# A Scaled Particle Theory of Aqueous and Nonaqueous Solutions

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## *I. Introduction*

The increasing trend on the part of chemists to endeavor to interpret the thermodynamic behavior of chemical systems in fluid media in terms of molecular parameters and intermolecular interactions has resulted in a need for new statistical thermodynamic approaches to fluids and fluid mixtures. While a number of such approaches have been developed, a particularly useful and intuitively attractive approach which yields important insight into the nature of such fluids is the scaled particle theory.[1-10] Although this theory was originally developed as a formal statistical mechanical theory of dense hard-sphere fluids, it became apparent that it provided relations which were relevant to the behavior of real fluids. The present article is not a review of the formalism of the scaled particle theory, but rather is an effort to select those aspects of the theory which make it important in understanding qualitatively and semiquantitatively the important contributions to the thermodynamic properties of nonaqueous and aqueous solutions. These solution properties have always been of interest to physical chemists, but in recent years there has been an unprecedented interest in solution thermodynamics by physical organic chemists, by inorganic chemists, by electrochemists, and, most notably, by biochemists. This interest stems in part from the importance of solvent effects on reaction rates and mechanisms, on the nature of ionic interactions in electrolyte solutions, and on the nature of hydrophobic interactions and the conformational properties of proteins and other biologically important molecules. Particular emphasis will be placed on the nature of dilute solutions, that is, on solutions in which the solubility of a substance is directly proportional to either the pressure or activity of the substance. These solutions are said to obey Henry's law, and one can show that the only molecular interactions that influence the system are the interactions of single solute molecules with the solvent. Experimental and theoretical studies of solutions obeying Henry's law give direct information about this interaction. If solubility studies of the deviations from Henry's law are made, then molecular information can be obtained involving not only the solute–solvent interaction but also the interaction between two or more solute molecules.

The following sections will (a) outline those aspects of the thermodynamics of solutions which are of particular interest in understanding intermolecular interactions in fluids, (b) develop those aspects of the scaled particle theory of fluids which will be of importance in studying solubility phenomena, and (c) apply the scaled particle theory to the interpretation of data pertaining to aqueous and nonaqueous solutions in terms of molecular and thermodynamic parameters.

## *II. Theory of Dilute Solutions*

### A. Thermodynamics of Dilute Solutions

The concentration of a solute dissolved in a liquid solvent can be expressed as a power series in the activity or fugacity of the solute. This power series is given as[11]

$$\rho_2 = \sum_{i \geq 1} B_{i+1,\ell}(f_2/kT)^i \tag{1}$$

where $\rho_2$ is the number density of the solute (i.e., the number of molecules of solute dissolved per unit volume of solution), $f_2$ is the fugacity of the solute (this is frequently replaced by the pressure of the solute), $kT$ is the Boltzmann constant times the absolute temperature, and $B_{2\ell}$, $B_{3\ell}$ etc., are functions of the temperature. It is possible to relate the quantities $B_{2\ell}$, $B_{3\ell}$, etc., to the molecular properties of the solute and the solvent through the application of the techniques of statistical mechanics.[11-13]

McMillan and Mayer[11] in considering the general problem of osmotic equilibrium showed that for constant solvent activity the coefficients of the terms in $(f_2/kT)$ are analogous to the virial coefficients in the virial equation of state of gases. The coefficient $B_{2\ell}$ is the second solute–solvent virial coefficient. These virial coefficients can be expressed in terms of integrals involving the configurations of one, two, etc., solute molecules and the configurations of the various molecules of the solvent. Of particular importance in this discussion is $B_{2\ell}$. It can be shown that[12]

$$B_{2\ell} = \frac{1}{V}\int_{\mathrm{vol}} (\mathrm{e}^{-W(\bar{r}_i)/kT} - 1)\,\mathrm{d}\bar{r}_i \tag{2}$$

where $\bar{r}_i$ is the position of the *i*th solute molecule under consideration, and $W(\bar{r}_i)$ is the average potential energy of the *i*th solute molecule whose center is at $\bar{r}_i$ and which interacts with the solvent. The averaging is over all allowable configurations of the solvent. The integral is over the entire volume of the solution. The importance of this coefficient is that it is dependent only upon one solute molecule interacting with the solvent, and hence solute–solute interactions do not enter into the first term in the expansion given by eq 1. We will see that this result is of great importance to our consideration in the following sections.

Although we will not be concerned in this article with the evaluation of $B_{3\ell}$, we present a few comments on it for the sake of completeness. The integral expressing $B_{3\ell}$ is considerably more complex than that for $B_{2\ell}$ and is given after a few approximations by[12]

$$B_{3\ell} = \frac{2B_{2\ell}^2}{V} \int \int_{\text{vol}} (e^{-\omega_2(\bar{r}_i,\bar{r}_j)/kT} - 1)\, d\bar{r}_i d\bar{r}_j \qquad (3)$$

where $B_{2\ell}$ is the second solute–solvent virial coefficient and $\omega_2(\bar{r}_i,\bar{r}_j)$ is the effective pair potential of two solute molecules, one located at position $\bar{r}_i$ and the second located at position $\bar{r}_j$. The effective pair potential is averaged over all configurations of the solvent molecules. The importance of $B_{3\ell}$ is that it is dependent only upon the interaction of two solute molecules with each other and with the solvent. It can be similarly shown that the $i$th virial coefficient in eq 1 is dependent upon $i$ molecules of solute interacting with each other and simultaneously with the solvent.

As can be seen, one can decompose the complex problem of solution equilibrium into its simplest parts and study these independently. The present article is concerned with a somewhat detailed examination of the effect of molecular type and temperature upon the second solute–solvent virial coefficient, $B_{2\ell}$.

The quantity of $B_{2\ell}$ is directly related to the experimental quantity called the Henry law constant which is usually expressed as

$$f_2 = K_H X_2 \qquad (4)$$

where $f_2$ is the fugacity of the solute, $K_H$ is the Henry law constant, and $X_2$ is the mole fraction of solute in the solution. Since the number density of solute molecules dissolved in a *dilute* solution is related to $X_2$ by

$$\rho_2 \bar{V}_1 = \boldsymbol{N} X_2 \qquad (5)$$

where $\bar{V}_1$ is the molar volume of solvent and $\boldsymbol{N}$ is Avogadro's number, we can see that the Henry law constant is given by

$$K_H = RT/\bar{V}_1 B_{2\ell} \qquad (6)$$

Since $B_{2\ell}$ represents the probability that a molecule of solute be found in the position $\bar{r}_i$ integrated over all possible positions in the solvent volume, it can be directly related to a Boltzmann equation[12-14]

$$B_{2\ell} = e^{-W/RT} \qquad (7)$$

where $W$ is the reversible work required to dissolve 1 mol of solute in an infinite amount of solvent at constant $P$ and $T$ or its equivalent, the partial molar free energy of the solute at infinite dilution. Substitution of this into eq 6 and rearranging yields

$$\ln K_H = W/RT + \ln (RT/\bar{V}_1) \qquad (8)$$

We will obtain this result in a more conventional manner in the next section. At this point it is worth noting the relationship between $K_H$ and $B_{2\ell}$ and between $B_{2\ell}$ and $W$.

The chemical potential of a solute in a liquid solvent can be expressed as[15]

$$\mu_{2,\text{soln}} = -\bar{U}_2 + P\bar{V}_2 + RT \ln \Lambda_2^3/j_2 + RT \ln (N_2/V) \qquad (9)$$

where $-\bar{U}_2$ is the molar potential energy of the solute in the solution relative to infinite separation, $P$ is the hydrostatic pressure, $\bar{V}_2$ is the partial molar volume of the solute, $V/\Lambda_2^3$ and $j_2$ are the partition functions per molecule for the translational and internal degrees of freedom of the solute, and $N_2$ is the number of solute molecules in the volume, $V$, of the solution. For very dilute solutions $V \approx \bar{V}_1$, the volume of the solvent, and $(N_2/N_1) \approx X_2$, the mole fraction of the solute.

