2000). Additionally, for Xe the experimental  $V_2^0$  values increase about  $15 \text{ cm}^3 \text{ mol}^{-1}$  between 299 and 376 K and  $P \approx 30$  MPa. By comparison, for  $\text{C}_2\text{H}_4$ , which is rather similar in size and polarity, this increase is only  $5\text{--}6 \text{ cm}^3 \text{ mol}^{-1}$  (values for both solutes are from Biggerstaff and Wood, 1988). If this is not from measurement errors, it may be some different physical effect such as the partial formation

Table 1. Parameters of Eqns. 4 and 6 for the solutes constituting the "basic" set. Parameters of Eqn. 4 obtained earlier only from  $V_2^0$  data (Plyasunov et al., 2000) are shown in italics for comparison. The uncertainty of the last digit is given in parentheses. SWD reflects the quality of the overall fit for a given solute,  $\text{SWD} = [\sum_i (\Delta_i/\delta_i)^2 / (Np - m)]^{0.5}$ , where  $\Delta$  stands for the difference between experimental and calculated data;  $\delta$  represents the uncertainty of the experimental point;  $Np$  stands for the total number of data points;  $m$  is the number of adjustable parameters. SWD for the present model is given in the last but one column of the table, and the SWD for the revised HKF model is given in the last column of the table, results in parentheses are for reduced data sets,  $T < 630$  K, see text.

Solute	$\Delta_h G^0$ <sup>a</sup>	$\Delta_h H^0$ <sup>a</sup>	$\Delta_h C_p^0$ <sup>b</sup>	$\sigma_{12}$ <sup>c</sup>	$\varepsilon_{12}/\kappa_B$ <sup>d</sup>	$N$	$a \times 10^{-9}$ <sup>e</sup>	$b \times 10^3$ <sup>f</sup>	$d_0 \times 10^{-2}$ <sup>g</sup>	$d_1$ <sup>h</sup>	$d_2 \times 10^7$ <sup>h</sup>	$d_3 \times 10^{-3}$ <sup>i</sup>	SWD (HKF)
CH <sub>4</sub>	16.29 (3) <sup>j</sup>	-13.1 (1) <sup>k</sup>	216 <sup>l</sup>	3.11 (15)	426 (10)	1.34 (7)	-2.8 (6)	2.10 (6)	4.656	-1.000	-1.7398	2.4322	1.07 (2.22)
CO <sub>2</sub>	8.28 (3) <sup>m</sup>	-19.7 (1) <sup>n</sup>	180 <sup>o</sup>	3.00 (8)	650 (18)	1.23 (8)	-2.0 (8)	2.18 (9)	3.846	-0.816	-1.0160	1.8204	0.88 (2.41)
H <sub>2</sub> S	5.66 (5) <sup>p</sup>	-18.0 (15) <sup>q</sup>	144 <sup>r</sup>	2.87 (13)	767 (32)	1.20 (6)	-1.8 (6)	1.79 (5)	3.149	-0.663	-0.7168	1.3692	0.86 (1.91)
NH <sub>3</sub>	-10.05 (10) <sup>s</sup>	-35.4 (3) <sup>t</sup>	39 <sup>u</sup>	2.90 (9)	945 (24)	1.53 (5)	-2.5 (4)	1.27 (4)	0.083	0.061	-0.4289	0.6410	0.58 (1.67)
C <sub>2</sub> H <sub>4</sub>	13.25 (10) <sup>v</sup>	-16.5 (2) <sup>w</sup>	237 <sup>x</sup>	3.16 (11)	573 (22)	1.22 (3)	-1.4 (2)	0.45 (2)	5.102	-1.048	-1.1106	1.9576	0.84 (1.45)
Ar	16.29 (3) <sup>x</sup>	-12.0 (1) <sup>y</sup>	200 <sup>z</sup>	2.95 (16)	349 (9)	1.97 (9)	-3.7 (8)	1.91 (8)	3.993	-0.907	-1.9037	2.6009	0.98 (2.57)
Xe	13.45 (5) <sup>x</sup>	-19.0 (1) <sup>y</sup>	250 <sup>z</sup>	3.03 (12)	584 (24)	0.68 (6)	0.0 (7)	2.22 (5)	5.334	-1.087	-0.9809	2.1034	1.04 (1.25)
						1.72 (5)	-2.5 (3)	2.19 (7)					
						0.73 (4)	-0.4 (4)	2.15 (4)					
						1.85 (15)	-3.8 (12)	2.27 (9)					
						1.44 (5)	-2.6 (5)	2.61 (24)					

<sup>a</sup> At 298.15 K, 0.1 MPa, kJ mol<sup>-1</sup>.

<sup>b</sup> At 298.15 K, 0.1 MPa, J K<sup>-1</sup> mol<sup>-1</sup>.

<sup>c</sup> Å, numerical values are from (Plyasunov et al., 2000).

<sup>d</sup> K, numerical values are from (Plyasunov et al., 2000).

<sup>e</sup> m<sup>3</sup> K<sup>5</sup> kg<sup>-1</sup>.

<sup>f</sup> m<sup>3</sup> kg<sup>-1</sup>.

<sup>g</sup> J K<sup>-1</sup> mol<sup>-1</sup>.

<sup>h</sup> J K<sup>-2</sup> mol<sup>-1</sup>.

<sup>i</sup> J K<sup>-n</sup> mol<sup>-1</sup>.

<sup>j</sup> Rettich et al. (1981); Wilhelm et al. (1977).

<sup>k</sup> Dec and Gill (1984); Olofsson et al. (1984).

<sup>l</sup> Dec and Gill (1985b); Hnedkovsky and Wood (1997).

<sup>m</sup> Carroll et al. (1991); Crovetto (1991).

<sup>n</sup> Berg and Vanderzee (1978); Gill and Wadsö (1982).

<sup>o</sup> Hnedkovsky and Wood (1997).

<sup>p</sup> Cox et al., 1989; Carroll and Mather, 1991.

<sup>q</sup> Cox et al. (1989).

<sup>r</sup> Barbero et al. (1982); Hnedkovsky and Wood (1997).

<sup>s</sup> Kawazuishi and Prausnitz (1987); Bieling et al. (1995).

<sup>t</sup> Vanderzee and King (1972).

<sup>u</sup> Allred and Woolley (1981); Hnedkovsky and Wood (1997).

<sup>v</sup> Wilhelm et al. (1977).

<sup>w</sup> Dec and Gill (1984).

<sup>x</sup> Krause and Benson (1989); Wilhelm et al. (1977).

<sup>y</sup> Dec and Gill (1985a); Olofsson et al. (1984); Krestov et al. (1982).

<sup>z</sup> Olofsson et al. (1984).

of clathrate-like structures at low  $T$  and elevated  $P$  in the Xe–H<sub>2</sub>O system, which affects measured values for this solute.

To emphasize the excellent description of the basic set, we have also fitted the revised HKF model to the same data over both the whole temperature and pressure range, and also for  $T < 630$  K. The standard weighted deviations are shown in the last column of Table 1. The performance of the model proposed is significantly better than the performance of the revised HKF, at least for solutes in the basic set.

