

Thermodynamics of Dissolution of Simple Gases in Water

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The thermodynamics of dissolution of simple non-polar gases in water has played historically a prominent role in signaling out the peculiar characteristics of solutions in aqueous medium. The pioneering work of Eley,¹ and of Frank and Evans² laid down the basis for the use by the latter authors of the large negative entropy of dissolution of noble gases in water as an indicator of the distinct type of ion-solvent interactions found in aqueous solutions. The large positive partial molar heat capacity of dissolution of the gases stands as another characteristic typical of aqueous solutions. These features of solutions in water are considered to be originated in the strong intermolecular interactions existing in the liquid due to extensive hydrogen bonding among neighboring water molecules.

Pierotti³ pointed out that the thermodynamics of dissolution of simple gases in water close to room temperature could be accounted for in terms of a hard-sphere fluid model with an added Lennard-Jones attractive term. For this purpose he used the scaled particle theory (SPT). The success of such a simple theory when applied to aqueous solutions has been considered fortuitous by Stillinger⁴ because SPT takes no account of the orientational correlation present in the solvent.

The significance of this point could in principle be assessed by testing the theory over a wide temperature range since it is known that the intermolecular orientational correlations in water are quite sensitive to a change in temperature. IR and dielectric constant studies⁵ have shown that the degree of intermolecular correlation in liquid water decreases appreciably with increasing temperature; however, even at 573 K water is a liquid with extensive intermolecular hydrogen bonding.

As a result of the research program of our laboratory related to the study of the thermodynamics of gas-liquid binary systems, we have determined Henry's constant for inert gases and for methane in light and heavy water^{6a} and for ethane,^{6b} nitrogen, and hydrogen^{6c} in H₂O, over a wide temperature range. In this work experimental results corresponding to a wide range of temperature (between room temperature and 473 K)

in which the thermodynamic quantities of dissolution obtained from the solubility data are reliable enough⁶ will be reviewed and compared with those predicted by perturbation theories applied to hard-sphere reference fluids. Arguments will be advanced to explain why perturbation theories, which do not take account of the intermolecular orientational correlation, are applicable to the solvent water. The rather controversial view advanced in the present work that introduction of small nonpolar solutes into water does not involve significant reorientation of the solvent molecules has the advantage of explaining the available experimental results and also of suggesting some further experiments which would help to support or reject this interpretation of the dissolution of simple gases in water.

Calculation of Henry's Constant by Perturbation Theories

In order to calculate the values of Henry's constants for gas-liquid binary systems, a hard-sphere reference fluid having a Lennard-Jones perturbation potential has been employed. As already mentioned, SPT is one of the simplest theories to be used; however, since it has been shown to underestimate the magnitude of the work necessary to create the solute cavity in the liquid,⁷ we have not used SPT in the present calculations.

With the assumption that a Lennard-Jones potential describes adequately the energy of non-hydrogen bonding interaction between solvent (1) and solute (2), u_{12} is given by⁸

$$u_{12} = 4\epsilon_{12}[x^{12} - x^6] \quad (1)$$

where $x = (\sigma_{12}/r)$ and the parameters ϵ_{12} and σ_{12} measure the strength and the range of the interaction. For the interactions of nonpolar molecules with water in the gas phase (low density fluid), eq 1 should include the contribution of the dipole-induced dipole interaction.⁸ On the other hand, these interactions in a high density (liquid-like) fluid can only be calculated if the instantaneous total electric field on the solute particle due to the solvent dipoles surrounding it is known. On the basis of symmetry considerations, this contribution to the total intermolecular energy is probably close to zero

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although there may be rather large fluctuation terms. This contention is supported by statistical mechanical calculations applied to fluid systems with liquid-like densities having a central point dipole. Employing the mean spherical approximation,⁹ or the hypernetted chain quadratic approximation,¹⁰ it has been found that for a nonpolar solute particle in this dipolar fluid the total electric field is zero. Consequently we have employed in eq 1 a Lennard–Jones potential without dipole-induced dipole interaction.