The sum of the two terms on the right-hand side of eq 9 represents the reversible work required to introduce one solute molecule into a solution of concentration $N_2/V$. For very dilute solutions the reversible work required to add a solute molecule to the solution is equivalent to that of adding one molecule to the pure solvent. It is convenient to consider the process of introducing the solute molecule into the solvent as consisting of two steps.[16-18]

*Step 1.* The creation of a cavity in the solvent of suitable size to accommodate the solute molecule. The reversible work or partial molar Gibbs free energy, $\bar{G}_c$, required to do this is identical with that required to introduce 1 mol of hard-sphere molecules of the appropriate radius such as to produce a mole of cavities in the solution.

*Step 2.* The introduction into the cavity of a solute molecule which interacts with the solvent according to some potential law. The molar reversible work here, $\bar{G}_i$, is identical with that of charging the hard spheres or cavities introduced in step 1 to the required potential; i.e., it is the work associated with giving each cavity or hard sphere the proper charge distribution and polarizability to simulate a real solute molecule.

Substitution of $\bar{G}_c + \bar{G}_i$ for $(-\bar{U}_2 + P\bar{V}_2)$ and $X_2/\bar{V}_1$ for $N_2/V$ in eq 9 yields

$$\mu_{2,\text{soln}} = \bar{G}_c + \bar{G}_i + RT \ln (\Lambda_2^3/j_2) + RT \ln (X_2/\bar{V}_1) \qquad (10)$$

The chemical potential of the solute in a gas phase in equilibrium with the solution is given by

$$\mu_{2,\text{gas}} = RT \ln (\Lambda_2^3/j_2) + RT \ln (f_2/RT) \qquad (11)$$

where $f_2$ is the fugacity of the solute.

Equating $\mu_{2,\text{soln}}$ to $\mu_{2,\text{gas}}$ yields

$$\ln (f_2/X_2) = \bar{G}_c/RT + \bar{G}_i/RT + \ln (RT/\bar{V}_1) \qquad (12)$$

or since for very dilute solutions $f_2 = K_H X_2$,

$$\ln K_H = \bar{G}_c/RT + \bar{G}_i/RT + \ln (RT/\bar{V}_1) \qquad (13)$$

The molar heat of solution is

$$\Delta H_S = \left(\frac{\partial \ln K_H}{\partial (1/RT)}\right)_P = \bar{H}_c + \bar{H}_i - RT + \alpha_P RT^2 \qquad (14)$$

where $\alpha_P$ is the coefficient of thermal expansion of the solvent; the partial molar volume of the solute is

$$\bar{V}_2 = (\partial \mu_{2,\text{soln}}/\partial P)_{T,N} = \bar{V}_c + \bar{V}_i + \beta_T RT \qquad (15)$$

where $\beta_T$ is the isothermal compressibility of the solvent.

## B. Scaled Particle Theory of Fluids

In a series of papers Reiss, Frisch, Helfand, Lebowitz, and Tully-Smith[1-9] have developed a statistical mechanical theory of fluids based upon the properties of the exact radial distribution function which yields an approximate expression for the reversible work required to introduce a spherical particle into a fluid of spherical particles. They consider the case of a system of $N$ particles obeying a pairwise additive potential and couple one additional particle obeying the same potential to this system by the procedure of distance scaling. The coupling procedure is used to obtain an expression for the chemical potential of the fluid in terms of a function related to the radial distribution function for the fluid.

The essence of the scaled particle theory is that work is required to exclude the centers of molecules from any specified region of space in a fluid. Consider a fluid consisting of $N$ spherically symmetrical molecules possessing a hard core of diameter $\sigma_1$ and exerting whatever attractive forces are consistent with the volume $V$ of the fluid. Imagine now excluding the centers of all $N$ molecules from a spherical region of space of radius $r$ in the volume $V$. This region of space would in fact be a cavity in the fluid. Suppose we denote the probability that such a cavity exists by $p_0(r,\rho)$, where $\rho$ is the number density of the fluid ($N/V$). The cavity could be created by a statistical fluctuation, and the probability that such a fluctuation would occur is given by[12-14]

$$p_0(r,\rho) = e^{-W(r,\rho)/kT} \tag{16}$$

where $W(r,\rho)$ is the reversible work required to produce a cavity of radius $r$ is the fluid. Note the similarity of eq 16 and 7. It is clear that $p_0(r,\rho)$ can be equated with $B_{2\ell}$ where the solute is a nonpenetrable cavity or its equivalent a hard sphere solute. The scaled particle theory attempts to determine $p_0(r,\rho)$ as accurately as possible based upon statistical mechanical and geometrical arguments. The general approach is to start with a cavity of zero radius and allow it to grow or be scaled up to the desired radius (see Figure 1a).

This is perhaps made more clear if one considers the probability of finding a molecular center just outside the cavity radius $r$, i.e., of finding the center in the fluid shell of thickness $r$ to $r + dr$. This probability is given by $4\pi r^2\rho\mathbf{G}(r,\rho)\,dr$, where $\rho\mathbf{G}(r,\rho)$ is the conditional probability that a molecular center is located in that region. The probability that there is no center in this spherical shell is simply $1 - 4\pi r^2\rho\mathbf{G}(r,\rho)\,dr$.

The probability that there is no molecular center in the range 0 to $r$ times the probability that there is no center in the range $r$ to $r + dr$ is just equal to the probability that there is no center in the range 0 to $r + dr$ or

$$p_0(r + dr) = p_0(r) + \left(\frac{\partial p_0(r)}{\partial r}\right) dr$$
$$= p_0(r)[1 - 4\pi r^2\rho\mathbf{G}(r,\rho)\,dr] \tag{17}$$

or

$$(\partial \ln p_0(r)/\partial r) = -4\pi r^2\rho\mathbf{G}(r,\rho) \tag{18}$$

Referring to eq 16, we find

$$(\partial W(r,\rho)/kT/\partial r) = 4\pi r^2\rho\mathbf{G}(r,\rho) \tag{19}$$

and consequently

$$W(r,\rho)/kT = 4\pi\rho\int_0^r r^2\mathbf{G}(r,\rho)\,dr \tag{20}$$

Hence the determination of the reversible work of introducing a cavity into a fluid is dependent upon the determination of a functional representation of the conditional probability $\mathbf{G}(r,\rho)$. Lengthy arguments[1-8] indicate that an asymptotic expansion in $1/r$ is a suitable representation; thus we can write

$$\mathbf{G}(r,\rho) = \sum_i \mathbf{G}_i(\rho)(1/r)^i \tag{21}$$

The task is now to evaluate the coefficients $\mathbf{G}_i(\rho)$, and this is done by seeking exact relationships that $\mathbf{G}(r,\rho)$ must possess and for each such relationship one coefficient $\mathbf{G}_i$ can be determined.

The first such exact relationship is a particularly interesting one. For all values of $r \le \sigma_1/2$, one and only one hard-core molecule can have its center in the spherical region of radius $r$, otherwise the hard cores would have to overlap. The probability that a molecular center is in this region is $\frac{4}{3}\pi r^3\rho$; hence

$$p_0 = 1 - \tfrac{4}{3}\pi r^3\rho \qquad r \le \sigma_1/2 \tag{22}$$

Reference to eq 18 indicates that

$$\mathbf{G}(r,\rho) = \frac{1}{(1 - \frac{4}{3}\pi r^3\rho)} \qquad r \le \sigma_1/2 \tag{23}$$

Substituting eq 18 into eq 20 and carrying out the integration yields

$$W_0(r,\rho) = kT\ln(1 - \tfrac{4}{3}\pi r^3\rho) \qquad r \le \sigma_1/2 \tag{24}$$

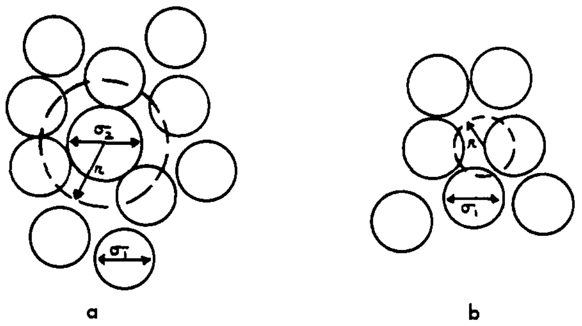

**Figure 1.** (a) Spherical cavity of radius $r$ caused by a hard-sphere solute of diameter $\sigma_2$ in a hard-sphere fluid of molecules of diameter $\sigma_1$. (b) A point solute creates a cavity of radius $\sigma_1/2$ by excluding the center of all solvent molecules.

where $W_0(r,\rho)$ is the reversible work of producing a cavity of radius $r \le \sigma_1/2$. In a way this is a curious result. A cavity of radius $\sigma_1/2$ in a fluid of hard spheres is in fact a point (see Figure 1b, and hence eq 24 with $r^3$ replaced by $(\sigma_1/2)^3$ represents the work required to introduce a point solute into the fluid. Furthermore, a solute of diameter $\sigma_2$ requires the creation of a cavity of radius $r = (\sigma_1 + \sigma_2)/2$. Geometrical considerations indicate that for $0 < r \le \sigma_1/2$ at most one molecular center can be found in the cavity, for $\sigma_1/2 < r \le \sigma_1/\sqrt{3}$ at most two molecular centers can be found in the cavity, etc., until at $r = \sigma_1$ twelve molecules can occupy the defined spherical region.