#### 4.1. The Infinite Dilution Partial Molar Volumes

Among the seven solutes considered here, three (C<sub>2</sub>H<sub>4</sub>, Ar, and Xe) were investigated more than 10 years ago (Biggerstaff and Wood, 1988). The experimental  $V_2^0$  and  $Cp_2^0$  data for these solutes have larger experimental errors than results for CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>S, and NH<sub>3</sub>, which were obtained using improved modifications of both densimeter and calorimeter (Hnedkovsky et al., 1996; Hnedkovsky and Wood, 1997). In Figs. 3a–c experimental data for the latter solutes can be compared with the fitting results at both 28 and 35 MPa over wide temperature ranges. It can be seen that the fitted values are always within a few percent of the experimental values. In Fig. 4 we plot experimental and fitted  $V_2^0$  values for aqueous ethylene, argon, and xenon at  $P = 34$  MPa. The experimental and fitted results are in close agreement, keeping in mind the lower accuracy of measurements for these three solutes.

#### 4.2. The Infinite Dilution Partial Molar Heat Capacities of Hydration

The quality of description of the infinite dilution partial molar heat capacities of hydration,  $\Delta_h Cp^0 = Cp_2^0 - Cp(id.gas)$ , for the accurately studied nonelectrolytes CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>S, and NH<sub>3</sub> is shown in Figs. 5a,b at  $P = 28$  MPa at 300–705 K, and for C<sub>2</sub>H<sub>4</sub>, Ar, and Xe in Fig. 6 at  $P = 31$  MPa. In all cases, apart from the minimum of the heat capacity, the differences between experimental and fitted values are comparable with the expected errors. The calculated minima in  $\Delta_h Cp^0$  seem to be more negative than the experimental ones for all solutes except NH<sub>3</sub>. There may be several sources for these discrepancies other than possible inadequacies of the model: (1) rather large uncertainties (up to 0.6 K, see Hnedkovsky and Wood, 1997) in the actual temperatures of measurements at extrema of heat capacities; (2) the assumption of equality of  $\Delta_h Cp^0$  at infinite dilution and at small finite concentrations, 0.1–0.3 m, where experimental results are obtained (Hnedkovsky and Wood, 1997) showed that at near-critical conditions the concentration dependence of the apparent molar heat capacities may not be negligible even at low molalities); (3) uncertainties in the values of the second derivative of the density of pure water with respect to temperature at near-critical conditions.

#### 4.3. The Infinite Dilution Partial Molar Enthalpies of Hydration

For CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, Ar, and Xe there are experimental determinations of enthalpies of hydration at  $P = 0.1$  MPa and temperatures other than 298.15 K from two independent laboratories (Olofsson et al., 1984; Dec and Gill, 1985a; 1985b;

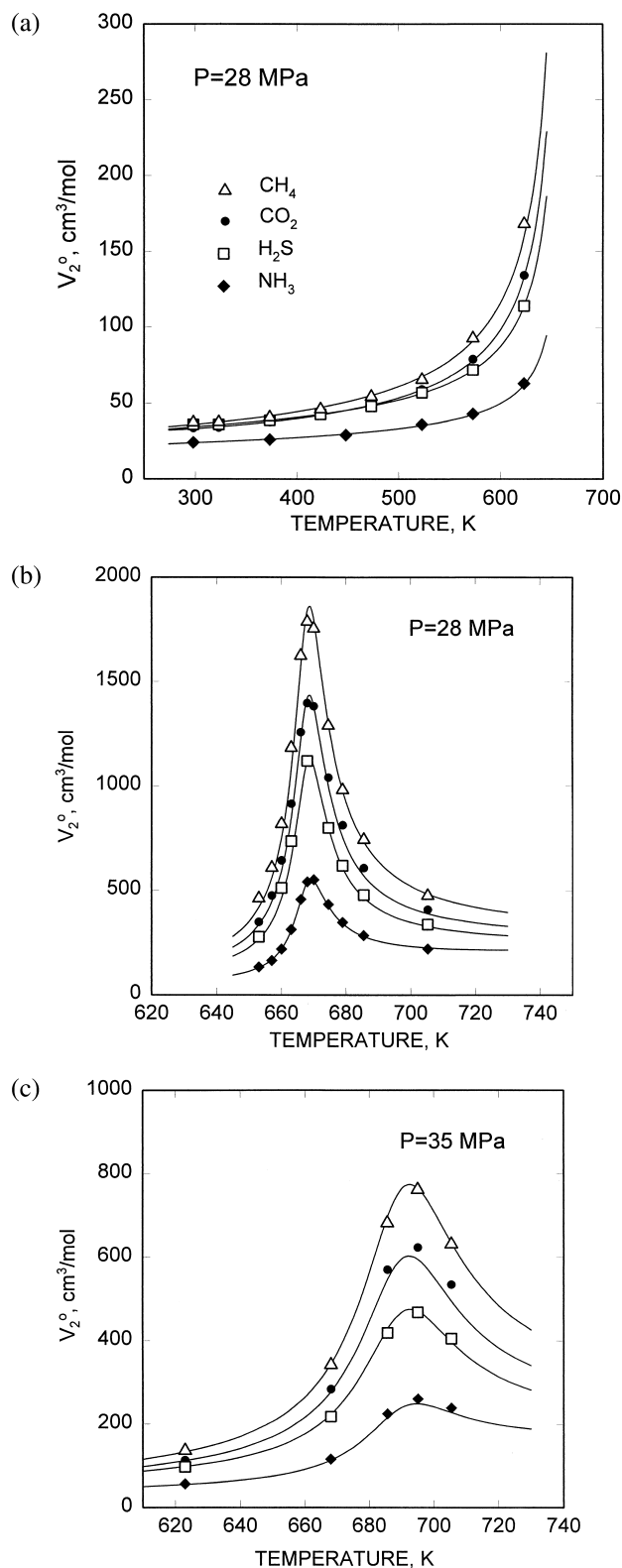


Fig. 3. Experimental (symbols, from Hnedkovsky et al., 1996) and fitted (solid curves) values of  $V_2^0$  for CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>S, and NH<sub>3</sub> at  $P = 28$  MPa at subcritical (a) and supercritical (b) temperatures, and at  $P = 35$  MPa (c).

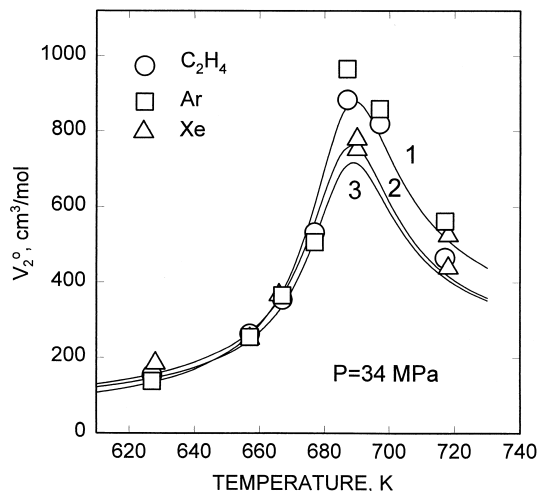


Fig. 4. Experimental (symbols, from Biggerstaff and Wood, 1988a) and fitted values of  $V_2^0$  at  $P = 34$  MPa for  $C_2H_4$ , Ar, and Xe. (1) Ar, (2) Xe, (3)  $C_2H_4$ .

Naghbi et al., 1986). As shown in Fig. 7, all experimental data are in close agreement with the calculated values.

#### 4.4. The Infinite Dilution Partial Molar Gibbs Energies of Hydration

A primary goal of this work is to provide an accurate description of the standard partial molar Gibbs energy of hydration of nonelectrolytes, as this is the most important property for geochemical modeling. In the next three sections we discuss separately the performance of the proposed approach for the description of Henry's constants at subcritical temperatures, the standard Gibbs energy of transfer (another measure of the infinite dilution partial molar Gibbs energies of hydration) at supercritical temperatures, and in the near-critical region.