The change of standard chemical potential of the solute, which characterizes the dissolution process (from ideal gas to infinitely dilute solution taken to a mole fraction of unity), may be expressed by

$$\Delta\mu^\circ_2 = \Delta\mu^{\text{id}}_2 + \Delta\mu^{\text{cav}}_2 + \Delta\mu^{\text{at}}_2 \quad (2)$$

The three terms represent the contributions to $\Delta\mu^\circ_2$ due respectively to changes in the density of an ideal gas when going from its standard state (0.1 MPa) to the density of the reference fluid, to the formation of a cavity in the reference fluid (solvent) large enough to accommodate the solute particle, and to the attractive Lennard–Jones solute–solvent intermolecular interaction.

We have employed two methods to calculate $\Delta\mu^\circ_2$. The first one is based on the Percus–Yevick (PY) hard-sphere equation of state which takes no explicit account of the intermolecular correlations existing in the real solvent. The other is the semiempirical perturbation method of Pratt and Chandler¹¹ (PC) which uses the experimental distribution function of the solvent to calculate the various terms in (eq 2). This second method is particularly attractive for the solvent water because the correlation among water molecules due to hydrogen bonding interactions is explicitly taken into account. The theory employs spherical correlation functions which are related to the thermodynamic properties of the system via the compressibility equation.¹² For PC the distribution function of the reference fluid is that corresponding to a hard-sphere particle introduced in *real* water.

According to the PY treatment, $\beta\Delta\mu^{\text{cav}}_2$ is given by

$$\beta\Delta\mu^{\text{cav}}_2 = -\ln(1-y) + \{3y(R+R^2)/(1-y) + (9/2)[yR/(1-y)]^2\} + \beta y P^{\text{HS}} R^3 / \rho_1 \quad (3)$$

where ρ_1 is the number density of the solvent, P^{HS} is the pressure of the hard-sphere reference fluid, y is the packing fraction of the solvent, and $R = d_2/d_1$ is the ratio of equivalent hard-sphere diameters.

For the PC treatment the cavity term is given by

$$\beta\Delta\mu^{\text{cav}}_2 = -\ln(1-y) + 2\pi\rho_1 \int_0^{d_2} G_{12}^\circ(z) z^2 dx \quad (4)$$

Where the second term gives the total work of creation of a cavity of size x which grows up to the diameter d_2 of the solute, $z = (d_1 + x)/2$ and $G_{12}^\circ(z)$ is the contact value of the radial distribution function of the solvent, $g_{12}^\circ(r)$, around the solute considered as hard sphere. It is $g_{12}^\circ(r)$ and consequently $G_{12}^\circ(z)$ which are calculated from the experimental radial distribution function of pure water measured by X-rays or neutron diffraction.¹¹

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Table I.
Molecular Parameters of the Gaseous Solutes Employed in the PY Treatment

gas	d_2 , Å	ϵ_2/k , K
Ne	2.900	36.3
Ar	3.412	121.8
Kr	3.709	174.7
Xe	4.054	229.9
CH ₄	3.681	151.7
C ₂ H ₆	4.377	236
H ₂	2.750	29.2
N ₂	3.400	95.0 ₅

For a fluid with the density of water eq 3 and 4 give values of $\Delta\mu^{\text{cav}}_2$ which are quite close especially at low temperatures.⁷

The contribution of the attractive solute–solvent interactions is given for both treatments by

$$\beta\Delta\mu^{\text{at}}_2 = 4\pi\rho_1\beta \int_0^\infty r^2 u'_{12}(r) g_{12}^\circ(r) dr \quad (5)$$

where $u'_{12}(r)$ is the perturbation Lennard–Jones potential. For PY $\Delta\mu^{\text{at}}_2$ was calculated from the Laplace transform of $rg_{12}^\circ(r)$ for mixtures of hard spheres derived by Lebowitz.¹³ For PC, $g_{12}^\circ(r)$ is obtained from a calculation involving the radial distribution function of the pure solvent and sphericalized Ornstein–Zernike expressions.¹¹

The use of perturbation theories based on hard-sphere reference fluids requires values for the d_i 's. These are determined essentially by the steepness of the repulsive branch of the intermolecular potentials; they may be calculated by either the Barker and Henderson¹⁴ or the Weeks, Chandler, and Andersen¹⁵ methods, for aqueous solutions the calculation is hampered by the need to decide upon the best water–water intermolecular potential.