There are a host of exact conditions that can be found in addition to that of eq 23. These have led to the evaluation of $\mathbf{G}_i$ in eq 21 through $\mathbf{G}_5$.[8] It has been shown that $\mathbf{G}_3$ is zero and $\mathbf{G}_4$ is likely to be zero. Examination of eq 20 and 21 indicates that an asymptotic expansion for $W(r,\rho)$ of the form

$$W(r,\rho) = K_0 + K_1r + K_2r^2 + K_3r^3 \tag{25}$$

might be an excellent approximation. This incidentally is the same form as required in classical thermodynamics, i.e.

$$W(r) = \frac{4}{3}\pi r^3P + 4\pi r^2\gamma\left(1 - \frac{4\delta}{r}\right) \tag{26}$$

where the term involving $P$ (the pressure) is just the volume work; the term involving $\gamma$ (the surface tension) is the surface work and the term involving $\delta/r$ is a term which corrects the surface tension for the effect of surface curvature. The only difference between these equations is the absence of the constant term $K_0$ in the thermodynamic equation. Since the thermodynamic equation is meant to account for macroscopic cavities, the absence of the $K_0$ term introduces negligible error but for microscopic cavities $K_0$ is an important term. Three of the exact conditions used to evaluate the $\mathbf{G}_i$ can also be used to evaluate the $K$'s in eq 25. In the original development of the scaled particle theory, the $K$'s were obtained by expanding $W(r,\rho)$ about $r = \sigma_1/2$ giving

$$W(r,\rho) = W_0 + W_0'(r - \sigma_1/2)$$
$$+ \frac{1}{2}W_0''(r - \sigma_1/2)^2 + \frac{1}{6}W_0'''(r - \sigma_1/2)^3 \tag{27}$$

where $W_0 = kT\ln(1 - \pi\sigma_1^3\rho/6)$ and where the first and second derivatives are known to be continuous and hence obtainable from eq 24. The coefficient of the cubic term was obtained by direct comparison with the thermodynamic equation and hence $K_3$ is equal to $\frac{4}{3}\pi P$. After suitable algebraic manipulations one obtains

$$\frac{W(\mathbf{R},\rho)}{kT} = -\ln(1 - y) + \left(\frac{3y}{1 - y}\right)\mathbf{R}$$
$$+ \left[\frac{3y}{1 - y} + \frac{9}{2}\left(\frac{y}{1 - y}\right)^2\right]\mathbf{R}^2 + \frac{yP}{\rho kT}\mathbf{R}^3 \tag{28}$$

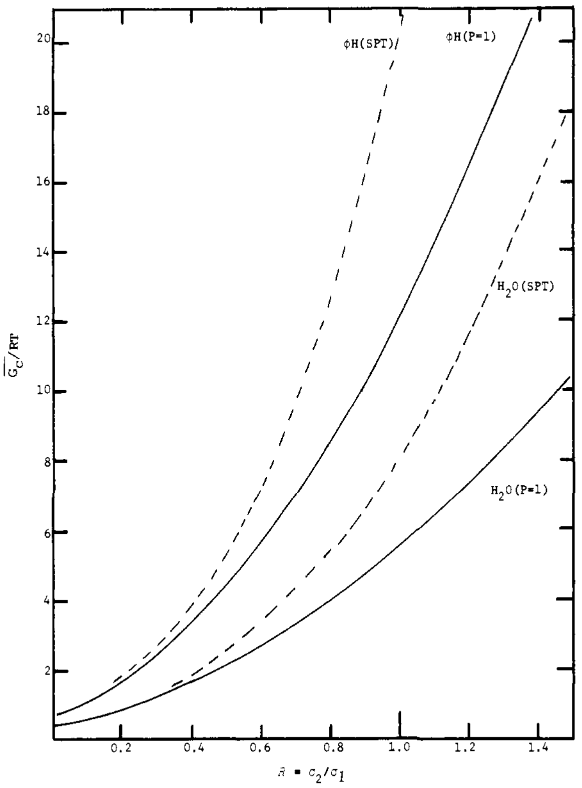

**Figure 2.** The free energy of cavity formation in water and benzene at 298.15 K.

where $y = \pi\rho\sigma_1^3/6$ is the reduced number density, $\boldsymbol{R} = \sigma_2/\sigma_1$, and $\sigma_2$ is the diameter of the hard-sphere solute molecule such that the cavity radius is $(\sigma_1 + \sigma_2)/2$. It is possible by incorporating a fourth exact relation to obtain an approximate equation of state for a hard-sphere fluid, and consequently the terms in the pressure above could also be expressed in terms of $y$ and $T$. As will be mentioned later, for our purposes of investigating the solubility of substances in real fluids there is considerable value in retaining as many experimentally known properties of the fluid (such as $\rho$, $P$, and their pressure and temperature derivatives) as possible. These quantities serve to preserve as much information as possible about the attractive interactions between the solvent molecules. In the application of the scaled particle theory to solutions, the theory is used primarily as a means of determining the reversible work required to introduce a hard-sphere molecule into a real fluid whose molecules behave as hard cores but whose volume and pressure at a given temperature are determined by the real intermolecular potentials existing among them.

## C. Henry Law Constants

The Henry law constant provides the basis for understanding the properties of dilute solutions because it separates out specifically the solute-solvent interactions. As shown in eq 13, the Henry law constant can be expressed as

$$\ln K_H = \overline{G}_c/RT + \overline{G}_i/RT + \ln (RT/\overline{V}_1) \qquad (29)$$

where $\overline{G}_c$ and $\overline{G}_i$ are the partial molar Gibbs free energy of cavity formation and interaction, respectively. The development of the scaled particle theory given above was directed at obtaining an expression for $\overline{G}_c$ which is equal to $W(\boldsymbol{R},\rho)$ and given by eq 28. The hydrostatic pressure in eq 28 can be replaced by the pressure from the theoretical equation of state for the scaled particle theory. As discussed above, it is preferable for the purpose at hand to use the experimental value of $P$ rather than the theoretical value for hard-sphere fluid. If the equation of state of the real fluid were known from theory, this would of course be preferred. For real fluids the term is of importance only for high-pressure studies and/or in considering the pressure derivatives of $\overline{G}_c$. Figure 2 shows curves of $\overline{G}_c/RT$ vs. $\boldsymbol{R}$ for values of $y$ corresponding to those for the solvents water and benzene at 298 K. Included in Figure 2 is a comparison of $\overline{G}_c/RT$ using the scaled particle theory equation of state for $P$ in the last term of eq 28 and using the "experimental value" of the hydrostatic pressure which in the curves shown was taken to be 1 atm. Actually for pressure around 1 atm the pressure term contributes a negligible amount to the free energy of cavity formation, and hence the curves labeled $P = 1$ are the equivalent to the sum of the first three terms in eq 28. Table I gives values of $y$ for a number of solvents.

