

A Model-Guided Determination of $\Delta_{\text{dis}}G_2^\infty$ for Slightly Soluble Gases in Water Using Solubility Data: From the Solvent's Freezing Point to Its Critical Point

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Abstract There is continuing interest in the description of the solubility of nonpolar gases in water over a wide range of temperatures. On one hand, the solubility data are used in many fields of science and technology; and on the other hand, simulation and theoretical calculations require experimental data to test their results and predictions. For these reasons it is important to have a means of calculating from the experimental solubility data the Gibbs energy of dissolution of gases ($\Delta_{\text{dis}}G_2^\infty$) and Henry's constant (k_{H}) over all the temperature range of existence of liquid water.

Under ambient conditions it is relatively easy to relate $\Delta_{\text{dis}}G_2^\infty$ and, hence, k_{H} to the solubility data of nonpolar gases. However, this simple procedure becomes increasingly complicated as the temperature approaches the critical temperature of the solvent and it is necessary to make important corrections to obtain the thermodynamic quantities for the dissolution process. This difficulty can be resolved with a procedure that employs a perturbation method applied to a simple model solvent to guide the correct determination of k_{H} and $\Delta_{\text{dis}}G_2^\infty$. We describe in this work an iterative calculation procedure whose correctness was validated with a thermodynamic relationship that uses only experimental data, hence it is model-free. Unfortunately this relationship can be applied only to a few systems due to its data requirements. The iterative procedure described in this work can be extended to higher pressures, $p \cong 50$ MPa above the solvent's vapor pressure, and also to gases dissolved in nonaqueous solvents.

Keywords Thermodynamic properties · Aqueous solutions · Solubility of gases

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1 Introduction

Information about the thermodynamic and structural properties of nonpolar gases dissolved in water is viewed as a cornerstone for many processes occurring in more complex systems, especially those involving hydrophobic solutes in aqueous solutions. Moreover, there is continuing interest in the description of the solubility of nonpolar gases in water over a wide range of temperatures due to the ubiquitous presence of these systems in nature as well as in many technologies. On one hand, experimental data are increasingly used in many fields of science and technology ranging from hydrophobic model-solute behavior at ambient temperatures [1] to geophysical processes over the complete temperature range of existence of liquid water [2, 3]. On the other hand, simulation studies and theoretical calculations [4–6] require experimental data to test their results and predictions. For these reasons it is very important to have a means of determining the values of $\Delta_{\text{dis}}G_2^\infty$ and Henry's constant from the available solubility data. Some twenty years ago we reviewed our experimental and theoretical studies of the solubility of nonreactive small gaseous solutes in H_2O and D_2O over a wide temperature range [7] and compared them with the dissolution of the same gases in slightly polar or nonpolar solvents. Since then we have developed a successful method that provides a description of the thermodynamic properties of the gaseous solutes in water from the melting point to the critical point of water, thus covering the complete range of existence of liquid H_2O . The method iterates between experimental solubility data and model equations so that in this way it is possible to determine k_{H} successfully.

Solubility data for nonpolar unreactive gases dissolved in water appear as a relatively direct way to determine Henry's constant and, hence, $\Delta_{\text{dis}}G_2^\infty$. However, the procedure that is simple under ambient conditions becomes increasingly complicated as the temperature approaches the critical temperature of the solvent, T_{c1} . This is due to the experimental requirements which are necessary to keep the precision of the solubility measurements within $\approx 2\%$ and also to the large contribution of the corrections necessary to obtain thermodynamically consistent data. The Poynting correction, due to the fact that the total pressure over the solutions is larger than the vapor pressure of water, and the excess chemical potential of the solutes, which is neglected under ambient conditions, become a significant contributions when the near-critical region is approached; these two effects constitute the main difficulties when trying to extend the simple Henry's law to high temperatures.

We have found that use of a robust procedure that iterates between experimental data and the results of a perturbation model to guide the correct calculation of k_{H} and $\Delta_{\text{dis}}G_2^\infty$ for a given (p , T) condition, is very efficient in fulfilling the goal of covering the complete temperature range of existence of liquid water. Furthermore, the thermodynamic consistency of the procedure we developed was validated using other thermodynamic relations that are model-free but require solubility data over a range of gas partial pressures at each temperature. The use of the iterative procedure provided us with expressions for k_{H} as a function of temperature over all the range of existence of liquid water, which we have already published [8, 9]. Moreover, we show in the present work that the iterative experimental–perturbation procedure can be extended to pressures that are at least 50 MPa above the solvent's partial pressure for solutions at high temperature.

It seems timely to give a short, but nonetheless detailed, review of the calculation procedure we have developed which has proved extremely successful for liquid water as a solvent over its complete range of existence. This procedure can be extended to pressures well above the solvent's vapor pressure, as well as to solutions of gases in nonaqueous solvents.