##### 4.4.1. Henry's law constants at subcritical temperatures

The infinite dilution partial molar Gibbs energy of hydration,  $\Delta_h G^0(T, P)$ , relates to Henry's constants,  $K_H(T, P)$ , as follows:  $\Delta_h G^0(T, P) = -RT \ln K_H(T, P)$ . There are abundant literature sources of Henry's constants for nonelectrolytes constituting our basic set. Low-temperature values, published before the mid-1970s, were reviewed by Wilhelm et al. (1977). These authors recommended the most reliable values of  $K_H$  up to 348 K for many gases. However, we did not use their values of the Henry's constants for  $NH_3$ , because they were not corrected for nonideality and hydrolysis, which are important effects for this solute. Instead, for  $NH_3$  we use values recommended by Edwards et al. (1978), Kawazuichi and Prausnitz (1987), and Bieling et al. (1995). Accurate values of  $K_H$  at low temperatures that appeared after the Wilhelm et al. (1977) review were also included in the fit (Cosgrove and Walkley, 1981; Rettich et al., 1982; Krause and Benson, 1989).

Over the past decade several investigators have compiled Henry's law constants. High-temperature (above 323 K) data on the solubility of gases in water were compiled and uniformly

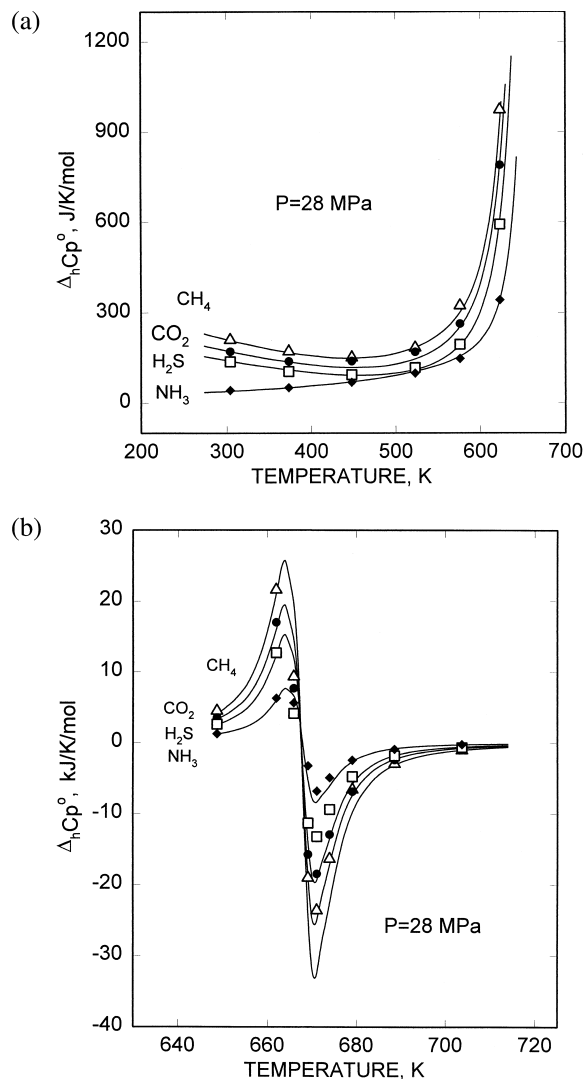


Fig. 5. Experimental (symbols, from Hnedkovsky and Wood, 1997) and fitted values of  $\Delta_h Cp^0$  for  $CH_4$ ,  $CO_2$ ,  $H_2S$ , and  $NH_3$  at  $P = 28$  MPa at subcritical (a) and supercritical (b) temperatures.

treated by Fernandez-Prini and Crovetto (1989) taking into account the nonideality of the gaseous phase and  $T$ - $P$  dependence of  $V_2^0$  for aqueous solutes. The same data set was used by Harvey and Levelt Sengers (1990). For  $CO_2$  there are two recent recommendations, one by Carroll et al. (1991) up to 433 K, and another by Crovetto (1991) up to temperatures close to the critical temperature of water. For  $H_2S$  Carroll and Mather (1989) reviewed the available low-temperature low-pressure experimental data and recommended  $K_H$  values for aqueous  $H_2S$  up to 363 K. Suleimenov and Krupp (1994) have determined values of the Henry's constants for hydrogen sulfide up to 593 K. Harvey (1996) used the sets of data from Fernandez-Prini and Crovetto (1989), Crovetto (1991), Suleimenov and Krupp (1994) to parametrize his new correlating equation. As a consequence, Henry's constants given in Fernandez-Prini and Crovetto (1989), Harvey and Levelt Sengers (1990), and Harvey (1996) are not independent, because they are based on the same data sets. However, despite the fact that all these models

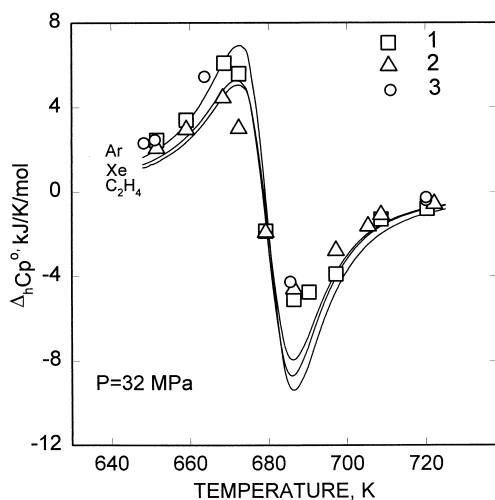


Fig. 6. Experimental (symbols, from Biggerstaff and Wood, 1988b) and fitted values of  $\Delta_h C_p^0$  for  $C_2H_4$ , Ar, and Xe at  $P = 31$  MPa and supercritical temperatures. (1) Ar, (2) Xe, (3)  $C_2H_4$ .

provide essentially the same quality of fit for all gases, there are some differences between  $K_H$  values calculated using these equations (see, for example, Fig. 8a for  $CH_4$ ). Values of Henry's constants from sources discussed above are indicated by different symbols in Fig. 8 over the temperature range where experimental determinations are available, i.e., none of the equations were used to generate values. Calculated results from the present approach are shown as solid lines, which extend to temperatures close to the critical temperature of water. Except for  $H_2S$ , all values refer to the saturation water vapor pressure. Only for  $H_2S$  are there direct experimental determinations of Henry's constants at elevated pressures through the measurement of concentration/fugacity ratios (Kishima, 1989).