**TABLE I. Selected Physical Properties of Various Liquid Substances at 298.15 K**[a]

| Substance | $\alpha \times 10^{24}$ cm$^3$ molecule$^{-1}$ | $\rho \times 10^3$ deg$^{-1}$ | $\beta_P \times 10^5$ atm$^{-1}$ | $\overline{V}_1$ cm$^3$/mol | $y$ |
|---|---|---|---|---|---|
| Ar | 1.63 | 4.49[b] | 22.7[b] | 28.66[b] | 0.436[b] |
| $CS_2$ | 8.57 (0.06)[c] | 1.17 | 10.73 | 60.65 | 0.483 |
| $CCl_4$ | 10.49 | 1.27 | 10.91 | 97.09 | 0.506 |
| $C_6H_6$ | 10.32 | 1.38 | 9.38 | 89.40 | 0.513 |
| c-$C_6H_{12}$ | 10.78 | 1.20 | 12.3 | 108.7 | 0.523 |
| *n*-$C_8H_{14}$ | 11.78 | 1.39 | 16.27 | 131.6 | C.502 |
| *n*-$C_8H_{18}$ | 15.44 | 1.15 | 12.14 | 163.5 | 0.542 |
| *n*-$C_7F_{16}$ | 14.57 | 1.56 | 29.98 | 225.87 | 0.502 |
| $C_6H_5CH_3$ | 12.33 | 1.08 | 9.40 | 106.8 | 0.532 |
| $C_6H_5F$ | 10.28 (1.42)[c] | 1.22 | | 94.03 | 0.453 |
| $N_2H_4$ | 3.51 (1.90)[c] | . . . | . . . | 52.97 | 0.472 |
| $(CH_3)_2CO$ | 8.67 (2.83)[c] | 1.42 | 12.55 | 74.05 | 0.468 |
| $CH_3OH$ | 3.26 (1.66)[c] | 1.20 | 12.58 | 40.73 | 0.395 |
| $C_2H_5OH$ | 5.13 (1.66)[c] | 1.10 | . . . | 58.69 | 0.445 |
| $H_2O$ | 1.47 (1.84)[c] | 0.257 | 4.46 | 18.07 | 0.371 |

[a] The entries in this table together with those of many more substances can be found compiled in ref 25. [b] These properties are for liquid argon at 87 K. [c] The number in parentheses is the dipole moment for the substance in debyes.

The partial molar Gibbs free energy for interaction, $\overline{G}_i$, can be approximated in the following manner. Suppose the interaction energy of a solute molecule with a given solvent molecule is $\epsilon_i(r)$, then the sum of the $\epsilon_i$ averaged over the configurations of the solvent for a mole of solute molecules will be $\overline{E}_i$. Since the solvent is a condensed phase, $\overline{E}_i$ is approximately equal to $\overline{H}_i$, and hence $\overline{G}_i$ can be determined in principle by integration of the Gibbs-Helmholtz relationship. This integration requires knowing the temperature dependence of the radial distribution function. This is not generally known and as an approximation it is assumed that $\rho g(r)$ is temperature independent and hence $\overline{G}_i \approx \overline{E}_i$. For spherically symmetric, pairwise-additive interactions

$$\overline{G}_i \simeq \overline{E}_i = \boldsymbol{N} \int_{\mathrm{vol}} \epsilon_i(r) 4\pi r^2 \rho g(\sigma_2,r)\, dr \qquad (30)$$

where $\rho$ is the number density of the fluid, $\boldsymbol{N}$ is Avogadro's number, and $g(\sigma_2,r)$ is a radial distribution function and measures the probability of finding a solvent molecular center at the distance $r$ from the center of a solute molecule of hard sphere radius $\sigma_2$. The most satisfactory and consistent approach here would be to obtain the radial distribution function directly from the scaled particle theory. Unfortunately this has not been done although significant progress in scaled particle theory has been made along these lines.[10] A number of approximate functions based upon physically intuitive notions could be used for $g(\sigma_2,r)$, but this has not been done either. The original papers on the scaled particle theory as applied to solutions used a uniformly distributed solvent; that is, $g(\sigma_2,r)$ was taken to be unity outside the radius $\sigma_2$. This is not a particularly poor approximation for

**TABLE II. Selected Properties and Parameters for the Inert Gases**[a]

| Substance | $\alpha \times 10^{24}$ cm$^3$/mol | $-\chi \times 10^{26}$ cm$^3$/molecule | $\epsilon/k$, K | $\sigma \times 10^8$ cm |
|---|---|---|---|---|
| He | 0.204 | 0.29 | 6.03 | 2.63 |
| Ne | 0.393 | 1.17 | 35.7 | 2.79 |
| Ar | 1.63 | 3.24 | 125 | 3.41 |
| Kr | 2.46 | 4.65 | 169 | 3.67 |
| Xe | 4.00 | 7.04 | 217 | 3.96 |
| Rn | 5.86 | | 290 | 4.23 |

[a] From ref 25.

obtaining the average energy, but it cannot be expected to account for small differences in properties between a given solvent and various solutes. If unit radial distribution function is assumed, then the integral in eq 30 can be carried out by assuming a functional form of $\epsilon_i(r)$. If one considers the interaction of a polarizable polar solute with a polarizable polar solvent, then a reasonable expression for $\epsilon_i(r)$ is[19]

$$\epsilon_i(r) = -C_{\text{dis}}[(1/r)^6 - (\sigma_{12}/r)^{12}/\sigma_{12}{}^6] - (C_{\text{ind}} + C_{\text{dip}})(1/r)^6 \tag{31}$$

where $C_{\text{dis}}$ is the dispersion (or London) energy constant, $C_{\text{ind}}$ is the inductive energy constant, $C_{\text{dip}}$ is the dipole-dipole energy constant, and $\sigma_{12}$ is the distance at which the dispersion and repulsive interactions are equal in magnitude. Substitution of eq 31 into eq 30 and integrating yields

$$\bar{G}_i/RT = -(16/3)(\epsilon^*_{\text{dis}}/kT) - 8(\epsilon^*_{\text{ind}} + \epsilon^*_{\text{dip}})/kT \tag{32}$$

where $\epsilon^*_i = \pi\rho C_i/6\sigma_{12}{}^3$ and where the integral has been evaluated from $\sigma_{12}$ to infinity. The expressions used for the dipole-dipole and inductive energy are, of course, the rotationally averaged terms, and, in those cases where these must be used, the adequacy of the approximation must be questioned.

The contribution of the dispersion energy may be estimated by several theoretical expressions. The Kirkwood-Muller formula[20] has been one of the more successful approximations[21] and is given by

$$C_{\text{dis}} = C_{\text{KM}} = -6mc^2 \frac{\alpha_1\alpha_2}{(\alpha_1/\chi_1) + (\alpha_2/\chi_2)} \tag{33}$$

where $m$ is the mass of an electron, $c$ is the velocity of light, $\alpha_1$ and $\alpha_2$ are the molecular polarizabilities of the solvent and solute, respectively, and $\chi_1$ and $\chi_2$ are the molecular magnetic susceptibilities of the solvent and solute (see Tables I and II).

Another useful form of $C_{\text{dis}}$ is that for the Lennard-Jones (6-12) potential

$$C_{\text{dis}} = C_{\text{LJ}} = 4\epsilon_{12}\sigma_{12}{}^6 = 4(\epsilon_1\epsilon_2)^{1/2}[(\sigma_1 + \sigma_2)/2]^6 \tag{34}$$

where $\epsilon_1$ and $\epsilon_2$ are the energy parameters for the solvent and solute, and $\sigma_1$ and $\sigma_2$ are the distance parameters of the solvent and solute (see Tables II and III).

The inductive energy constant $C_{\text{ind}}$ is given by[22]

$$C_{\text{ind}} = \mu_1{}^2\alpha_2 + \mu_2{}^2\alpha_1 \tag{35}$$

where $\mu_1$ and $\mu_2$ are the dipole moments of the solvent and solute, and $\alpha_1$ and $\alpha_2$ are the polarizabilities of the solvent and solute.

The dipole-dipole interaction constant is the coefficient of $r^{-6}$ in the so-called Keesom orientation energy and is given by[22]

$$C_{\text{dip}} = (2/3)\mu_1{}^2\mu_2{}^2/kT \tag{36}$$

where $\mu_1$ and $\mu_2$ are the dipole moments of the solvent and solute, respectively.

For a nonpolar solute and solvent only the dispersion energy in eq 32 contributes. If either the solvent or the solute is dipolar but not the other, then only the dispersion term and one term in the inductive energy expression contribute. If both solute and solvent are dipolar, the entire expression given by eq 32 must be used. We can combine eq 28, 29, and 32 to obtain the final expression for the Henry law constant given by

$$\begin{aligned} \ln K_{\text{H}} = {} & \ln (RT/\bar{V}_1) - (16/3)\epsilon^*_{\text{dis}}/kT - 8(\epsilon^*_{\text{ind}} + \epsilon^*_{\text{dip}})/kT \\ & - \ln (1 - y) + \left(\frac{3y}{1 - y}\right) R \\ & + \left[\frac{3y}{1 - y} + \frac{9}{2}\left(\frac{y}{1 - y}\right)^2\right] R^2 + \frac{yP}{\rho kT} R^3 \end{aligned} \tag{37}$$

where $y = \pi\rho\sigma_1{}^3/6$, $R = \sigma_2/\sigma_1$, $\epsilon^*_i = \pi\rho C_i/6\sigma_{12}{}^3$, and where the $C_i$ are given by eq 34, 35, and 36.