The value of ϵ_{12} in eq 1 can be expressed for nonpolar gas–water interactions by the geometric mean combination rule, i.e., $\epsilon_{12} = (\epsilon_1\epsilon_2)^{1/2}$, only if ϵ_1 denotes the water–water intermolecular energy *when all hydrogen bonding contributions are eliminated*. This parameter is not readily available, but we have estimated its value from gas-phase studies.⁸ On account of the difficulties to obtain rigorously the molecular parameters when dealing with solvents having strong intermolecular interactions, we have employed a more pragmatic semiempirical approach.

Method of Calculation and Results

The values employed for the molecular parameters of the solute gases for the PY treatment are given in Table I, the values for PC being only slightly different; the diameter of water was taken to be 2.70 Å at all temperatures. With these parameters and with use of the experimental values of the solubilities of Ar, Kr, Xe, and CH₄ in H₂O at 298 K, the best value for ϵ_1/k was determined. This quantity resulted 217 K for the PY treatment and 135 K for the PC treatment. Employing these values for ϵ_1 , the values of d_2 for each gas at each temperature were adjusted so that the PY and PC treatments fitted the corresponding experimental $\ln(k^0_{\text{H}})$.

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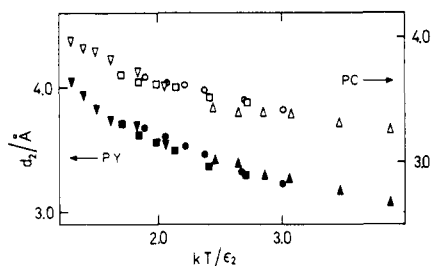


Figure 1. Change of d_2 with temperature: open symbols, PC treatment; closed symbols, PY treatment; ∇ , Xe; \square , Kr; \circ , CH_4 ; Δ , Ar.

Figure 1 illustrates the changes of d_2 with temperature which were determined with each procedure. The values calculated are quite reasonable when compared with those predicted by theory.¹¹

These results indicate that perturbation theories based on a hard-sphere reference fluid can be successfully applied to describe the dissolution of nonpolar gases in a solvent like water. The experimental data were fitted by using d_2 as an adjustable parameter due to the difficulties in knowing the intermolecular potential of the pure solvent; this is an apparent limitation of these theoretical treatments. However, on the basis of these calculations it is possible to predict several features which are usually considered typical of aqueous solutions and attributed to the peculiar structure of this solvent.

Using the available cross-second virial coefficient data for gaseous binary mixtures of water with Ar, CH_4 , N_2 , and C_2H_6 , Alvarez, Crovetto, and Fernandez-Prini⁸ have calculated a value of 220 ± 10 K for ϵ_1/k . The closeness of the value obtained from cross virial coefficients with those calculated with the PY treatment is remarkable and probably partially fortuitous. Nevertheless it supports the contention that in the liquid the induced dipole-dipole interaction is negligible. On the other hand, the value obtained from gas-phase studies is larger than that calculated with PC. For this reason and the fact that the PC treatment involves a more complicated calculation and requires experimental X-ray data at all the temperatures, we employ only the PY method in what follows.