2 Molecular Background

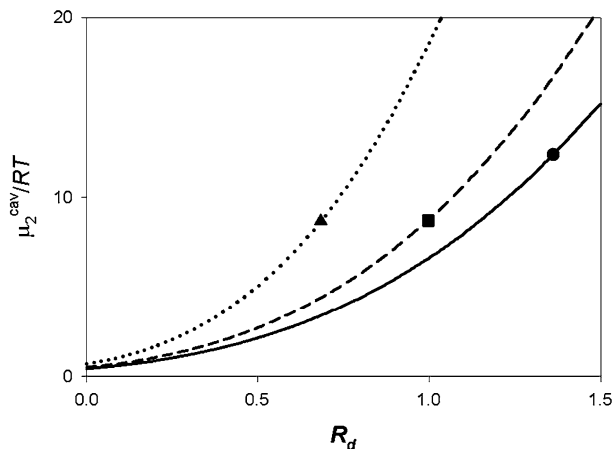
It is frequently mentioned that water is not a typical solvent medium, but this truism applies only to ambient conditions, a feature that has been summarized, unfortunately, by saying that water becomes hydrophobic as temperature increases. This somewhat confusing statement seems to put into question the possibility of having a general method able to describe quantitatively the behavior of solutes in water, and it appears that it can only be deemed possible at high temperatures. However, for gaseous solutes at those temperatures the simplicity of Henry's original formulation of the solubility of gases in liquids is lost, as we shall show below. Not only that, also the description would be different for aqueous and nonaqueous solutions of the gases, implying a complete loss of generality in the description of these rather simple solutions. Thus it is important to inquire about the molecular picture that describes the dissolution process of nonpolar gases in a liquid.

Pierotti's classical work first described the dissolution of small nonpolar solutes in several nonaqueous solvents [10] with the scaled particle theory (SPT), a perturbation method that uses a hard-sphere reference fluid perturbed by the solute-solvent interaction. In spite of the structural features of liquid water at ambient temperature, he also showed that SPT could be applied successfully to solutions of gases in water at ambient temperature [11]. The success of such a simple theory to deal with aqueous, as well as nonaqueous, solutions of gaseous solutes was supported by evidence that these solutes affect very slightly, if at all, the solvent's structure. This has been proposed [7] by comparing the gas-(oxygen atom of H₂O) pair correlation function $g_{12}(r)$ for the water molecules surrounding the solute, and also by molecular dynamics simulations of Xe dissolved in water [12] that will be discussed below.

Recently an important revival of the field has taken place with a much deeper *molecular* insight in connection with the behavior of typically hydrophobic solutes in aqueous solutions, usually having larger molecules than the nonpolar gases. Theoretical and simulation studies have confirmed that the predictions of the perturbation method developed in our laboratory were accurate if the size of the (spherical) solute dissolved in H₂O does not exceed about 0.5 nm [13].

This wealth of information is summarized partially in Fig. 1 where the work for the formation of a cavity, a repulsive contribution to $\Delta_{\text{dis}}G_2^\infty$, for CH₄ in three liquid solvents is plotted as function of the ratio of solute-to-solvent size. Figure 1 is very revealing of the molecular features that support the perturbation method; the process of cavity formation in the liquid solvent is essentially determined by the probability that a cavity of appropriate size may be spontaneously formed in the solvent through fluctuations in the number density of H₂O molecules, n_1 . This probability depends on the solvent's packing fraction ($\eta = \pi n_1 d_1^3/6$, d_1 being the molecular diameter of the solvent) and on the ratio of solute to solvent diameters $R_d = (d_2/d_1)$. The curves in Fig. 1 show how the repulsive term changes with R_d at room temperature for three solvents having different packing fractions: water ($\eta = 0.34$), methanol ($\eta = 0.39$) and CCl₄ ($\eta = 0.50$). It is clear from the figure that the low solubility of nonpolar gases in water is due to the small size of the H₂O molecule which produces a large R_d . Since d_1 for water is small, the probability of local fluctuations in n_1 that produce cavities large enough to hold a given solute particle is much smaller than in other liquids, even for those having a much larger value of the packing fraction but also a much larger d_1 , like CCl₄; hence, it is less probable to find water cavities having the size of a given solute particle than in a typical nonpolar liquid. The case of methanol is interesting, it also has a relatively low packing fraction but the size of its molecule is large enough to make it easier to find in methanol a cavity spontaneously generated by molecular density fluctuations compared to the case for water.

Fig. 1 The term μ_2^{cav}/RT against R_d for three solvents: water (solid line), CH_3OH (dashed line); CCl_4 (dotted line). The symbols indicate values for CH_4 as a solute



On the basis of the molecular picture described above, it should be possible in principle to use a perturbation method to describe the solubility over the complete temperature range of liquid water existence. It is a simple method which also shows great flexibility, e.g., the procedure can easily be extended beyond the solvent's vapor pressure and can also be used to describe the dissolution of gases in nonpolar liquids.

3 Thermodynamic Relationships

As stated in the introduction, in order to achieve our goal it was necessary to use rigorous thermodynamic equations to describe the dissolution process. Starting with the equality of the chemical potentials of the solute and solvent in both coexisting fluid phases it is possible to obtain the full thermodynamic expression for $\Delta_{\text{dis}}G_2^\infty = RT \ln(k_{\text{H}}/p^\theta)$ [8, 9], where p^θ is the standard pressure (0.1 MPa). If fugacities are used to express the chemical potentials of the two components in the vapor phase, it is possible to get the following equation for k_{H} [8]:

$$k_{\text{H}} = \frac{\phi_2 p}{x_2 \gamma_2^{\text{H}}} \exp\left(-\int_{p_1^*}^p \frac{V_2^\infty}{RT} dp\right) \left[1 - \frac{\phi_1^* p_1^*}{\phi_1 p} \exp\int_{p_1^*}^p \frac{V_1^*}{RT} dp\right] \quad (1)$$

In this equation ϕ_i is the fugacity coefficient of component i ($i = 1$ denotes solvent and $i = 2$ solute) in the vapor phase, V_i is the partial molar volume of component i in the solution, and the superscripts * and ∞ indicate pure substance and infinity dilution, respectively. Finally, γ_2^{H} is the solute's activity coefficient in solution using Henry scale of activities. The fugacity coefficients in the gas phase can be calculated with some of the equations of state which account satisfactorily for the behavior of aqueous gaseous mixtures; in our work we have employed the Peng and Robinson equation of state [14, 15].