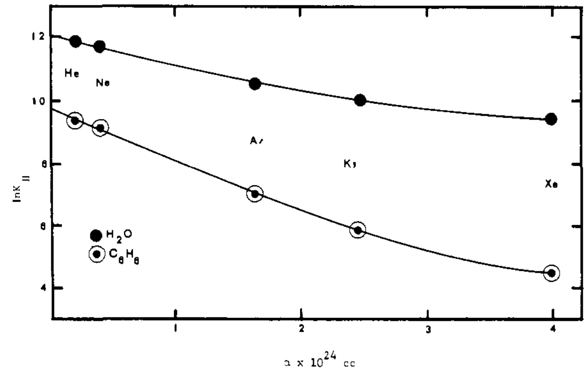

**Figure** 3. Ln $K_{\text{H}}$ vs. polarizability of inert gases in water and benzene at 298.15 K.

**TABLE III. Lennard-Jones Parameters for Solvents from Gas Solubility**[a]

| | $\sigma_1{}^b$ | $\sigma_1{}^c$ | $\sigma_1{}^d$ | $\sigma_1{}^e$ | $\epsilon_1/k^b$ | $\epsilon_1/k^d$ | $\epsilon_1/k^e$ |
|---|---|---|---|---|---|---|---|
| Ar | 3.41 | 3.42 | 3.41 | 3.42 | 120 | 122 | 120 |
| $CS_2$ | 4.53 | 4.55 | 4.53 | 4.44 | 466 | 466 | 468 |
| $CCl_4$ | 5.38 | | 5.35 | 5.88 | 530 | 490 | 327 |
| $C_6H_6$ | 5.26 | 5.25 | 5.22 | 5.26 | 496 | 504 | 440 |
| c-$C_6H_{12}$ | 5.65 | 5.60 | | 6.09 | 589 | | 324 |
| *n*-$C_6H_{14}$ | 5.94 | 5.87 | | 5.91 | 543 | | 413 |
| *n*-$C_8H_{12}$ | 6.55 | 6.56 | | 7.41 | 607 | | 333 |
| *i*-$C_8H_{18}$ | 6.53 | 6.48 | 6.44 | | 584 | 519 | |
| $C_7F_{16}$ | 7.11 | 7.03 | 7.11 | | 495 | 505 | |
| $C_6H_5CH_3$ | 5.65 | 5.68 | | 5.93 | 573 | | 377 |
| $C_6H_5F$ | 5.31 | 5.31 | | | 410 | | |
| $N_2H_4$ | 3.63 | | | | 142 | | |
| $(CH_3)_2CO$ | 4.79 | | | 4.67 | 384 | | 519 |
| $CH_3OH$ | 3.71 | *f* | | 3.67 | 255 | | 452 |
| $C_2H_5OH$ | 4.36 | *f* | | 4.31 | 339 | | 431 |
| $H_2O$ | 2.77 | *f* | | | 79.3 | | |

[a] Units of $\sigma$ are $10^{-8}$ cm, units for $\epsilon/k$ are K. [b] Obtained from gas solubility; see ref 25. [c] Obtained from the heat of vaporization based upon the scaled particle theory: $\Delta H_v = RT + \alpha_p RT^2[(1 + 2y)^2/(1 - y)^3]$. [d] Obtained from ref 65 from liquid-state properties using a cell theory. [e] Obtained from ref 66 from gas-phase virial coefficients and viscosities. [f] Heat of vaporization expression is not applicable to hydrogen-bonded liquids.

## D. Solubility of a Hard Sphere

It has long been realized that a plot of the logarithm of the experimental Henry law constant vs. the polarizability of the solute for a given solvent yielded a reasonably smooth curve.[23] Equations 37 and 33 indicates that one should expect such a correlation and that the inert gases should define the curve because they are monatomic and spherically symmetric. Figure 3 shows such a curve for the inert gases dissolved in benzene and in water. Similar curves are obtained for all solvents studied thus far. The extrapolation to zero $\alpha_2$ of the curve through the inet gas points yields a finite value of $\ln K_{\text{H}}$ and, therefore, a nonzero solubility even though the interaction term has gone to

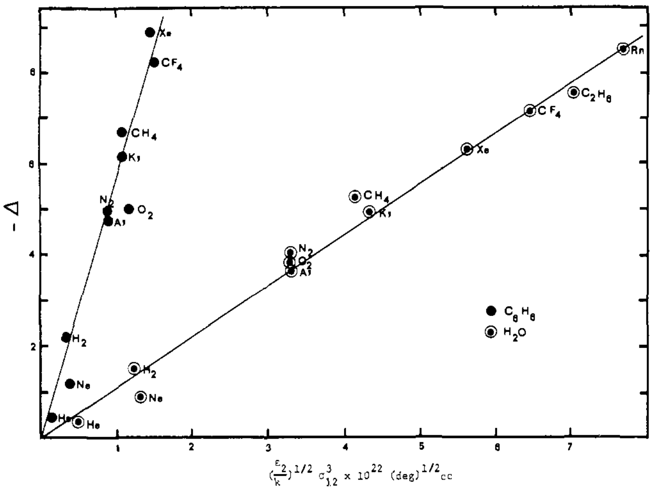

**Figure 4.** $-\Delta$ vs. solubility interaction parameter for water and benzene at 298.15 K.

zero. The change from one solute to another is accompanied not only by a change in polarizability and hence interaction energy, but also by a change in hard-sphere diameter, $\sigma_2$. A plot of $\sigma_2$ vs. $\alpha_2$ for the inert gases also describes a smooth function, and extrapolation of this curve to $\alpha_2 = 0$ gives a value of $\sigma_2{}^0$ of 2.55 Å.[24,25] The extrapolation of ln $K_H$ vs. $\alpha_2$ is thus equivalent to determining the solubility of a hard sphere of diameter 2.55 Å in the particular solvent. This can be expressed as

$$\lim_{\substack{\alpha_2 \to 0 \\ \sigma_2 \to 2.55\ \text{Å}}} \ln K_H = \ln K_H{}^0 \qquad (38)$$

where $K_H{}^0$ is the Henry law constant for hard spheres of diameter 2.55 Å.

This ability to determine from experimental data the solubility of a hard sphere in a real solvent makes it possible to directly test the adequacy of the scaled particle theory to calculate the reversible work required to introduce a hard sphere into a *real* liquid solvent. Table IV compares values of ln $K_H{}^0$ obtained from the extrapolation techniques described above for various solvents with values of ln $K_H{}^0$ determined from the theory. The agreement is excellent and represents a strong confirmation of the validity of eq 28 as derived by the scaled particle theory. The results in fact are such that there is good reason to believe that we are now in possession of a much better method for calculating $\overline{G}_c$ than for calculating $\overline{G}_i$.

## E. Determination of an Effective Hard-Sphere Diameter, $\sigma_1$

As stated above, there is good reason to have confidence in the scaled particle calculation of the energy of cavity formation of a hard sphere in a liquid solvent. A consequence of this is that if one has the solubility of the inert gases in a solvent, it is possible to carry out the extrapolation described above and determine ln $K_H{}^0$ in the solvent. Since the value of ln $K_H{}^0$ determined by this extrapolation is simply equal to $\overline{G}_c/RT$ + ln $(RT/\overline{V}_1)$, it is clear that its value is determined only by the properties of the solvent $\sigma_1$, $\overline{V}_1$, $T$, and the hard-sphere diameter $\sigma_2{}^0$ = 2.55 Å. If one takes $\sigma_1$ to be an unknown, then it is possible, from the intercept of the ln $K_H$ vs. $\alpha_2$ curve, to determine the hard-sphere diameter of the solvent $\sigma_1$, and Table III indicates values of $\sigma_1$ for a number of solvents including water[24-26] determined in this manner. Also included there are values of $\sigma_1$ determined from other more standard methods. It is of particular interest that "effective" hard-sphere diameters for solvent molecules have been determined for alkanes, cycloalkanes, aromatics, alcohols, amines, etc., by Wilhelm and Battino,[27] deLigny and van derVeen,[28] and Liabastre and Pierotti.[24-26] DeLigny and van derVeen believe the values of $\sigma_1$ determined from solubility data are probably more accurate than values from vapor viscosities or second virial coefficients. Of course, one of the advantages of determining $\sigma_1$ from solubilities is that for many liquids it is frequently not practicable to determine their vapor phase properties.