Hydrophobic Effect

From experimental measurements of the solubilities of CH_4 and C_2H_6 in water, it is possible to calculate the thermodynamic quantities of dissolution of these two gases in water up to 473 K.^{6b} We have also calculated the quantity

$$\beta\Delta\mu^\circ_{\text{Hyd}} = \beta\Delta\mu^\circ_2(\text{C}_2\text{H}_6) - 2\beta\Delta\mu^\circ_2(\text{CH}_4) + \ln(\rho_1/\beta) \quad (6)$$

which, as suggested by Ben-Naim,¹⁶ may be taken as an indicator of the presence of hydrophobic effects. [Strictly the definition of Ben-Naim involves another term in eq 6 which contains the cross second virial coefficients of the gases and water. This term has been neglected because it is too small even at 473 K.] Table II records values of $\Delta\mu^\circ_{\text{Hyd}}$ and related thermodynamic quantities at various temperatures. The last row in Table II gives the typical values of $\Delta X^\circ_{\text{Hyd}}$ found in

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Table II.
Experimental Values of $\Delta X^\circ_{\text{Hyd}}$ As Defined by Eq 6

T, K	$-\Delta\mu^\circ_{\text{Hyd}}, \text{kJ}\cdot\text{mol}^{-1}$	$\Delta S^\circ_{\text{Hyd}}, \text{J}\cdot(\text{mol}\cdot\text{K})^{-1}$	$-\Delta C_p^\circ_{\text{Hyd}}, \text{J}\cdot(\text{mol}\cdot\text{K})^{-1}$
298.2	9.08	45.6	205
323.2	10.00	31.8	142
373.2	11.18	17.3	67
423.2	11.87	11.6	28
473.2	12.40	9.7	8
a	(5-7)	(-14 to +4)	

^aThese row quotes typical range for $\Delta X^\circ_{\text{Hyd}}$ for nonaqueous solvents.

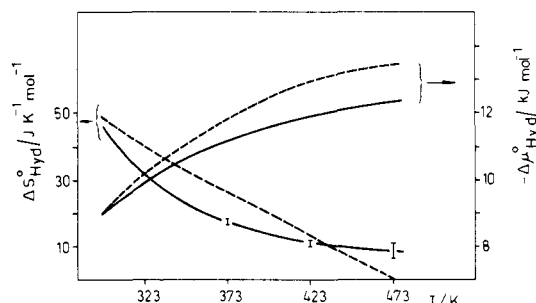


Figure 2. $\Delta\mu^\circ_{\text{Hyd}}$ and $\Delta S^\circ_{\text{Hyd}}$ against temperature: full curves, experimental (the vertical bars represent the magnitude of the uncertainty); dashed curves, calculated with PY treatment using temperature-independent d_2 's.

nonaqueous solvents. The results obtained show that in water $\Delta\mu^\circ_{\text{Hyd}}$ is more negative as the temperature increases. This feature, as already noted,¹¹ casts doubts on a straightforward interpretation of this quantity because the intermolecular structure of water is weaker at higher temperature and, consequently, any effect related to it should decrease with temperature. On the other hand, $\Delta S^\circ_{\text{Hyd}}$ and $\Delta C_p^\circ_{\text{Hyd}}$ become smaller with increasing temperature and probably closer to the values in other solvents.

It is interesting now to evaluate how the PY perturbation theory explains the experimental results shown in Table II. $\Delta\mu^\circ_{\text{Hyd}}$ and $\Delta S^\circ_{\text{Hyd}}$ have been calculated by using temperature-independent d_2 's having the values required by PY theory to reproduce the experimental $\ln(k^0_{\text{H}})$ at 298 K for each gas. Figure 2 compares a plot of the thermodynamic properties calculated with a constant d_2 to the experimental quantities. The observed trends in the experimental $\Delta X^\circ_{\text{Hyd}}$ are correctly described by the PY theory; this is especially clear for the case of the entropy because it has been calculated by differentiation of the PY chemical potential with respect to temperature without further adjustment of d_2 .

Gas Transfer from Light to Heavy Water

A critical point for any theory which claims to describe the thermodynamics of simple solutes in water is its ability to predict the magnitude of the thermodynamic quantities corresponding to the transfer of the solute between light and heavy water. According to the perturbation theories used to calculate thermodynamic quantities of dissolution of gases in liquids, the molecular properties of the solvent are expressed by the parameters d_1 and ϵ_1 which should be the same for D_2O and for H_2O .