Equation 1 lets us individualize the quantities that are more difficult to obtain experimentally, but which become very important contributions at high temperature. These are V_2^∞ and γ_2^{H} , and both quantities diverge at the solvent's critical point making a significant contribution to Henry's constant in that temperature range [16, 17]. It is noteworthy that, according to Eq. 1, the values of V_2^∞ have to be known for the pressure interval going from p_1^* to p , the experimental total pressure. However, there is only a very limited number of

published values of partial molar volumes of gaseous solutes in water as functions of temperature and pressure. Nonetheless, it should be mentioned that recently formulations have been proposed to estimate values of V_2^∞ and other thermodynamic infinite dilution standard properties of volatile solutes in water over wider ranges of temperature and pressure [2, 18]. On the other hand, for the activity coefficients of the gaseous solutes there are practically no experimental data. This lack of experimental information was the reason for adopting the iterative model-guided method to calculate the values of Henry's constant over the complete range of temperature of existence of liquid water.

The calculations start with the ambient temperature data where the corrections for the Poynting effect and for the excess chemical potential of the slightly soluble solutes are small or negligible (it should be remembered that the high-temperature technique for gas solubility determination has an overall precision that is not better than 1% at present). As the solution's temperature rises, it becomes increasingly important to take into account both corrections: To implement our procedure we have resorted to the use of a simple perturbation model which gives the first-order approximation of the perturbation according to the Percus-Yevik (PY) equations as the starting point of the calculation. The expressions used to calculate the corrections are more clearly applicable to the temperatures where the structural features of water solvent are not the determining factor for the values of V_2^∞ and γ_2^H , i.e., outside of the ambient temperature range.

A very general and thermodynamically correct way of defining Henry's constant is through the following limiting expression,

$$k_H = \lim_{x_2 \rightarrow 0} (f_2/x_2) \quad (2)$$

where f_2 is the fugacity of the gaseous solute. This limiting expression also allows us to relate k_H to the distribution equilibrium constant K_D defined by,

$$K_D = \lim_{x_2 \rightarrow 0} (y_2/x_2) \quad (3)$$

where y_2 and x_2 are the mole fractions of solute in the coexisting vapor and liquid phases, respectively. It is easily shown that,

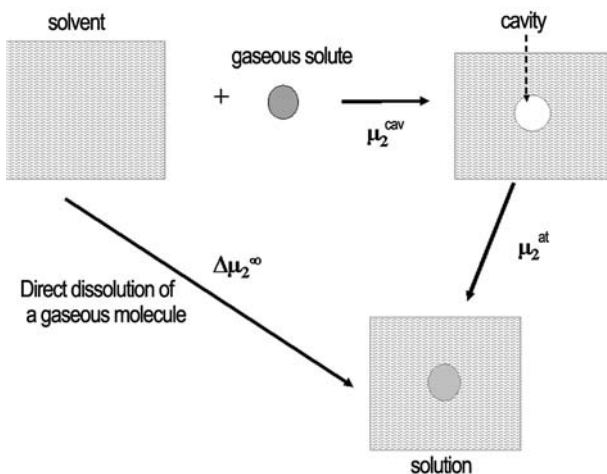
$$k_H = \phi_2^\infty p_1^* K_D \quad (4)$$

As already mentioned there are some quantities in Eq. 1 that seldom are reported in experimental studies, namely V_2^∞ and γ_2^H . This is why it is impossible to calculate $\Delta_{\text{dis}} G_2^\infty$ directly from the solubility data at all temperatures.

4 Perturbation Theory

The approach followed by us makes use of the perturbation method applied to a reference solvent formed by a hard-sphere liquid having the actual solvent density at all temperatures. The adequacy of such a simple reference fluid is based upon the evidence that small non-polar solutes have a negligible effect on the water structure, as discussed below. The first very successful perturbation method to describe the solubility of small gaseous solutes in liquids was the scaled particle theory (SPT) developed by Lebowitz and coworkers [19, 20] who described by means of statistical mechanics the work necessary to introduce a hard-sphere into a liquid. Shortly afterwards, Pierotti used the SPT to describe the solubility of

Fig. 2 The perturbation scheme of dissolution of a gas particle



small gases in nonpolar liquids [10], a work which he extended afterwards to the solvent water [11]. We have employed another version of the same perturbation method which uses the PY approximation to express the reference term to account for the work necessary to introduce a hard-sphere into the solvent. This procedure has been shown to be better than SPT [21, 22].

The basis of the application of perturbation methods to dissolution processes consists in dividing them in two successive steps, as depicted in Fig. 2. First a cavity large enough to hold the solute is created in the hard-sphere liquid solvent that gives a repulsive contribution (μ_2^{cav}) to the solute's chemical potential μ_2 . The second step consists in switching on the interactions between solvent and solute. This step leads to an attractive contribution (μ_2^{at}) which we considered to be given by the Lennard-Jones intermolecular potential between solute and solvent molecules. Thus, $\Delta_{\text{dis}}G_2^\infty$ is given by,

$$\frac{\Delta_{\text{dis}}G_2^\infty}{RT} \equiv \frac{\Delta\mu_2^\infty}{RT} = \frac{\mu_2^{\text{cav}} + \mu_2^{\text{at}}}{RT} + \ln\left(\frac{\rho_1 RT}{p^\theta}\right) \quad (5)$$

where the last term is an ideal contribution due to a change in standard state, from the standard pressure p^θ to the solvent's molar density ρ_1 , and the first two terms for the PY approximation, are given by:

$$\frac{\mu_2^{\text{cav}}}{RT} = -\ln(1 - \eta) + 3\eta \frac{R_d + R_d^2}{1 - \eta} + \frac{9}{2} \left[\frac{\eta R_d}{1 - \eta} \right]^2 + \frac{\beta \eta p^{\text{HS}} R_d^3}{n_1} \quad (6)$$

with $\beta = (1/kT)$ where k is Boltzmann's constant. The attractive contribution is given by,

$$\mu_2^{\text{at}} = 4\pi\rho_1 \int_0^\infty r^2 u_{12}(r) g_{12}(r) dr \quad (7)$$

where $g_{12}(r)$ is the radial distribution function of the H_2O molecules surrounding a solute particle and $u_{12}(r)$ is the solute-solvent interaction energy.