**TABLE IV. Theoretical and Experimental Values of Ln $K_H{}^0$**

| Solvent ($\sigma_1 \times 10^8$ cm) | $T$, K | Ln $K_H{}^0$ (calcd) | Ln $K_H{}^0$ (obsd) |
|---|---|---|---|
| Ar (3.40)[a] | 87.3 | 10.56 | 10.50 |
| $C_6H_6$ (5.27)[a] | 298 | 9.84 | 9.78 |
| $CCl_4$ (5.35)[b] | 298 | 9.31 | 9.43 |
| *n*-$C_6H_{14}$ (5.92)[a] | 298 | 8.56 | 8.62 |
| $C_7F_{16}$ (7.11)[b] | 298 | 7.44 | 7.44 |

[a] From ref 66. [b] From ref 65.

## F. A New Solubility Parameter and the Determination of $\epsilon_1/k$

There has been a trend in recent years to search for parameters composed of physical quantities related to interaction energy which are linearly related to solubility. If eq 37 is rewritten in the form

$$\Delta = \ln K_H + 8(\epsilon^*_{\text{ind}} + \epsilon^*_{\text{dip}})/kT - \overline{G}_c/RT - \ln (RT/\overline{V}_1)$$
$$= -32\pi\rho(\epsilon_1\epsilon_2)^{1/2}\sigma_{12}{}^3/9kT \qquad (39)$$

then it is possible to relate $\Delta$ to the interaction energy of the solute with the solvent. For a given solvent $(\epsilon_1/k)^{1/2}$ is a constant, and hence a plot of $-\Delta$ vs. $(\epsilon_2/k)^{1/2}\sigma_{12}{}^3$ should be a straight line of slope $32\pi\rho(\epsilon_1/k)^{1/2}/kT$. Figure 4 shows typical plots of $-\Delta$ vs. this new solubility parameter, $(\epsilon_2/k)^{1/2}\sigma_{12}{}^3$, for a number of solutes in benzene and water. The present theory is the only one which correlates solubility data for solvents as diverse as water and benzene using a single nonadjusted solubility parameter.

As indicated, the slope of the $-\Delta$ plot is proportional to $(\epsilon_1/k)^{1/2}$; hence the experimentally determined slope permits the evaluation of the interaction parameter for the solvent. Table III gives values of $\epsilon_1/k$ determined from solubilities as described as well as values determined in other ways. It should be pointed out that the value of $(\epsilon_1/k)$ determined in the solution is not necessarily equal to that determined in the gas phase because of nonadditivity effects in condensed media.[29] In general, the more dense the solvent and the more polarizable its molecules, the greater the nonadditivity correction would be and the correction is in the direction such that $(\epsilon_{1,\text{soln}}/\epsilon_{1,\text{gas}})$ is less than unity. In general, the values of $(\epsilon_1/k)$ determined from solubility measurements for nonpolar molecules are in good accord with values from gas-phase virial coefficients and viscosities. It is a direct benefit of the present theory that the Lennard-Jones parameters of a solvent ($\sigma$ and $\epsilon/k$) can be determined directly from the solubility of the inert gases in that solvent.

## G. Thermal Properties of Dilute Solution Processes

The Gibbs free energy of solution can be calculated directly from

$$\Delta G_s = RT \ln K_H = \overline{G}_c + \overline{G}_i + RT \ln (RT/\overline{V}_1) \qquad (40)$$

where $\overline{G}_c$ and $\overline{G}_i$ are given by eq 28 and 32, respectively. It is worth noting that $\Delta G_s$ corresponds to the Gibbs free energy change in transferring 1 mol of gaseous solute at unit fugacity in atmospheres to a hypothetical unit mole fraction state for the solute determined from the properties of an infinitely dilute solution of the solute in a given solvent. The molar enthalpy of solution is given by eq 14, where $\overline{H}_c$ is given by

$$\overline{H}_c = y\alpha_p RT^2(1-y)^{-3}[(1-y)^2$$
$$+ 3(1-y)\boldsymbol{R} + 3(1+2y)\boldsymbol{R}^2] + y(RP/\rho k)\boldsymbol{R}^3 \qquad (41)$$

**TABLE V. Comparison of Contributions to the Solubility of Ar and $N_2$ in Benzene and Water at 298.15 K**[a]

| Solute/solvent | | $G_c$ | $H_c$ | $G_i$ and $H_i$ | $\Delta G_s$ | $\Delta H_s$ | $\Delta S_s$ | $\bar V_2$ |
|---|---|---|---|---|---|---|---|---|
| Ar/benzene | Calcd | 3677 | 4060 | −3033 | 3969 | 678 | −11.0 | 43 |
| | Obsd | ... | ... | ... | 4167 | 297 | −13.0 | 43 |
| Ar/$H_2O$ | Calcd | 5268 | 840 | −3248 | 6291 | −2757 | −31.0 | 26 |
| | Obsd | ... | ... | ... | 6274 | −2680 | −30.0 | 27 |
| $N_2$/benzene | Calcd | 4142 | 4640 | −2919 | 4548 | 1372 | −10.7 | 52 |
| | Obsd | ... | ... | ... | 4571 | 1016 | −11.9 | 53 |
| $N_2$/$H_2O$ | Calcd | 5199 | 828 | −2528 | 6943 | −2249 | −30.8 | 32 |
| | Obsd | ... | ... | ... | 6720 | −2681 | −31.5 | 32 |

[a] Units of $G$ and $H$ are cal/mol, $S$ is in cal/(mol deg), and $\bar V_2$ is cm³/mol.

where $\alpha_P$ is the thermal expansion coefficient of the solvent and $\mathbf{R} = \sigma_2/\sigma_1$.

The partial molar enthalpy of interaction, $\bar H_i$, is given by eq 32 since $\bar G_i$ has been assumed equal to $\bar H_i$. This assumption amounts to assuming the entropy change associated with the charging of the cavity, $\bar S_i$, is zero. This is certainly not correct and $\bar S_i$ should be a small negative quantity. The molar entropy of solution is given by

$$\Delta S_s = -(\partial \Delta G_s/\partial T)_P = \bar S_c + \bar S_i - R\ln(RT/\bar V_1) + \alpha_P RT \quad (42)$$

where

$$\bar S_c = (\bar H_c - \bar G_c)/T \quad (43)$$

and $\bar S_i$ is usually taken equal to zero as discussed above. The result of this is that the calculated values of $\Delta S_s$ should be slightly more negative. The molar heat capacity of solution is[26,30]

$$\Delta C_P = \bar C_c + \bar C_i - R + 2\alpha_P RT + RT^2(\partial\alpha_P/\partial T)_P \quad (44)$$

where

$$\bar C_c = [2/T - \alpha_P + \alpha_P^{-1}(\partial\alpha_P/\partial T)_P]\bar H_c' - R[y\alpha_P T/(1-y)^2]^2[(1-y)^2 + 6(1-y)\mathbf{R} + 3(4y+5)\mathbf{R}^2] \quad (45)$$

and

$$\bar C_i = \alpha_P \bar H_i \quad (46)$$

The partial molar volume of the solute at infinite dilution is given by eq 15 where

$$\bar V_c = 82.05(\beta_T/\alpha_P)(\bar H_c'/RT) + N\pi\sigma_2^3/6 \quad (47)$$

and

$$\bar V_i = \beta_T \bar G_i \quad (48)$$

$\bar H_c'$ is given by $\bar H_c$ less the cubic term in $\mathbf{R}$ and eq 48 applies for systems not involving dipole–dipole interactions.