The difference between H_2O and D_2O as solvents for a nonpolar gas are expected to be greater at lower temperatures. For this reason we have employed our

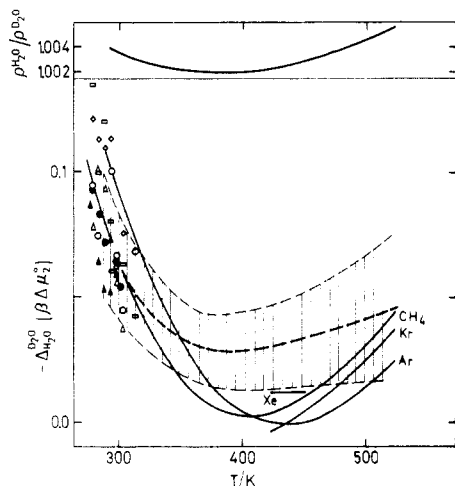


Figure 3. Chemical potential for transfer of gaseous solutes from H_2O to D_2O as a function of temperature: full curves, experimental; heavy dashed curve, calculated with PY treatment for Ar; the hatched region gives the magnitude of experimental error; \square Kr,¹⁸ \diamond Ar,¹⁸ \circ CH₄,¹⁸ ∇ C₂H₆,¹⁸ \bullet CH₄,¹⁶ \blacktriangledown C₂H₆.¹⁶

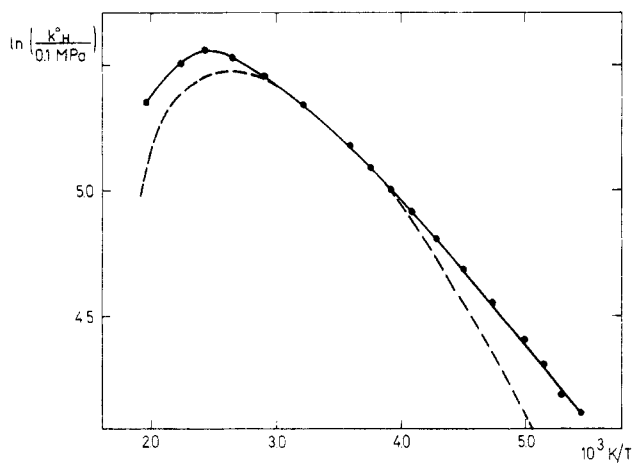


Figure 4. $\ln(k^0_{\text{H}})$ against $(1/T)$ for CH_4 dissolved in $n\text{-C}_7\text{H}_{16}$: full curve and points, experimental data;¹⁹ dashed curve, calculated with PY treatment using temperature-independent d_2 .

data combined with those reported by Battino et al.¹⁷ for Ar and CH_4 from 278 to 520 K in order to calculate the change of chemical potential of these gases upon transfer to heavy water. These data are given as full curves in Figure 3 together with those for Xe and Kr obtained for the high temperature range in our laboratory.^{6a} Figure 4 also contains the data for Ar, Kr, and CH_4 reported by Cosgrove and Walkley¹⁶ for low temperatures as well as data for C_2H_6 .^{16,18} The experimental values are compared in Figure 3 with those calculated with the PY perturbation theory for Ar (dashed curve) using the same values of the molecular parameters for both solvents and the value of $d_2(T)$ found for Ar in H_2O . As the solute size increases, the calculated curves are displaced upwards up to 0.05 unit for a change in size equivalent to that between Ar and C_2H_6 .

The calculated change in $\Delta\mu^{\circ}_2$ for Ar when it is transferred from D_2O to H_2O passes through a shallow minimum; its value increases again at higher temperatures. This unexpected behavior is due to the relative

change of densities in the two liquids which is represented in the upper part of Figure 3. The agreement between predicted and experimental $\Delta(\beta\Delta\mu^{\circ}_2)$ for transfer is quite good. Unfortunately this conclusion cannot be tested more accurately because the experimental error in our high-temperature setup (hatched region in Figure 3) is close to the expected value of $\Delta(\beta\Delta\mu^{\circ}_2)(\text{D}_2\text{O} \rightarrow \text{H}_2\text{O})$ at high temperature. The general trend of the experiment is predicted well although more accurate determinations at higher temperatures would be of considerable interest.