The pressure of a hard-sphere fluid having the experimental water density at each temperature, $p^{\text{HS}}(T)$, is given by,

$$\beta p^{\text{HS}} = n_1 \frac{1 + \eta + \eta^2}{(1 - \eta)^3} \quad (8)$$

The only variables appearing in the equations used to calculate $\Delta_{\text{dis}}G_2^\infty$ are the solvent's packing fraction and the ratio of the solute to solvent hard-sphere diameters R_d . This is a very convenient feature for a general procedure. For the attractive term it is also necessary to have a value for the Lennard-Jones cross-interaction energy ε_{12} . These points will be discussed below.

5 High-Temperature Corrections

Following the same strategy we calculated the corrections due to the effect of pressure upon the solute's chemical potential and the excess chemical potential due to solute-solute interactions that is neglected in the Henrian range. For this purpose we used the hard-sphere model to calculate the first-order corrections which are necessary according to Eq. 1.

V_2^∞ is related to the solvent's isothermal compressibility, κ_T , and the Fourier transform of the direct correlation function for a hard-sphere having the solute's diameter, $\hat{c}_{12}^{\text{HS}}(0)$, by,

$$V_2^\infty = RT\kappa_T \left[1 - n_1 \hat{c}_{12}^{\text{HS}}(0) \right] \quad (9)$$

We used the experimental κ_T for water for each (p, T) value. The expression for $\hat{c}_{12}^{\text{HS}}(0)$ given by Boublik et al. [23] was substituted in Eq. 9 to obtain the final equation of V_2^∞ as function of η and R_d ,

$$V_2^\infty = RT\kappa_T \left\{ 1 + \frac{\eta}{1-\eta} \left[1 + 3 \frac{R_d + R_d^2}{1-\eta} + 9 \frac{\eta R^2}{(1-\eta)^2} + \frac{(1+2\eta)^2}{(1-\eta)^3} R_d^3 \right] \right\} \quad (10)$$

It should be mentioned that when the solubility data correspond to temperatures close to the critical temperature of water, it is impossible to assume that V_2^∞ is pressure independent. Figure 3 shows that for N_2 dissolved in water at 620 K there is a large difference between the Poynting correction when V_2^∞ is taken as a constant independent of temperature and when its change with pressure is accounted for. In the first case the correction was greatly overestimated.

The excess chemical potential of the solute can often be neglected below approximately 520 K, but this quantity can be shown [17] to diverge at the solvent's critical point where the solvent compressibility is high. Furthermore, the solubility of the gaseous solutes increases substantially at higher temperature and at the higher solute's partial pressures; this condition must be used for its measurement in order to keep a good precision. We have dealt with this problem [9, 24] considering that the solutions are still sufficiently dilute so that it is possible to use a linear relation between solubility and $\ln \gamma_2^{\text{H}}$,

$$\ln \gamma_2^{\text{H}} = b_2(T, p)x_2 \quad (11)$$

The coefficient b_2 was shown by Kirkwood and Buff [25] to be related to B_2^* , the osmotic second virial coefficient, by,

$$b_2 = \left(\frac{2}{V_1^*} \right) \left[B_2^* + \frac{V_1^*}{2} - V_2^\infty + \frac{RT\kappa_T^*}{2} \right] \quad (12)$$

The osmotic second virial coefficient is also related to the integral of the total correlation function of two solute particles, $h_{22}(r)$. This correction was made as if the molecules of the solutes were hard-spheres. This is consistent with the procedure we employed. Following

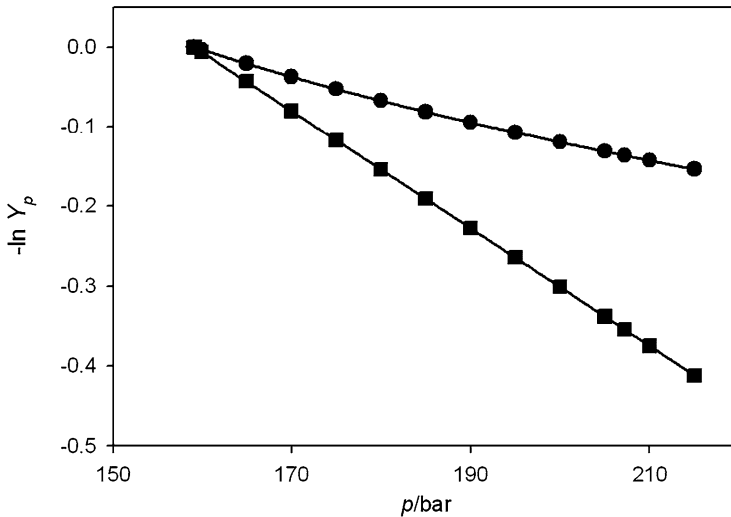


Fig. 3 Poynting effect in the N_2 – H_2O system at 620 K, expressed as $\ln Y_p$ [see Eq. 14]. Pressure dependent V_2^∞ (●); pressure-independent V_2^∞ (■)