Figure 5 illustrates the importance of cavity thermodynamics for water and benzene at 298 K. Although water is frequently referred to as an abnormal solvent, one sees in Figure 5 that the reversible work of cavity formation for water and benzene are functionally very similar; only the magnitudes differ. The enthalpy and entropies of cavity formation, however, behave quite differently. In benzene most of the work of cavity formation goes toward the enthalpic maintenance of the excluded volume and only a small contribution to the entropy or configurational exclusion of volume. Just the opposite is the case with water. This difference shows up not specifically because of the scaled particle theory, but because of the use of the experimental value of the thermal expansion coefficients which introduces implicit information about the liquid structure of the solvent into the theory. The importance of the scaled particle theory is that it makes it natural to consider cavity thermodynamics explicitly in terms of molecular properties of the solute and the thermodynamics properties of the solvent.

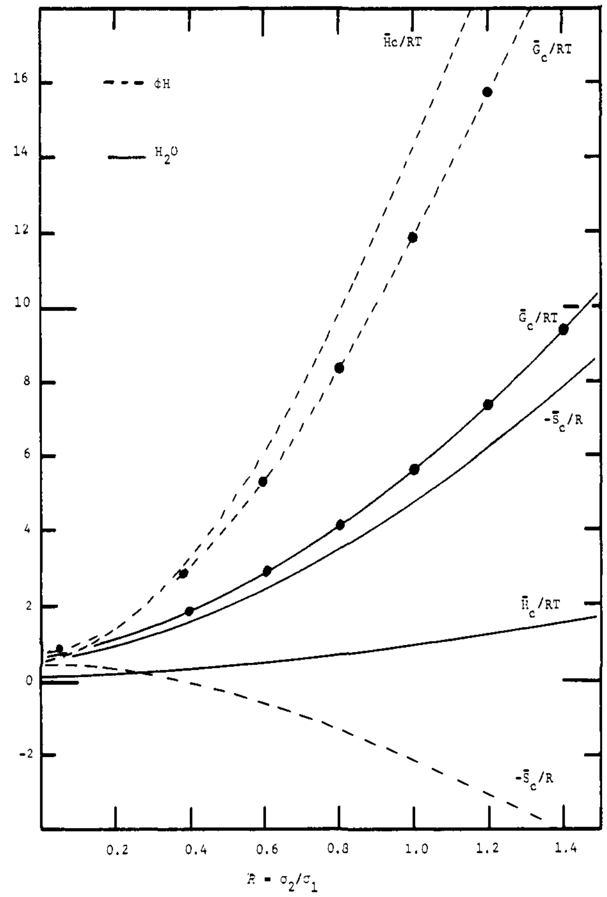

**Figure 5.** Thermodynamic properties of cavity formation in water and benzene at 298.15 K.

Table V compares the contributions of the various cavity and interaction terms to the solution properties of argon and nitrogen in benzene and water as examples of two diverse solvent systems. It should be pointed out that the equations given above do not take into account the variation of $\sigma$ with temperature.[31,32] Although the effect is not large over small temperare ranges,[33,34] it can be important for nonspherical molecules over any extended temperature range.

## H. Mixed Solvents, Electrolyte Solutions, and Salt Effects

The reversible work of introducing a hard-sphere solute into a fluid mixture containing $m$ components whose molecules have hard cores can be obtained in a manner similar to that used to obtain eq 28. The result is[6,29]

$$\bar G_c = -RT\left\{\ln(1-y_3) - \left(\frac{3y_2}{1-y_3}\right)\sigma_s - \left[\left(\frac{3y_1}{1-y_3}\right) + \frac{9y_2^2}{2(1-y_3)^2}\right]\sigma_s^2\right\} - \frac{1}{6}\pi \mathbf{N} P\sigma_s^3 \quad (49)$$

where $\sigma_s$ is the diameter of the solute molecule, $y_i = (\pi/6)\cdot\Sigma_j\rho_j\sigma_j^i$, and $\rho_j$ and $\sigma_j$ are the number density and the hard-sphere diameter of the $j$th component. The contribution from the interaction term is similarly given by

$$\overline{G}_i = -\frac{32}{9}\sum_{j=1}^{m}\rho_j\epsilon_{sj}\sigma_{sj}^3 - \frac{4}{3} \times \left(\sum_{j=1}^{m}\rho_j\mu_i^2\alpha_s/\sigma_{sj}^3 + \sum_{j=i}^{m}\rho_j\alpha_j\mu_s^2/\sigma_{sj}^3\right) - \frac{8}{9}\pi\sum_{j=1}^{m}\rho_j\mu_j^2\mu_s^2/\sigma_{sj}^3 \quad (50)$$

where $\mu_j$ and $\mu_s$ are the dipole moments of the solute and solvent, respectively, and $\epsilon_{sj}$ and $\sigma_{sj}$ are the mixed pair potential parameters for the solute and the $j$th component. The Henry law constant is then

$$\ln K_H = \overline{G}_c + \overline{G}_i + \ln\left(RT\sum_j \rho_j\right) \quad (51)$$

The relationships given above can be used to calculate solution properties of a solute in a mixed solvent. Shoor and Gubbins[35] used them to investigate the nature of the solubility of a nonpolar gas (argon) in a concentrated electrolyte solution (KOH) as a function of concentration and temperature. They found the salting-out effect well predicted by the theory and that the theory proved superior to the standard electrostatic theories of Debye and McAulay[36] and Conway, Desnoyers, and Smith.[37]

Masterton and Lee[38] also applied this theory to the salting-out of nonpolar solutes from electrolytes including in their study of NaCl and KI solutions. They found the theory gave excellent results for systems in which the molecular and ionic diameters were small. For larger molecules the quantitative agreement was less good, but qualitatively the behavior was still correct and adjustments to the molecular diameters were capable of bringing about good agreement. As a result, Masterton suggests obtaining the ionic radii of ions in solution from the theory.[39] Schrier et al.[40,41] found the theory applicable to salting-out of polar molecules from alcohol–water solutions containing NaCl, NaBr, and NaI.

Hirata and Arakawa[42] used eq 47 to determine $\overline{V}_c$ of ionic solutions, and they were able to show that $\overline{V}_c$ corresponds to the intrinsic volume of ions in dilute aqueous solution. They indicate that the expressions for the intrinsic volume of Stokes and Robinson,[43] Hepler,[44] Conway et al.,[45] and Glueckauf[46] were incomplete and inferior to that obtained from the scaled particle theory. They then subtract $\overline{V}_c$ from the experimental $\overline{V}_2$ and obtain $\overline{V}_i$, the interaction volume. For salt solutions $\overline{V}_i$ is frequently a large negative number corresponding to electrostriction.

## III. Discussion and Concluding Remarks

As stated at the outset no effort has been made to review the formalism of the scaled particle theory. Instead one aspect of the scaled particle theory (that aspect which permits the calculation of cavity work) has been used to calculate one term, $\overline{G}_c$, in the theory of dilute solutions. Contrary to comments in the literature that the scaled particle theory as applied to solutions refers specifically to hard-sphere fluids, the theory as developed above applies to fluids whose molecules have "effective" spherical hard cores but whose soft potential determines the pressure, density, and their derivatives. The theory is not a rigorous statistical mechanical theory derived from the molecular properties of the solute and solvent. Such a theory would be unlikely to yield the agreement for the diversity of molecules that have been treated with the present theory. Neff and McQuarrie[47] have attempted to develop a more rigorous theory based upon the perturbation theory of Barker and Henderson.[48] They start with the equation of state of a reference hard-sphere fluid mixture from which they obtain