The successful account of the thermodynamics of transfer of nonpolar spherical gases from light to heavy water by the PY treatment is remarkable. According to the theory this is due to the differences in the number density and their temperature dependences in both liquids.

The arguments which explain the small solubility of nonpolar gases in H_2O by the extensive hydrogen bonded structure prevailing in this liquid would naturally lead to expect an even smaller solubility in D_2O , since this is generally considered as being more structured than H_2O . This expectation is contrary to observation, because the nonpolar gases are more soluble at low temperature in D_2O . This apparent paradox and the relative increase of solubilities in D_2O compared to H_2O for temperatures higher than 400 K are correctly explained by PY perturbation theory.

Dissolution of Gases in Nonaqueous Media

It seems important to test the applicability of the PY theory in describing the behavior of solutions of gases in nonpolar solvents where no "structural effects" should be expected. Thus we have examined the solubility of methane in n -heptane, which is known over a very wide temperature range (between 183 and 511 K).

The $\ln(k^0_{\text{H}})$ data reported by Gunn, Yamada, and Whitman¹⁹ have been compared to those calculated with the PY perturbation theory over the entire experimental temperature range. We have employed the value of $\ln(k^0_{\text{H}})$ at 310.94 K to determine $(\epsilon_1/k) = 525$ K with the PY treatment using $d_1 = 6.25$ Å, $d_2 = 3.70$ Å, and $(\epsilon_2/k) = 157$ K. We have performed the calculations assuming that d_2 was temperature independent. The effect of such an assumption is illustrated in the curves given in Figure 4. The calculated values of Henry's constants agree quite well with the experimental data between 230 and 400 K, and the maximum of the curve is correctly reproduced. Above and below that temperature range, however, the calculated solubility is larger than that observed. We have not tried to fit the results more closely by adjusting ϵ_1 and d_2 because the most important conclusion of this comparison is attained with this simple calculation: the PY perturbation theory is very successful in explaining the solubility of CH_4 in n -heptane over all the experimental temperature range. The values of $\ln(k^0_{\text{H}})$ obtained with PY result from a rather delicate cancellation of the contribution of the cavity and the attractive terms in eq 2 which are very close in magnitude.

Figure 5 shows the difference in experimental ΔS°_2 and $\Delta C_p^{\circ}_2$ for methane dissolution in H_2O and in n -heptane as function of the reduced temperature. The

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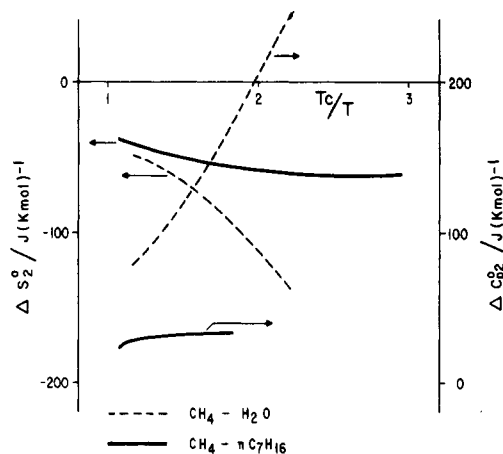


Figure 5. ΔS^\ddagger and ΔC_p^\ddagger for CH_4 dissolved in water and in *n*-heptane as function of the reciprocal reduced temperature (T_c/T).

figure shows clearly the different behavior encountered in both solvents which is usually attributed to the structural effects present in the aqueous media. As the temperature increases ΔS^\ddagger and ΔC_p^\ddagger for water and *n*-heptane solvents approach each other. However, even at 500 K the difference between water and heptane stands out clearly. These differences are correctly predicted by the PY perturbation treatment.