Examination of Figs. 8a–g shows that in most cases the

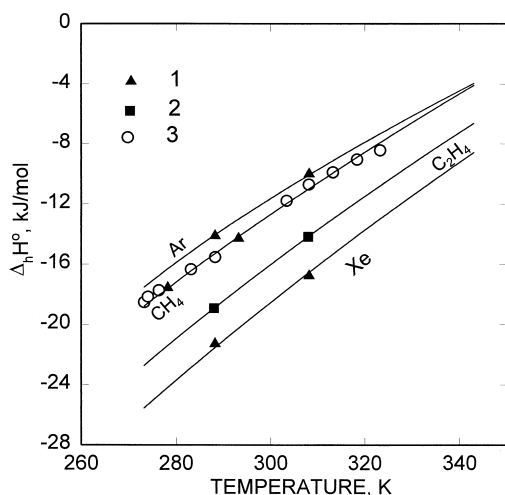


Fig. 7. Experimental and fitted values of  $\Delta_h H^0$  for Ar,  $CH_4$ ,  $C_2H_4$ , and Xe at various temperatures and atmospheric pressure. Experimental data are taken from: (1) Oloffson et al. (1984); (2) Dec and Gill (1985); (3) Naghibi et al. (1986).

differences between experimental and fitted results for  $\ln K_H$  are close to the expected experimental uncertainties, which vary from less than 0.01 at  $T < 323$  K to about 0.05 at  $T > 500$  K. Only for  $H_2S$  are there systematic deviations between recent experimental results of Suleimenov and Krupp (1994), and the results by Kozintseva (1964) and Drummond (1981). Our model, which successfully describes experimental  $V_2^0$  and  $Cp_2^0$  data for  $H_2S$  at elevated temperatures and pressures, is closer to the Kozintseva (1964) results, see Fig. 8g. Drummond's (1981) data (many experimental points) are close to Kozintseva's values, and they were not shown in Fig. 8g for better clarity. This result is found even if Kozintseva's and Drummond's  $K_H$  values are not used to determine the model parameters. Perhaps new experimental determinations at high temperatures are needed for this geochemically important solute,  $H_2S$ .

#### 4.4.2. The Gibbs energies of transfer at supercritical temperatures

At supercritical temperatures the infinite dilution partial molar Gibbs energy of hydration can be obtained from equations of state for water–gas systems (for instance, “SUPERFLUID” by Belonoshko et al., 1992) or from computer simulations (Lin and Wood, 1996). As discussed in the Introduction, it is convenient to represent the supercritical results as  $\Delta_h^V G^0$ , the Gibbs energy of transfer of solute from the gas phase to an equal volume of solution. Fitted results for  $CH_4$  and  $CO_2$  are very close to the values shown in Fig. 1 by the solid curves. For  $NH_3$  and Ar comparison is made in Fig. 9 with the “SUPERFLUID” values which are only available at  $P > 500$  MPa (Belonoshko et al., 1992). In addition to values calculated with “SUPERFLUID” at higher temperatures there are experimental data for  $H_2S$  by Kishima (1989) at 673 K (results from “SUPERFLUID” at 673 K are systematically more positive than experimental values up to 8 kJ mol<sup>-1</sup> and are not shown in Fig. 9).

We believe that the comparisons shown in Fig. 9 demonstrate that  $\Delta_h^V G^0$  values calculated by our approach are in close agreement with experimental results at temperatures up to at least 1300 K and density up to 1000 kg m<sup>-3</sup>.

#### 4.4.3. Near-critical behavior

During the last decade there were notable developments in the thermodynamics of infinitely dilute solutions near the solvent's critical point (SCP), the foundations of which were developed by Krichevskii (1967) and Rozen (1976). Many important results were first derived by Japas and Levelt Sengers (1989). As shown by Levelt Sengers (1991), the thermodynamic properties of dilute solutions near the SCP are governed by the derivative

$$A_{Kr} = \left( \frac{\partial P}{\partial X} \right)_{T,V,X=0}^c, \quad (10)$$

which Levelt Sengers has called the Krichevskii parameter,  $A_{Kr}$ . In Eqn. 10,  $X$  stands for the mole fraction of solute, and the superscript  $c$  indicates that this derivative is the limiting condition of the SCP. Some relations valid for infinitely dilute solutions in the vicinity of the SCP obtained by Harvey and

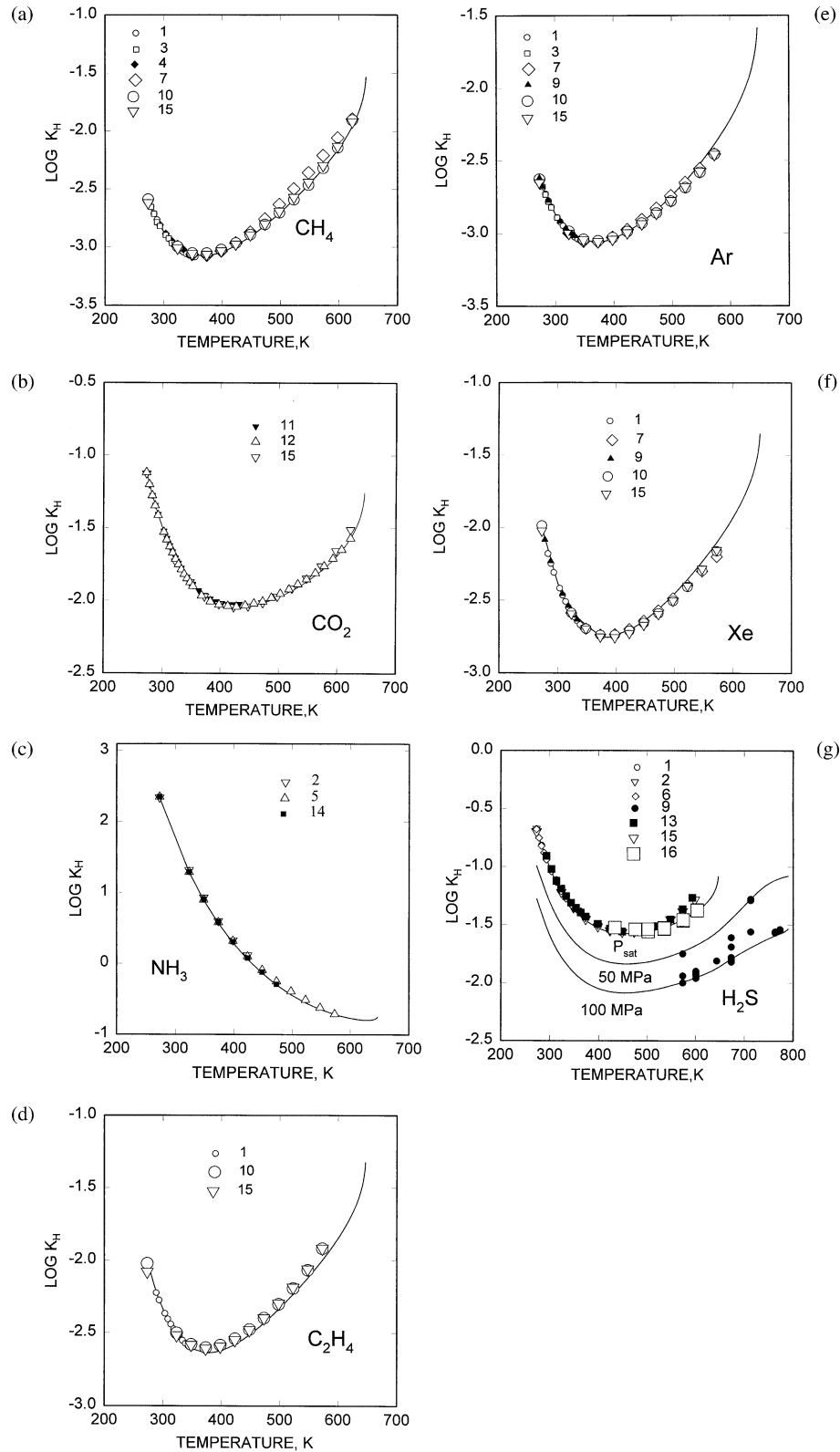


Fig. 8. "Experimental" (symbols) and fitted results for Henry's law constants of  $\text{CH}_4$  (a),  $\text{CO}_2$  (b),  $\text{NH}_3$  (c),  $\text{C}_2\text{H}_4$  (d), Ar (e), Xe (f), and  $\text{H}_2\text{S}$  (g). Symbols: (1) Wilhelm et al. (1977); (2) Edwards et al. (1978); (3) Cosgrove and Walkley (1981); (4) Rettich et al. (1981); (5) Kawazuishi and Prausnitz (1987); (6) Carroll and Mather (1989); (7) Fernandez-Prini and Crovetto (1989); (8) Kishima (1989); (9) Krause and Benson (1989); (10) Harvey and Levelt Sengers (1990); (11) Carroll et al. (1991); (12) Crovetto (1991); (13) Suleimenov and Krupp (1994); (14) Bieling et al. (1995); (15) Harvey (1996); (16) Kozintseva (1964).