Pratt and Chandler [26] we have used the Ornstein-Zernike equation to relate B_2^* to the short-ranged direct correlation function according to,

$$B_2^* = -\frac{N_A}{2} \left[\hat{c}_{22}^{\text{HS}}(0) + (n_1 \hat{c}_{12}^{\text{HS}}(0))^2 kT \kappa_T^* \right] \quad (13)$$

where N_A denotes Avogadro's number and the expressions for $\hat{c}_{ij}^{\text{HS}}(0)$ are given in reference [23]. In this calculation the density and isothermal compressibility of the reference fluid are taken from the values for actual water at each temperature, and $d_1 = 2.70 \text{ \AA}$ at all temperatures.

Table 1 reports the values of the typical contributions of the two corrections for the system CH_4 in water as temperature increases. The calculation corresponds to a solute having a partial pressure of 2.0 MPa.

$$\ln \left(\frac{k_H}{p_1^*} \right) = \ln Y - \ln Y_p - \ln Y_\gamma \quad (14)$$

The quantity Y is obtained with Eq. 1 ignoring the Poynting (Y_p) and the activity coefficient (Y_γ) corrections. Table 1 shows that below 473 K the magnitude of the Poynting correction is around 2% of k_H , whereas the excess chemical potential of the solute is still negligible. At higher temperatures the corrections become increasingly more important; they are greater than 20% of Henry's constant at 15 K from T_{c1} . It should be noted that the two corrections have opposite signs, so they cancel each other partially. The size of the individual corrections and the fact they are partially cancelled emphasize the importance of validating the results obtained with our iterative calculation procedure; this validation is described in Sect. 7.

Table 1 Effect of the corrections to $\ln(k_{\text{H}}/p^\theta)$ at different temperatures for CH_4 dissolved in water. The partial pressure of methane was 2.0 MPa

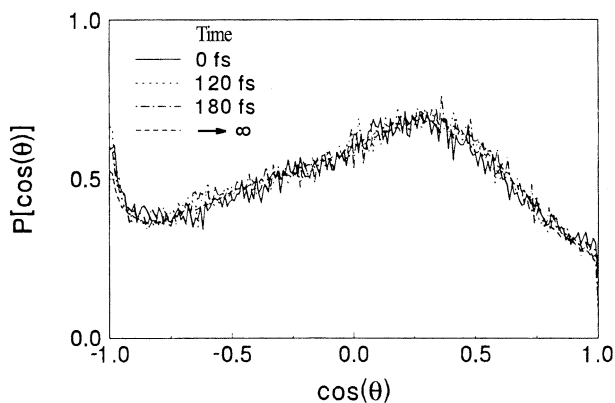
T/K	$\ln Y_{\text{p}}$	$\ln Y_{\gamma}$	$\ln(k_{\text{H}}/p^\theta)$
303.14	0.026	0	13.822
323.15	0.024	0	12.989
373.12	0.022	0	11.060
423.11	0.023	0	9.328
473.16	0.025	−0.007	7.758
523.11	0.031	−0.018	6.317
537.51	0.034	−0.021	5.917
554.11	0.038	−0.027	5.460
603.11	0.076	−0.086	4.081
623.11	0.135	−0.160	3.439
633.11	0.218	−0.245	3.051

6 Overview of the Calculation Procedure and Comparison with other Perturbation Methods

An apparent drawback of using a hard-sphere reference system to describe the behavior of aqueous solutions is the fact that the solvent, at least under ambient conditions, has a molecular structure that is very different from that present in a hard-sphere liquid, e.g., water has a packing fraction of 30%, appreciably smaller than that for the average nonpolar solvent. The fact that small nonpolar solutes have a negligible effect upon the water structure is supported by Fig. 4 which was taken from reference [12] where the Xe– H_2O system at room temperature was studied by molecular dynamics. The simulations were run until a spontaneously formed cavity in H_2O large enough to hold a Xe atom was detected, then the run was stopped and the Xe atom was introduced into the cavity and the simulation trajectory was continued fixing the centers of mass of the H_2O molecules vicinal to the Xe atom, but allowing them to reorient freely. It was observed that their orientations did not change when the vicinal H_2O molecules were allowed to relax, as illustrated in Fig. 4 where $P(\cos \theta)$, the normalized distribution of the $\cos \theta$ for vicinal water molecules, is plotted against $\cos \theta$, with θ being the angle formed by the dipole of the vicinal H_2O 's with the distance of their centers of mass. The curves indicated that the presence of the Xe atom did not influence the structure of the solvent surrounding the original cavity formed by density fluctuations since at all times after Xe was introduced into the cavity the distribution was the same. Moreover this is supported by a perturbation method proposed by Pratt and Chandler (PC) [26] that uses the real water structure to calculate the work of cavity formation. Thus, the probability of cavity formation may be calculated using the radial distribution function of H_2O determined experimentally by X-ray or neutron scattering. We have shown the similarity of the results obtained by the PY approximation and by the PC method [21, 22] and have adopted the first one because the range of temperatures over which experimental radial distribution functions are available is limited.

In order to compare the method used by us with the more classical SPT method it is necessary to identify the differences between them. In Eq. 6, which describes the cavity formation, the pressure in the last term p^{HS} is replaced in SPT by the experimental pressure. However, for the case of water this difference is particularly important because it makes an

Fig. 4 Molecular dynamics study of Xe–H₂O system at room temperature (reproduced by permission of Elsevier from Ref. [12]). The average orientation of the vicinal molecules is plotted at different times after a Xe was introduced into the spontaneously formed cavity; the curve labeled $\rightarrow \infty$ corresponds to the completely relaxed system



appreciable contribution to μ_2^{cav} due to the factor $(R_d)^3$ appearing in the pressure term of Eq. 8, which is large because of the small size of the H₂O molecule.