The origin of the bell-shaped curve of $\ln(k_H^\ddagger)$ against $1/T$ for CH_4 in *n*- C_7H_{16} is quite different from that for the aqueous system. For water the change of sign in ΔH^\ddagger is due to the rapidly increasing contribution of the cavity formation term which is zero at the temperature where the expansivity of water is zero. For *n*-heptane the change in sign of the enthalpy of dissolution is due to an appreciable decrease in the attractive contribution with increasing temperature which originates in the reduction of the number density of solvent molecules with temperature. It is usually considered that the dissolution of solutes in water is governed by the large negative values of ΔS^\ddagger which characterizes the dissolution process. According to PY theory the magnitude of ΔS^\ddagger in water results from the balance between the large work necessary to create a cavity in liquid water (manifested in a large $\Delta\mu^\ddagger$ due to the large size ratio R in eq 3) and the very small enthalpy of cavity formation in the vicinity of room temperature as a consequence of the small expansivity of the solvent. Thus ΔS^\ddagger is large and negative due to a large $\Delta\mu^\ddagger$ and a small $\Delta H^{\text{cav},\ddagger}$, rather than due to a structural rearrangement of the solvent itself. This may be interpreted as implying that the introduction of small nonpolar spherical solutes in water does not entail a substantial reorientation of the surrounding water molecules.

Concluding Remarks

We have performed additional calculations in order to understand more clearly how is it that a perturbation theory based on a hard-sphere reference fluid can account for the results of nonpolar gas dissolution in water. In particular we have calculated²⁰ the radial distribution function of a hard-sphere fluid having both the diameter (2.70 Å) and number density of liquid

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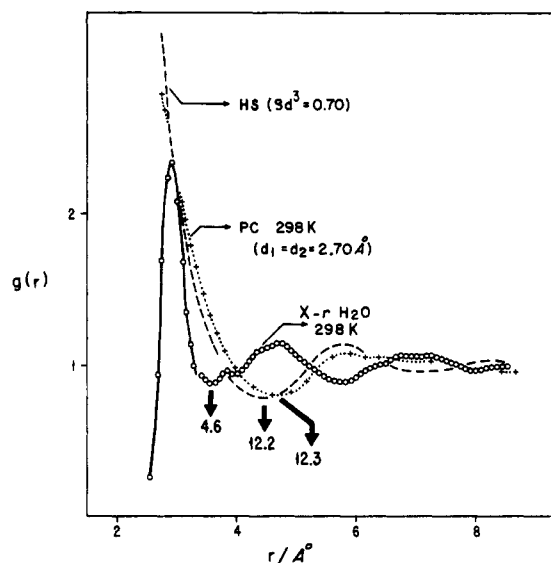


Figure 6. Radial distribution functions: O, experimental for water,²² ---, hard-sphere fluid with $d = 2.70 \text{ \AA}$ and $\rho d^3 = 0.70$; ...+, solute-water radial distribution function according to PC treatment¹¹ at 298 K ($d_1 = d_2 = 2.70 \text{ \AA}$). The number of first neighbors calculated for each distribution function are shown under each curve.

water close to room temperature using the self-consistent method.²¹ In Figure 6 we compare the radial distribution functions of pure water (298 K)²² with that of its hard-sphere analogue. There we also exhibit results based on the PC¹¹ method which gives the radial distribution function of water molecules surrounding a hard-sphere solute having its same diameter. It must be borne in mind that the PC method starts from the experimental value of the radial distribution function of the solvent. As a consequence it would be expected to reflect the structural properties of water. The great similarity of the curves obtained for a hard-sphere fluid and for a hard-sphere solute immersed in actual water is remarkable. The similarity probably holds the answer to the question posed at the beginning of this section. Furthermore, the number of first neighbors calculated with both curves are very similar and, obviously, very different from that corresponding to a central water molecule. That is, a hard-sphere solute immersed in water has practically the same number of first neighbor H_2O molecules as a particle of a pure hard-sphere liquid having the same number density and size as water. Moreover the calculated number of first neighbors compares very well with those determined by Monte Carlo²³ and molecular dynamic²⁴ simulation studies of water with nonpolar solutes (usually noble gases or methane).

With use of the Pratt and Chandler method, we have also determined the number of first neighbors in water as a function of solute size. The results show that for a solute having zero diameter the number of first

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neighbors H₂O molecules is 7.2; this quantity increases with d_2 leading to the numbers reported in Figure 6 and in simulation studies for simple gaseous solutes.