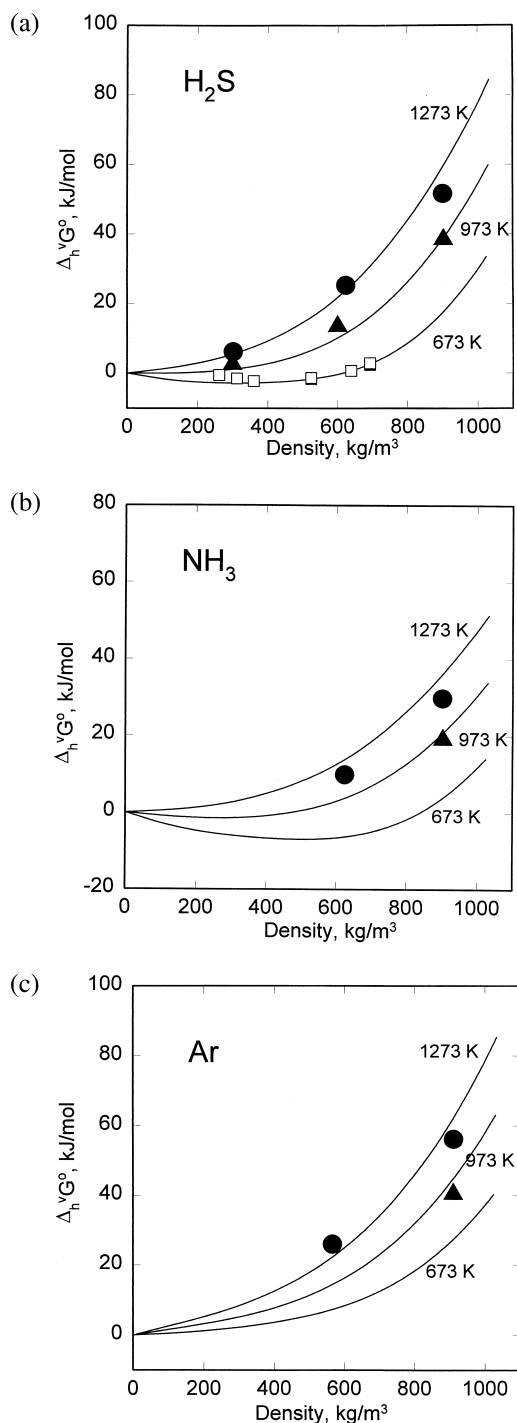


Fig. 9. Predicted (solid lines) and literature values (symbols) of  $\Delta_h^V G^0$  for  $\text{H}_2\text{S}$  (a),  $\text{NH}_3$  (b), and Ar (c) as a function of water density at some representative isotherms. Symbols: open squares—Kishima (1989), 673 K; filled triangles—Belonoshko et al. (1992), 973 K; filled circles—Belonoshko et al. (1992), 1273 K.

Levelt Sengers (1990), Harvey et al. (1990), and Levelt Sengers (1991), and relevant to the purposes of the present work, bear repetition.

(1) For the partial molar volume of a solute:

Table 2. Values of the Krichevskii parameter  $A_{\text{Kr}}$  (MPa) estimated from the initial slopes of the critical lines (CRL), the infinite dilution distribution constants (DISTR), and calculated from the present model parameters (MODEL).

Solute	CRL <sup>a</sup>	DISTR <sup>b</sup>	MODEL
$\text{CH}_4$	150	158	166.1
$\text{CO}_2$	100	118	127.2
$\text{H}_2\text{S}$		103	100.9
$\text{NH}_3$		40	47.1
Ar	130	171	170.1
Xe		149	150.6

<sup>a</sup> Harvey et al. (1990), may have uncertainty up to 25% of the value.

<sup>b</sup> Recommended in Alvarez et al., 1994.

$$V_2^0 = A_{\text{Kr}} V_1^0 \kappa_T. \quad (11)$$

(2) For the near-critical variation of  $k_H$  ( $k_H$  stands for the Henry's law constant in the mole fraction concentration scale and it is defined as solely a temperature-dependent function along the saturation water–vapor curve):

$$T \ln \left( \frac{k_H}{f_1^0} \right) = A + B(\rho - \rho_c), \quad (12)$$

where  $A$  and  $B$  stand for proportionality coefficients, and  $\rho_c$  represents the pure water density at the critical point. The coefficient  $B$  in Eqn. 12 relates to the Krichevskii parameter as follows (Harvey and Levelt Sengers, 1990):

$$B = \frac{A_{\text{Kr}}}{R\rho_c^2}. \quad (13)$$

In addition, the value of the Krichevskii parameter can be evaluated from the initial slopes of the critical line in a solute–solvent system and the temperature dependence of the vapor–liquid distribution coefficients for a solute at infinite dilution (see Krichevskii, 1967; Harvey and Levelt Sengers, 1990; Harvey et al., 1990; Alvarez et al., 1994). Numerical values of  $A_{\text{Kr}}$  have been estimated from different sets of data by Harvey et al. (1990) and Alvarez et al. (1994). The conclusion reached by these authors is that self-consistent values of the Krichevskii parameters can be obtained from the infinite dilution distribution coefficients and the initial slopes of the critical line, but not from  $k_H$  (Harvey et al., 1990). Alvarez et al. (1994) recommended the most reliable values of the parameter  $B$  (and consequently  $A_{\text{Kr}}$  through Eqn. 13) for a number of water–gas systems, including all solutes in our set except  $\text{C}_2\text{H}_4$ .

The value of the Krichevskii parameter can also be calculated in the framework of the model presented here. Comparing Eqns. 3 and 11 at the critical point of pure water, we obtain the following relationship:

$$A_{\text{Kr}} = A_{12}(T_c, P_c) \frac{RT_c}{V_1^c}, \quad (14)$$

where  $V_1^c$  represents the critical value of the molar volume of water ( $V_1^c = 55.96 \text{ cm}^3 \text{ mol}^{-1}$  to be consistent with  $\rho_c = 17.87 \text{ mol dm}^{-3}$  used by Harvey et al., 1990);  $A_{12}(T_c, \rho_c)$  is the value of the parameter  $A_{12}$  at the critical point of pure water.