Other differences occur in the calculation of the solute-solvent attractive term for which we employ Eq. 7 and the Lennard-Jones potential for the interaction energy. SPT assumes $g_{12}(r) = 1$ and adds to the solute-solvent intermolecular potential a term for the dipole induced (polarizability) in the solute particle by the H₂O dipole, which is identical to that used for the vapor phase. Thus, the very small value given to the Lennard-Jones solute-solvent interaction energy ε_{12} in SPT is compensated by including an extra term that originates in the dipole induced on the solute by the polar aqueous environment. The effect of the solvent's electric field, which is a multi-body field, on the polarizability of the solute is however very small. A molecular dynamics simulation study [12] showed that the effect of induced dipoles in Xe is much smaller in dense water than predicted for a single Xe–H₂O interaction (vapor phase). The results illustrated in Fig. 4 also suggest that in a dense polar liquid phase the induced dipole has a negligible contribution compared with the value used in SPT. In the latter theory the induced dipole contribution is calculated on the basis of the energy of the induced dipole when only one H₂O molecule is close to a solute particle, which is the case in the gas-phase, but this will overestimate the attraction in the liquid phase.

We have shown that both differences in μ_2^{at} will affect the final value of $\Delta_{\text{dis}}G_2^\infty$, albeit they compensate each other partially at room temperature because a very low value of ε_{12} is used in SPT. For the solvent-solute Lennard-Jones interaction energy ε_{12} we have used the value calculated with the geometric mean combining rule and the interaction energy for the pure solute ε_{22} [22]. For the solvent we fixed $(\varepsilon_{11}/k) = 217$ K, which is very close to the value of 220 K obtained for this quantity from the second virial coefficients of mixtures of H₂O vapor and nonpolar gases [28]. It should be remembered that hydrogen bonding and dipolar interactions will not manifest themselves in the interaction of a water molecule with a nonpolar solute. The calculation with Eq. 7 was done using the Laplace transform of $rg(r_{ij})$ [29].

Now we shall describe the steps of the iterative procedure that we have followed to calculate $\Delta_{\text{dis}}G_2^\infty$ at all temperatures and at the saturation pressure of water. Calculations are started with solubility values at ambient temperature that are very precise and, more relevant for the iterative calculation procedure, the corrections to the simple Henry's law are either small or negligible. The solubilities were compared with those calculated with the value of k_H predicted by Eqs. 6–8; it should be remarked that the only adjustable parameter is the hard-sphere equivalent diameter of the solute d_2 . The Lennard-Jones parameters ε_{22} and d_2 [22] were used to calculate the solubility at 298 K, employing then the Lorentz-Berthelot

combining rules to get the molecular parameters for the solute-solvent interaction. Using the values of the solubilities at increasingly higher temperature, the calculation was repeated and the value of $d_2(T)$ was determined at each temperature; obviously when the corrections of pressure and excess chemical potential were required they were included in the calculation of d_2 .

Summarizing the procedure, the solubility data were used to obtain the hard-sphere diameters of the solutes at each temperature by means of the perturbation theory [Eqs. 6–8] using for the Henry's constant the values obtained with Eq. 1 neglecting the two corrections (Poynting and excess chemical potential). Then the values of d_2 were used to calculate the correction terms required by Eq. 1 and a new value was obtained for k_H , as well as a new d_2 . The process was repeated until two successive values of the calculated Henry's constant were close enough, i.e., until the difference was $\approx 0.5\%$. The iterative procedure always converges and looks robust. However, it is convenient to have an independent method of testing that the final value of Henry's constant is correct as shown in the following section.

7 Thermodynamic Validation of the Procedure

In order to test the consistency of the iterative procedure we used a rigorous thermodynamic relationship. It has been shown [30] that on the basis of Eqs. 2 and 3 the expression,

$$K_D = 1 + \frac{V_1^*(g) - V_1^*(l)}{RT} \left(\frac{\partial p}{\partial x_2} \right)_{T,\sigma}^{\infty} \quad (15)$$

is thermodynamically exact in the limit of infinite dilution. In order to use Eq. 15 the solubility of the gaseous solute at a given temperature must be known over a range of solute partial pressures that are used to extrapolate the change of pressure with composition when $p \rightarrow p_1^*$. The partial derivative of pressure with composition has to be taken along the path of coexistence of the two fluid phases, indicated by subscript σ , and then extrapolated to infinite dilution; this is a practical limitation for such a simple and exact equation. Even in the few systems for which the required information is available, the uncertainty of the calculated K_D is somewhat larger than when it is calculated from Henry's constant according to Eq. 4.

Another important requirement that must be fulfilled is the asymptotic dependence of $T \ln K_D$ close to T_{c1} . The way in which K_D approaches unity as $T \rightarrow T_{c1}$ was derived by Japas and Levelt Sengers [31]. They showed that $T \ln K_D$ becomes asymptotically proportional to the difference between the density of the coexisting liquid phase and its critical density $\rho_{1,cr}$ and goes to zero when the temperature attains the value of the solvent's critical point. The asymptotic expression is,

$$RT \ln K_D = \frac{2}{(\rho_{1,cr})^2} \left(\frac{\partial p}{\partial x_2} \right)_{T,V}^{\infty,cr} [\rho_1(l) - \rho_{1,cr}] \quad (16)$$

The possibility of knowing the limiting behavior of $T \ln K_D$ at the critical point proved to be a very important tool to identify data that do not comply with the expected asymptotic behavior. Equation 15 together with Eq. 16 have validated the results obtained with the iterative procedure and also helped to discriminate those sets of data that do not show the expected asymptotic behavior when the temperature approaches the critical temperature of the solvent, where $K_D = 1$.