The dissolution of nonpolar gases in water is successfully reproduced by the hard-sphere perturbation treatments for the simple reason that dissolution entails the creation of a cavity which starts growing from a natural void in the liquid. Viewed from the positions occupied by the nonpolar solutes, water does not differ too much from a hard-sphere fluid having the same molecular size and number density. Furthermore, the temperature dependence of the dissolution properties is correctly given if the experimental change of density with temperature for the pure solvent is employed.

In other words, the dissolution of small nonpolar solutes in water does not involve significant reorientation of the neighboring water molecules. If this were the case, a hard-sphere perturbation theory would not be capable of describing the thermodynamics of the process over a wide temperature range. This is in agreement with the view expressed above that the large negative ΔS°_2 is not the origin of the low solubility in aqueous medium, but rather the consequence. The orientation of H₂O molecules surrounding an empty point or a nonpolar solute in liquid water is obviously

very different from that of the solvent molecules surrounding a lattice point where a central H₂O molecule is sited. It seems that in many instances reorientation of water molecules has been invoked because this point has been overlooked.

In order to verify our description of the dissolution of nonpolar solutes in water, the following points could be studied either by simulation or experiment: (1) the average orientation of the first H₂O neighbors to empty points in the pure liquid, compared to the distribution of first neighbor water molecules surrounding spherical nonpolar solutes of variable size (including $d_2 = 0$); (2) accurate determination of the thermodynamics of transfer of an inert gas from D₂O to H₂O over a wide temperature range; (3) the average total electric field on a nonpolar spherical molecule.

Note Added in Proof. Recently Wood and co-workers (*J. Phys. Chem.*, in press) have determined experimentally $C_p^\circ_2$ for Ar in H₂O up to 578 K. These important experimental data can be successfully reproduced by the perturbation treatment presented here by using the same molecular parameters (work to be submitted for publication). This is strong evidence in favor of the views expressed in this article.

The Single Electron Shift as a Fundamental Process in Organic Chemistry: The Relationship between Polar and Electron-Transfer Pathways

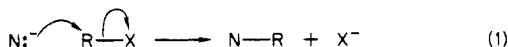
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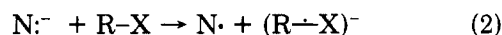
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The concept of electronic reorganization is a fundamental tenet of chemistry. Chemical reactions come about through the rearrangement of valence electrons. It is these electrons that hold the atoms together in the reacting molecules and which, by redistribution, govern the structure of the product molecules.

Yet a strange dichotomy concerning the movement of electrons during chemical reactions has emerged over the years. In electron-transfer theory a fundamental postulate is that electrons may only be transferred one at a time.^{1,2} But, within organic chemistry, for polar reactions at least, electrons are considered to move about in pairs, as illustrated by the S_N2 process (eq 1).



It is only for radical producing reactions that the idea of a single electron transfer (SET) is widely entertained, as illustrated by the first step of the S_{RN}1 pathway for nucleophilic substitution (eq 2).³ This subdivision of



nucleophilic substitution reactions into either polar or SET pathways is equally applicable to all the other fundamental organic mechanisms. Thus hydride reduction, electrophilic, and nucleophilic aromatic substitution, and nucleophilic addition, to quote a few examples, may also be formulated in terms of either SET or polar mechanisms.

Recognition of the SET pathway in organic reactions has grown enormously over the last 20 years, primarily following the pioneering work of Kornblum, Russell, and Bunnett.³⁻⁷ The impact of SET pathways on organometallic chemistry has been extensive, largely due to the contributions of Kochi and co-workers.^{8,9} More

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(7) Application of electron transfer concepts in organic chemistry by Soviet workers has been popular for many years. For reviews, see: (a) Todres, Z. V. *Russ. Chem. Rev. (Engl. Transl.)* 1978, 47, 148; (b) Bilevich, K. A.; Okhlobystin, O. Y. *Russ. Chem. Rev. (Engl. Transl.)* 1968, 37, 1.