In Table 2 we compare values of the Krichevskii parameter calculated using parameters of the present model with the

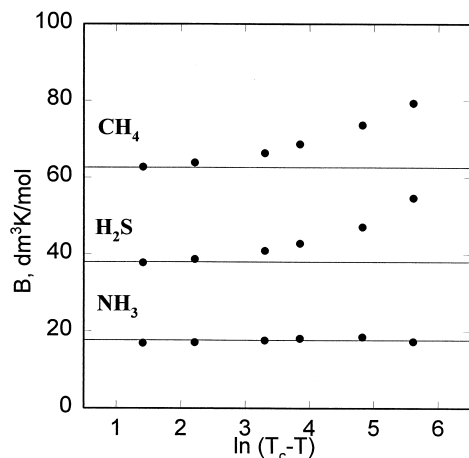


Fig. 10. Values of the slope,  $B$ , for  $\text{CH}_4$ ,  $\text{H}_2\text{S}$ , and  $\text{NH}_3$  (circles) calculated using Eq. (13) at temperatures from  $T_c$  to  $T$ , plotted versus  $\ln(T_c - T)$ . Solid lines represent the asymptotic values of  $B$  calculated in the framework of the present model.

Harvey et al. (1990) and Alvarez et al. (1994) recommendations. Parameters of our model were evaluated using large and diverse arrays of experimental data over wide temperature and pressure ranges, however, with no “asymptotic” near-critical relations and data included. Our estimates of the Krichevskii parameter are in close agreement with the recommendations of Alvarez et al. (1994), which are based mainly on high-temperature distribution coefficients and available information about the initial slopes of critical lines in binary water–gas systems. This agreement between the numerical values of the Krichevskii parameter calculated within the framework of our approach and independent literature evaluations gives us additional confidence in the correctness of the proposed model at near-critical conditions.

Another interesting question concerns the temperature interval of the applicability of Eqn. 12. This relation must be asymptotically correct at near-critical conditions as discussed by Japas and Levelt Sengers (1989). Later, Harvey and Levelt Sengers (1990) found that the linear relation is valid over an unexpectedly wide range of temperature, down to 373 K; however, the slopes ( $B$  parameter) differ from ones estimated from the distribution coefficients or initial slopes of the critical lines in binary water–solute systems (Harvey et al., 1990; Harvey, 1998). To address this problem we used the parameters of our approach to evaluate the left-hand side of Eqn. 12 at various temperatures along the saturated vapor pressure curve. Then for each substance we took all values within specific temperature distances from the critical point of pure water (six groups within approximately 4, 9, 30, 50, 120 or 270 K from  $T_c$ ) and correlated each set of results by means of Eqn. 12. Values of  $B$  calculated from each group of data treated in this manner are plotted in Fig. 10 as symbols, and the solid lines correspond to the “true” asymptotic values of  $B$  as given in the last column of Table 2. It is worth noting that Eqn. 13 provides an accurate description of the data within each of the selected temperature distances. In all cases the size of each symbol in Fig. 10 is equal to or less than its uncertainty for the 95% confidence level. However, it can be seen that numerical values

of the  $B$  parameter for  $\text{CH}_4$  and  $\text{H}_2\text{S}$  depend strongly on the temperature interval used for parametrization. For these solutes the true slopes are observed only within 10–20 K from the critical point of water, which is broadly consistent with findings of Harvey et al. (1990) and Harvey (1998).

## 5. DISCUSSION

The extension of the Plyasunov et al. (2000) model to sub-critical temperatures has been accomplished without introducing new fitting parameters, but by using the four-coefficient Eqn. 6 in combination with the four constraints discussed above. The novel feature of the model is that it uses the values of  $\Delta_h G^0$ ,  $\Delta_h H^0$ ,  $\Delta_h C_p^0$  at one selected supercritical temperature  $T_s = 658$  K, generated “inside” the model, to evaluate the course of the  $\Delta_h C_p^0(T, P_r)$  function from ambient to supercritical temperatures. The particular analytical form of Eqn. 6 was found empirically using the trial and error method by global fitting of all available data for the basic set of solutes:  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ , Ar, Xe, and  $\text{C}_2\text{H}_4$ . Can the same approach be used for all the various neutral volatile species? It is difficult to have a definite answer, which depends in part whether the compounds in the basic set are representative for all nonelectrolytes. Note that the solutes in the basic set have relatively small excluded volumes, ranging approximately from 25 to 50  $\text{cm}^3 \text{mol}^{-1}$  and exist as gases in their pure states at ambient temperatures. They do represent a wide variation in polarity, from polar  $\text{NH}_3$  (high dipole moment in the gas phase, low value of the Gibbs energy of hydration) to a typical nonpolar compound such as  $\text{CH}_4$  (zero dipole moment in the gas phase, relatively high value of the Gibbs energy of hydration). So, we expect that this approach can be applied to many gases of different polarity. Preliminary results show the applicability to large compounds that exist in condensed form at ambient temperatures, such as benzene, hexane, etc.

For some solutes there are no experimental  $\Delta_h C_p^0$  results even at 298.15 K, 0.1 MPa. To determine the parameters of the model for these compounds we suggest using only three constraints [without  $\Delta_h C_p^0(T_s, P_r)$ ] and setting the value of the coefficient  $d_2$  in Eqn. 6 to zero. As a result, a predicted value of the partial molar heat capacity of hydration at 298.15 K, 0.1 MPa will be calculated. We recommend checking its consistency with estimates available from literature correlations and empirical knowledge of the magnitude of  $\Delta_h C_p^0$  (298.15, 0.1 MPa) depending on the polarity and size characteristics of compounds. All of the above discussion is restricted to solutes with positive values of the  $A_{12}$  parameter, i.e., not to solutes that interact strongly with water such as aqueous silica, or neutral ion pairs like HCl, etc.

The present model is also limited to the standard state of infinite dilution. However, since it is formulated in terms of the  $A_{12}$  parameter, related to the integral of the infinite dilution solute–solvent correlation function, extensions to finite concentrations may be accomplished following the methods of Liu and O’Connell (1998) and O’Connell et al. (1999).

## 6. CONCLUDING REMARKS

The primary goal of this paper is to outline a new model for calculating infinite dilution partial molar properties of volatile nonelectrolytes over wide ranges of temperature and pressure

(or density). Partial molar properties estimated with this model provide useful input for thermodynamic interpretations of geochemical processes. Traditionally, two methods have been used to represent the thermodynamic properties (mostly Gibbs energy) for aqueous volatile nonelectrolytes: one at subcritical temperatures based on evaluating Henry's law constants, and the other at supercritical conditions based on equations of state. Neither of these methods can be extended to include the region close to the critical point of pure water in any straightforward manner. As a result it is often difficult to relate models of metamorphic or magmatic fluids to those for hydrothermal fluids, basinal brines, or seawater. The new model presented here covers both subcritical and supercritical temperature ranges with a single framework, and we have checked in considerable detail its ability to return useful results in the challenging near-critical region. Another point to underscore is the high accuracy of the model at all conditions and for all thermodynamic properties. At least at supercritical conditions it represents a notable improvement over the revised-HKF model, and especially for partial molar volumes and heat capacities. As the model contains only a few parameters and can be successfully employed far outside the  $T$ - $P$  range of experimental data used for parametrization, we believe that predictions may be made for many aqueous compounds of geochemical significance with this approach. The development of the corresponding estimation strategy is an aspect of our ongoing research.