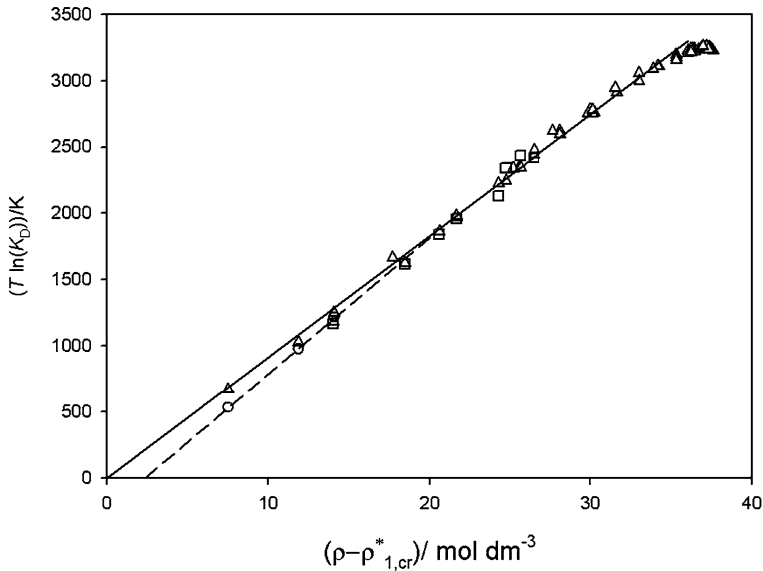


Fig. 5 The $\text{CO}_2\text{-H}_2\text{O}$ system. Δ using Eq. 1; \circ from Ref. [34], with no correction for γ_2^{H} ; \square using Eq. 15

The advantage of using the asymptotic relationship given by Eq. 16 is clear in the examples illustrated in the following two figures. Figure 5 shows $T \ln K_D$ plotted against water density for the $\text{CO}_2\text{-H}_2\text{O}$ system where the values of K_D were calculated with different equations [30]. The solubility data in the literature (the actual data sources are identified in reference [8]) were calculated with the complete Eq. 1. Figure 5 shows that these data agree with those obtained using Eq. 15 [32] and that they follow the functional behavior required by the asymptotic Eq. 16; however, we remark once more that the values of K_D obtained with the latter equation have somewhat larger uncertainties than those obtained with Eq. 1. Crovetto and Wood [33] made determinations of k_{H} for this system very close to the T_{c1} . They measured the solubilities and they could also apply the rigorous Poynting correction using their experimental volumetric results, but they assumed that $\gamma_2^{\text{H}} = 1$. Figure 5 shows that their final results were close to the asymptotic slope but were somewhat low and do not appear to extrapolate to the $\lim_{\rho \rightarrow \rho_{1,\text{cr}}} (T \ln K_D) = 0$. Using their solubility data that we recalculated with Eq. 1, which takes account of γ_2^{H} , the values for k_{H} and thence K_D were calculated; it is seen that they follow more closely the expected asymptotic behavior.

Figure 6 shows data for the system $\text{CO-H}_2\text{O}$ [34] extending to 573 K. It is quite clear from the graph that when $T \rightarrow T_{\text{c1}}$ the data do not go to the asymptotic limit for the quantity $T \ln K_D$, suggesting that there was some systematic error in the measurements, hence they could not be used to calculate the thermodynamic quantities of aqueous CO at high temperature [8, 9].

8 Extension of the Procedure to Higher Pressures

The procedure described in the present work to calculate the thermodynamics of gases dissolved in water at high temperature can be extended to pressures substantially larger than the solvent's vapor pressure. We have used as an example the data for solutions of methane

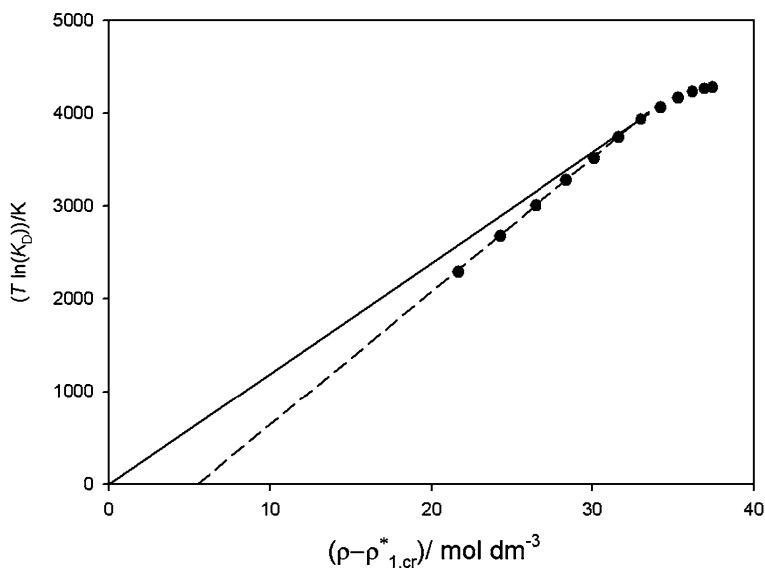


Fig. 6 The CO–H₂O system, Ref. [34]

in water reported by Sultanov et al. [35] who determined the CH₄ solubilities up to pressures of almost 100 MPa above the vapor pressure of water. This system was chosen because there are several isotherms for which the procedure could be checked; the extension is valid also for other gaseous solutes.

In order to make this comparison we have employed the values $d_2(T)$ for CH₄ which we had determined for conditions of liquid-vapor coexistence [22]. With that value we calculated the Poynting and excess chemical potential contributions to solubility according to Eq. 1. Thus, it was possible to determine the solubilities as function of pressure for the isotherms of 573, 603, 623 and 633 K.

As examples of the performance of the extended procedure, Fig. 7 shows plots of the experimental solubilities of CH₄ in water as function of pressure for two isotherms. They are compared with the solubilities calculated with our procedure; the agreement is quite good (within 10%). In the case of the two isotherms of 573 and 603 K the agreement extends up to 100 MPa total pressure. It should be mentioned that the isotherm of 573 K has some experimental problems which impeded its inclusion in our comprehensive compilation of the k_H [8]. As the temperature of the solutions increased the pressure range over which the agreement was good was observed to be progressively reduced, as expected, but even at 633 K it extends up to 50 MPa. This behavior suggests that the agreement should be better at 603 K, however, the extremely good agreement shown in Fig. 7 for this isotherm seems to be partially fortuitous, although we do not know the reason for the excellent description of the experimental solubilities at 603 K.

It should be noted that at higher pressure the calculated solubilities were bigger than the experimental ones, probably due to the fact that $\ln \gamma_2^H$ in Eq. 11 considers only the first-order approximation, thus overestimating the attractive interaction between two solute particles. If we consider that the solutions of methane are already quite concentrated ($x_2 \geq 0.1$ implies a concentration larger than 3 mol·dm⁻³) at the higher temperatures, then in order to improve the pressure range over which there is good agreement it would be necessary to add more

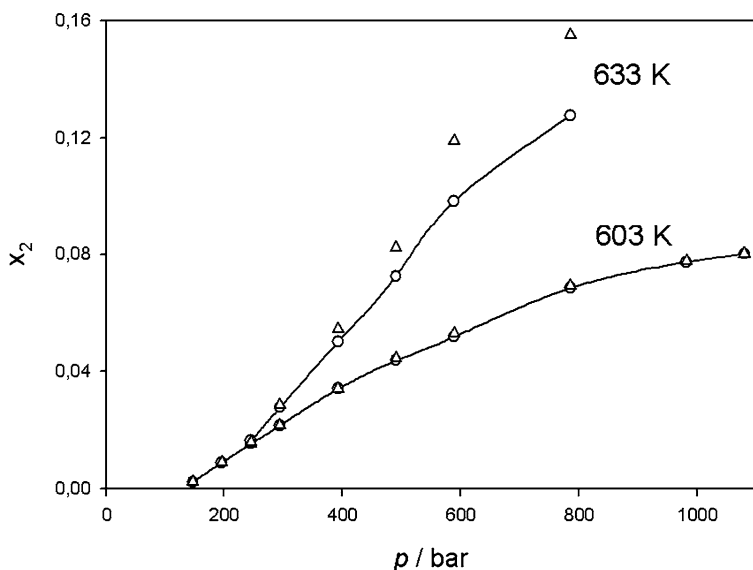


Fig. 7 The CH₄–H₂O system at 603 and 633 K. Experimental solubilities: Δ ; calculated with the perturbation procedure: \circ

terms to the approximate Eq. 11. Moreover, the observed deviations of the calculated and experimental solubilities imply that the next term in the expression for $\ln \gamma_2^H$ would have the opposite sign to the first one, thus decreasing the attraction between two solute molecules.

It is interesting to note that since the relative error in k_H is proportional to the absolute uncertainty of $\Delta_{\text{dis}}G_2^\infty$, this one will not be greater than $500 \text{ J}\cdot\text{mol}^{-1}$ up to 50 MPa of excess pressure at all temperatures. The application of the procedure to pressures far in excess of the solvent's vapor pressure makes it a very flexible method to deal with systems of interest for technological and geophysical processes which often take place at larger pressures than that of the solvent's coexistence curve.

9 Conclusions

It is possible to describe the thermodynamics of dissolution of nonpolar gases in water over the complete range of existence of the liquid solvent by means of a calculation procedure that iterates between experimental solubility data with model equations. The reason for this is that the direct determination of $\Delta_{\text{dis}}G_2^\infty$ from solubility data employing the simple Henry's law cannot be used at high temperatures without taking into account two important corrections. Moreover, because there is not enough experimental information to allow the determination of these corrections, it is necessary to employ model equations in order to calculate them.

The model adopted for the dissolution process is based upon the perturbation of the properties of a hard-sphere reference fluid which represents the solvent. This is possible because the presence of a small nonpolar particle does not affect the molecular structure of liquid water that surrounds it. The procedure that has been devised depends only on the temperature dependent ratio of the diameters of solute to solvent molecules and uses their

interaction energy; the density, compressibility and expansion coefficient of the reference fluids are considered equal to those of water at each temperature.

This procedure describes the observed behavior satisfactorily. Its results were checked against results from thermodynamic relationships that do not use any model equations. The procedure developed affords consistency between the molecular parameters used to describe the dissolution of a gas molecule in water and the properties of the gaseous mixtures of the two compounds. On the other hand, it is a very general and flexible procedure, e.g., it enables the calculation of gas solubilities at total pressures ≤ 50 MPa above the vapor pressure of the solvent, and it can also be applied for the dissolution of gaseous solutes in nonpolar solvents.

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