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#### APPENDIX A. STANDARD PARTIAL MOLAR THERMODYNAMIC FUNCTIONS OF HYDRATION CONSISTENT WITH EQ. (4)

(1) The equation for the standard partial molar fugacity coefficient of a solute is written as follows:

$$\ln \Phi_2^0 = \ln \Phi_2^0(\text{I}) + \ln \Phi_2^0(\text{II}) + \ln \Phi_2^0(\text{III}) + \ln \Phi_2^0(\text{IV}), \quad (\text{A1})$$

where

$$\ln \Phi_2^0(\text{I}) = N \ln \Phi_1^0, \quad (\text{A2})$$

$$\ln \Phi_2^0(\text{II}) = (N-1) \ln \frac{PV_1^0}{RT}, \quad (\text{A3})$$

$$\ln \Phi_2^0(\text{III}) = -\frac{2\Omega}{c_1} \{B_{12}(T) - NB_{11}(T)\} \exp[-c_1\rho] - 1, \quad (\text{A4})$$

and

$$\ln \Phi_2^0(\text{IV}) = \left( \frac{a}{T^3} + b \right) \left[ \frac{1}{c_2} (\exp[c_2\rho] - 1) - \rho \right]. \quad (\text{A5})$$

(2) The equation for the standard Gibbs energy of hydration of a solute,  $\Delta_h G^0$ , is

$$\frac{\Delta_h G^0}{RT} = \ln \left( \frac{\Phi_2^0 P}{P^\ominus} \right) - \ln \left( \frac{1000}{M_w} \right), \quad (\text{A6})$$

where  $P^\ominus = 0.1$  MPa is the ideal gas reference pressure,  $M_w$  stands for the molecular mass of water. The second term on the right-hand side of Eqn. A6 is the conversion factor from the mole fraction to the molality concentration scale.

(3) The equation for the standard partial molar enthalpy of hydration,  $\Delta_h H^0$ , is given by

$$\frac{\Delta_h H^0}{R} = -T^2 \left( \frac{\partial}{\partial T} \left\{ \frac{\Delta_h G^0}{RT} \right\} \right)_p = \frac{\Delta_h H^0(\text{I})}{R} + \frac{\Delta_h H^0(\text{II})}{R} + \frac{\Delta_h H^0(\text{III})}{R} + \frac{\Delta_h H^0(\text{IV})}{R}, \quad (\text{A7})$$

where

$$\frac{\Delta_h H^0(\text{I})}{R} = N \frac{H_1^0 - H_1^\ominus}{R}, \quad (\text{A8})$$

$$\frac{\Delta_h H^0(\text{II})}{R} = (N-1)(T - \alpha T^2), \quad (\text{A9})$$

$$\frac{\Delta_h H^0(\text{III})}{R} = -T^2 2\Omega \{B_{12}(T) - NB_{11}(T)\} \exp[-c_1\rho] \left( \frac{\partial \rho}{\partial T} \right)_p + \frac{T^2}{c_1} 2\Omega \left( \frac{\partial}{\partial T} \{B_{12}(T) - NB_{11}(T)\} \right)_p (\exp[-c_1\rho] - 1), \quad (\text{A10})$$

and

$$\frac{\Delta_h H^0(\text{IV})}{R} = (\exp[c_2\rho] - 1) \left\{ \frac{5a}{c_2 T^4} - \left( \frac{a}{T^3} + bT^2 \right) \left( \frac{\partial \rho}{\partial T} \right)_p \right\} - \frac{5a\rho}{T^4}, \quad (\text{A11})$$

where  $H_1^0$  stands for the molar enthalpy of water at specified  $T$  and  $P$ ,  $H_1^\ominus$  represents the molar enthalpy of water in the ideal-gas state, and  $\alpha = (1/V_1^0)(\partial V_1^0/\partial T)_p$  indicates the thermal expansion coefficient of pure water. The values of the standard partial molar entropy of hydration can be obtained from the relation:

$$\Delta_h S^0 = \frac{\Delta_h H^0 - \Delta_h G^0}{T}. \quad (\text{A12})$$

(4) The equation for the standard partial molar heat capacity of hydration is given by

$$\frac{\Delta_h Cp^0}{R} = \left( \frac{\partial}{\partial T} \left\{ \frac{\Delta_h H^0}{R} \right\} \right)_p = \frac{\Delta_h Cp^0(\text{I})}{R} + \frac{\Delta_h Cp^0(\text{II})}{R} + \frac{\Delta_h Cp^0(\text{III})}{R} + \frac{\Delta_h Cp^0(\text{IV})}{R}, \quad (\text{A13})$$

where

$$\frac{\Delta_h Cp^0(\text{I})}{R} = N \frac{Cp_1^0 - Cp_1^\ominus}{R}, \quad (\text{A14})$$

$$\frac{\Delta_h Cp^0(\text{II})}{R} = (N-1) \left( 1 - T^2 \left( \frac{\partial \alpha}{\partial T} \right)_p - 2\alpha T \right), \quad (\text{A15})$$

$$\begin{aligned} \frac{\Delta_h Cp^0(\text{III})}{R} = & -T2\Omega \{B_{12}(T) - NB_{11}(T)\} \exp[-c_1\rho] \\ & \times \left\{ 2 \left( \frac{\partial \rho}{\partial T} \right)_p - c_1 T \left( \frac{\partial \rho}{\partial T} \right)_p^2 + T \left( \frac{\partial^2 \rho}{\partial T^2} \right)_p \right\} + 2T2\Omega \\ & \left( \frac{\partial}{\partial T} \{B_{12}(T) - NB_{11}(T)\} \right)_p \left( \frac{1}{c_1} (\exp[-c_1\rho] - 1) - T \exp[-c_1\rho] \right) \\ & \times \left( \frac{\partial \rho}{\partial T} \right)_p + \frac{T^2}{c_1} 2\Omega \left( \frac{\partial^2}{\partial T^2} \{B_{12}(T) - NB_{11}(T)\} \right)_p (\exp[-c_1\rho] - 1), \end{aligned} \quad (\text{A16})$$

and

$$\begin{aligned} \frac{\Delta_h C p^0(\text{IV})}{R} &= c_2 \exp[c_2 \rho] \left( \frac{\partial \rho}{\partial T} \right)_p \left\{ \frac{5a}{c_2 T^4} - \left( \frac{a}{T^3} + b T^2 \right) \left( \frac{\partial \rho}{\partial T} \right)_p \right\} \\ &+ \frac{5a}{T^4} \left\{ 4\rho - T \left( \frac{\partial \rho}{\partial T} \right)_p \right\} - (\exp[c_2 \rho] - 1) \left\{ \frac{20a}{c_2 T^5} + \left( 2bT - \frac{3a}{T^4} \right) \right. \\ &\quad \left. \times \left( \frac{\partial \rho}{\partial T} \right)_p + \left( \frac{a}{T^3} + b T^2 \right) \left( \frac{\partial^2 \rho}{\partial T^2} \right)_p \right\}, \quad (\text{A17}) \end{aligned}$$

where  $C p_1^0$  designates the molar enthalpy of water at specified  $T$  and  $P$ ,  $C p_1^\infty$  stands for the molar enthalpy of water in the ideal gas state.

(5) The temperature derivatives of  $B_{ij}$  are given by

$$\left( \frac{\partial B_{ij}(T)}{\partial T} \right)_p = \frac{2\pi N_A \sigma_{ij}^3 (\lambda^3 - 1)}{3} \frac{\varepsilon_{ij}}{T^2} \frac{\varepsilon_{ij}}{\kappa_B} \exp \left[ \frac{\varepsilon_{ij}}{\kappa_B T} \right] \quad (\text{A18})$$

and

$$\left( \frac{\partial^2 B_{ij}(T)}{\partial T^2} \right)_p = - \left( \frac{\partial B_{ij}(T)}{\partial T} \right)_p \left\{ \frac{\varepsilon_{ij}}{\kappa_B T^2} + \frac{2}{T} \right\}. \quad (\text{A19})$$

### APPENDIX B. EQUATIONS FOR THE PRESSURE DEPENDENCIES OF THE STANDARD PARTIAL MOLAR THERMODYNAMIC FUNCTIONS OF A SOLUTE CONSISTENT WITH EQ. (4)

An isothermal pressure increment of any standard (infinite dilution) thermodynamic function  $Y^0$ ,  $\Delta Y^0$ , is defined as the difference between the values of the function  $Y^0$  at pressure  $P$ ,  $Y^0(P)$ , and at any reference pressure  $P_r$ ,  $Y^0(P_r)$ . Any of the thermodynamic functions of hydration,  $\Delta_h Y^0$ , is defined as the difference between the standard partial molar property,  $Y^0$ , of a compound in an aqueous solution at any  $T$  and  $P$ , and the same property of the compound in the ideal gas state at any temperature and pressure  $P^\infty = 0.1$  MPa. As a result the pressure increment is identical for both hydration functions and partial molar properties of a solute:

$$\Delta Y^0 = \Delta_h Y^0(T, P) - \Delta_h Y^0(T, P_r) \equiv Y_2^0(T, P) - Y_2^0(T, P_r). \quad (\text{B1})$$

(1) The equation for the isothermal pressure increment of the standard partial molar Gibbs energy is

$$\Delta G^0 = \int_{P_r}^P V_2^0 dP = \Delta G^0(\text{I}) + \Delta G^0(\text{II}) + \Delta G^0(\text{III}) + \Delta G^0(\text{IV}), \quad (\text{B2})$$

where

$$\Delta G^0(\text{I}) = RT N \langle \ln(\Phi_1^0 P) \rangle_{P_r}^P, \quad (\text{B3})$$

$$\Delta G^0(\text{II}) = RT(1 - N) \langle \ln(\rho) \rangle_{P_r}^P, \quad (\text{B4})$$

$$\Delta G^0(\text{III}) = -RT \frac{2\Omega}{c_1} \{B_{12}(T) - NB_{11}(T)\} \langle \exp[-c_1 \rho] \rangle_{P_r}^P, \quad (\text{B5})$$

and

$$\Delta G^0(\text{IV}) = RT \left( \frac{a}{T^5} + b \right) \left\langle \left\{ \frac{1}{c_2} \right\} \exp[c_2 \rho] - \rho \right\rangle_{P_r}^P. \quad (\text{B6})$$

(2) The equation for the isothermal pressure increment of the standard partial molar enthalpy is

$$\begin{aligned} \Delta H^0 &= \int_{P_r}^P \left( V_2^0 - T \left( \frac{\partial V_2^0}{\partial T} \right)_p \right) dP = \Delta H^0(\text{I}) + \Delta H^0(\text{II}) + \Delta H^0(\text{III}) \\ &+ \Delta H^0(\text{IV}), \quad (\text{B7}) \end{aligned}$$

where

$$\Delta H^0(\text{I}) = N \langle H_1^0 \rangle_{P_r}^P, \quad (\text{B8})$$

$$\Delta H^0(\text{II}) = RT^2(1 - N) \langle \alpha \rangle_{P_r}^P, \quad (\text{B9})$$

$$\begin{aligned} \Delta H^0(\text{III}) &= -RT^2 2\Omega \{B_{12}(T) - NB_{11}(T)\} \left\langle \exp[-c_1 \rho] \left( \frac{\partial \rho}{\partial T} \right)_p \right\rangle_{P_r}^P \\ &+ RT^2 \frac{2\Omega}{c_1} \left( \frac{\partial}{\partial T} \{B_{12}(T) - NB_{11}(T)\} \right) \langle \exp[-c_1 \rho] \rangle_{P_r}^P, \quad (\text{B10}) \end{aligned}$$

and

$$\begin{aligned} \Delta H^0(\text{IV}) &= -RT^2 \left( \frac{a}{T^5} + b \right) \left\langle \left( \frac{\partial \rho}{\partial T} \right)_p (\exp[c_2 \rho] - 1) \right\rangle_{P_r}^P \\ &+ RT^2 \frac{5a}{T^6} \left\langle \left( \frac{\partial \rho}{\partial T} \right)_p \left( \frac{1}{c_2} \exp[c_2 \rho] - \rho \right) \right\rangle_{P_r}^P. \quad (\text{B11}) \end{aligned}$$

(3) The equation for the isothermal pressure increment of the standard partial molar heat capacity is

$$\begin{aligned} \Delta C p^0 &= -T \int_{P_r}^P \left( \frac{\partial^2 V_2^0}{\partial T^2} \right)_p dP = \Delta C p^0(\text{I}) + \Delta C p^0(\text{II}) + \Delta C p^0(\text{III}) \\ &+ \Delta C p^0(\text{IV}), \quad (\text{B12}) \end{aligned}$$

where

$$\Delta C p^0(\text{I}) = N \langle C p_1^0 \rangle_{P_r}^P, \quad (\text{B13})$$

$$\Delta C p^0(\text{II}) = RT(1 - N) \left\langle 2\alpha + T \left( \frac{\partial \alpha}{\partial T} \right)_p \right\rangle_{P_r}^P, \quad (\text{B14})$$

$$\begin{aligned} \Delta C p^0(\text{III}) &= 2\Omega RT \{B_{12}(T) - NB_{11}(T)\} \left\langle \exp[-c_1 \rho] \left[ c_1 T \left( \frac{\partial \rho}{\partial T} \right)_p^2 \right. \right. \\ &\quad \left. \left. - 2 \left( \frac{\partial \rho}{\partial T} \right)_p - T \left( \frac{\partial^2 \rho}{\partial T^2} \right)_p \right] \right\rangle_{P_r}^P + 2\Omega RT^2 \left( \frac{\partial}{\partial T} \{B_{12}(T) \right. \\ &\quad \left. - NB_{11}(T)\} \right) \left\langle \exp[-c_1 \rho] \left[ \frac{1}{c_1} - T \left( \frac{\partial \rho}{\partial T} \right)_p \right] \right\rangle_{P_r}^P \\ &+ 2\Omega RT \frac{T}{c_1} \left( \frac{\partial^2}{\partial T^2} \{B_{12}(T) - NB_{11}(T)\} \right) \langle \exp[-c_1 \rho] \rangle_{P_r}^P, \quad (\text{B15}) \end{aligned}$$

$$\begin{aligned} \Delta C p^0(\text{IV}) &= RT \left( \frac{20a}{T^6} \left( \rho - \frac{1}{c_2} \exp[c_2 \rho] \right) - 2 \left( \frac{\partial \rho}{\partial T} \right)_p \left( b - \frac{4a}{T^5} \right) \right. \\ &\quad \left. \times (\exp[c_2 \rho] - 1) - c_2 T \left( \frac{a}{T^5} + b \right) \exp[c_2 \rho] \left( \frac{\partial \rho}{\partial T} \right)_p^2 - T \left( \frac{a}{T^5} + b \right) \right. \\ &\quad \left. \times (\exp[c_2 \rho] - 1) \left( \frac{\partial^2 \rho}{\partial T^2} \right)_p \right\rangle_{P_r}^P. \quad (\text{B16}) \end{aligned}$$