$$\ln K_H = \mu_2^{HS}/RT + \mu_2^{cor}/RT + \ln(RT/\overline{V}_1) \quad (52)$$

where $\mu_s^{HS}$ is the chemical potential of the solute in the reference hard-sphere fluid and $\mu_2^{cor}$ is the correction for the soft potential which exists between the solute and solvent. $\mu_2^{HS}$ is obtained directly from he equation of state of a hard-sphere mixture as approximated by the Percus–Yevick compressibility equation. The expression they obtain for $\mu_2^{HS}/RT$ is identical with $\overline{G}_c/RT$ given by eq 23 except that consistency in their derivation requires that the pressure term in eq 28 be given by the hard-sphere pressure which may be orders of magnitude greater than the experimental pressure. The effect of retaining the theoretical SPT pressure in the cubic term in $\boldsymbol{R}$ is illustrated in Figure 1. For water as a solvent and for $\boldsymbol{R}$ equal to unity $\overline{G}_c/RT$ is 6.9 using the SPT pressure, whereas it is 4.6 using the experimental pressure of 1 atm. The deviation for benzene as the solvent is even greater, the value of $\overline{G}_c/RT$ calculated using the theoretical pressure being almost a factor of 2 larger than that calculated using $P$ equal to 1 atm. The reason for this is that the pressure required to confine a fluid of hard spheres to the molar volume of most liquids is very great. The pressure–volume work required to produce a cavity under these conditions is correspondingly very large. The Neff and McQuarrie approach must correct for this difference in the term $\mu_2^{cor}$. They show that $\mu_2^{cor}$ is made up of a number of terms including the term $\overline{G}_i$ and a term involving an integral they designate as $I_{11}$ which accounts for the change in the interaction among the solvent molecules as a result of the disturbance in the radial distribution function of the solvent by the solute. This term is required explicitly in the Neff and McQuarrie treatment because they have used a true hard-sphere reference state. The major contribution of this term is included in the term $\overline{G}_c$ as obtained by the scaled particle theory when the experimental properties of the real fluid including the pressure terms are used. Their approach, which is computationally complex, requires calculating the integral $I_{11}$ whose integrand contains the product of the solvent–solvent pair potential and the derivative of solvent radial distribution function with respect to the number of solute molecules. In light of the uncertainty of both the pair potential and radial distribution function for most real fluids, it is doubtful that one can evaluate this integral as well as would be required to correct for the high PV work contribution in $\mu_2^{HS}$ caused by using the hard-sphere equation of state rather than using the experimental hydrostatic pressure. Neff and McQuarrie treated the system neon in liquid argon where the effect of the solvent–solvent term is somewhat less important and the approximation in $I_{11}$ is somewhat less demanding than for most solvents. In this case they found their approach yielded somewhat better results than the approach discussed here. The slightly better agreement with experiment may be fortuitous, but there is no doubt that their theory has the satisfying element of not mixing theoretical and empirical results in the free energy expression. They do nevertheless use empirical expansivities and compressibilities for the heat and volume expressions similar to the method presented here rather than using hard-sphere theoretical values. Hermann[49] has used the Neff–McQuarrie approach in considering hydrocarbon solubility in water, but the number of approximations, assumptions, etc., makes it difficult to evaluate its success, but it appears to be substantially poorer than the simpler approach suggested here.

Tiepel and Gubbins[50] have also used eq 49 to treat solubility in fluid mixtures including electrolytes. They use the hard-sphere equation of state suggested by Carnahan and Starling[51] to obtain $\mu_2^{HS}/RT$ and include the theoretical hard-sphere pressure term. They do not, however, include the solvent disturbance term in $\mu_2^{cor}/RT$ as required by Neff and McQuarrie. Ignoring this term makes the computation simpler, but the approach does not have theoretical consistency. Although the Carnahan and Starling equation of states agrees with machine calculations for a rigid sphere fluid better than does scaled particle theory, it is worth mentioning that when used to calculate the cavity work term, it has not been shown to have the correct thermodynamic limit for cavities of large radius. Although no careful examination of the work of Tiepel and Gubbins has been made, the values of $\sigma$ and $\epsilon/k$ used in their work are not those usually found in the literature, and there is reason to believe that without careful selection of $\sigma$ and $\epsilon/k$ for both the solute and the solvent it would yield poorer results than the scaled particle approach.

The scaled particle theory of nonaqueous and aqueous solutions has been applied to a host of solution problems, many of which have been referred to above. Additional applications include examining (1) the problem of solubility in fused salts[52] and liquid metals;[53] (2) the problems correlating transfer properties between solvents, for instance, between $H_2O$ and $D_2O$[24,25,54] or between water and nonaqueous solvents (the transfer between $H_2O$ and nonaqueous solvents could be useful in establishing criteria for a generalized pH scale);[55] (3) the problem of theoretically relating partition coefficients to molecular parameters (these can be further related to biomedical problems);[56] (4) the problem of relating ionization kinetics and thermodynamics to molecular properties and isolating those contributions which originate from ionized species or neutral molecules;[57] (5) the properties of a well-defined reference molecule (a hard sphere) in a *real* solvent[58] and hence separating the solvolysis[59] process into a part which can be calculated with reasonably high accuracy (the cavity term) and a less well-defined term involving solute–solvent interactions.

There are a number of ways in which the present theory can be further investigated and possibly improved. Clearly the scaled particle theory itself can be extended to calculate $W(\mathbf{R},\rho)$ more accurately by utilizing more of the exact relationships which have been discovered and/or utilizing more structural information as suggested by Stillinger for aqueous solutions.[60] Another improvement could be made for nonspherical molecules by including terms describing the properties of rigid convex bodies.[61,62] The improvement here is not likely to be great since the effective diameter of a molecule cannot be determined to better than a few hundredths of an angstrom, and this is enough to mask the effects of a nonspherical core. The inclusion of a temperature variation in the effective $\sigma$ may aide in correlating enthalpy changes for nonspherical, nonrigid molecules. The greatest improvement could be obtained by utilizing more realistic intermolecular potentials in $\overline{G}_i$[63,63] and by using the scaled particle theory or some other means to provide a more realistic radial distribution function in the evaluation of $\overline{G}_i$.

In conclusion, the scaled particle theory has been applied to aqueous and nonaqueous solutions. There can be no question that it provides an opportunity to investigate solution thermodynamics in a manner which has not been available up to this time. This comes about because there is no comparable way to account for the enthalpy and entropy changes associated with the exclusion of volume in a solvent. This is the main reason the continuum electrostatic theories are lacking in interpreting dilute solutions of molecules in electrolytes. One important feature of the present theory is that the structure of the solvent (other than its pressure, density, and diameter and their temperature derivatives) are not explicitly considered, and hence water and other solvents are equally well handled by the theory.

## *IV. Addendum*

Since the submission of the original manuscript, a number of significant contributions have been made to the general area of the scaled particle theory of fluids and its application to the investigation solution properties. A few of these are:

(1) Mandell and Reiss[67] have utilized a set of six conditions required by the scaled particle theory to determine six coefficients in $\mathbf{G}(r,\rho)$ (eq 21). They find $\mathbf{G}_3 = 0$ as required and $\mathbf{G}_4$ and $\mathbf{G}_5$ are nonzero but small. The equation of state determined using all of these conditions is somewhat improved over that obtained using $\mathbf{G}_3$ and $\mathbf{G}_4$ equal to zero. These results could be used to generate a presumably improved but more complex expression for the cavity work term.

(2) Philip and Jolicoeur[68] used the scaled particle approach to calculate the thermodynamic changes associated with the transfer of a hard-sphere solute from several isotopic water and methanol solvents. They conclude that the overall importance of solvent structural effects on the properties of nonpolar solutes in aqueous solution seem overstated and also that the isotope effect on trensfer functions appears built into the bulk properties of the solvents.

Desroiers and Lucas[69] calculated the transfer properties of salts from $H_2O$ to 3 m urea and to $D_2O$ with apparent good success.

(3) Masterton, Polizzotti, and Welles[70] investigated the salt effects of the complex-ion electrolyte *t*-$[CO(en)_2NCSCl]Br$ on the solubility of argon. They use the experimental salting coefficients to determine the ionic radius of the complex ion and find it proves a useful method of interpreting the molar volumes of electrolytes in agreement with the conclusion of Hirata and Arakawa.[42] Conway, Novak, and Laliberte[71] discuss the applicability of the scaled particle approach to salting-out behavior on the basis that it obscures the structural aspects of the phenomenon. They do not make any comparisons or calculations using the theory.

Masterton[72] has considered salting coefficients for gases dissolved in seawater using the scaled particle approach and finds reasonably good agreement between theory and experiment. The predicted temperature coefficients have the right sign but are only about half the observed values.

(4) Lucas[73] has made model calculations for the transfer of a hard-sphere solute from water to other solvents using the scaled particle approach and also the modification suggested by Stillinger. The author concludes that the solvent dimensions are the important parameters in determining the sign of the free energy transfer from one solvent to another.

(5) The application of the theory with modification to the calculation of Henry's law constant has been published by Saito et al.,[74] Benson and Krause,[75] Geller, Battino, and Wilhelm,[76] and deLigny and van derVeen.[77] The latter work is concerned with a system in which one component is very polar. They find that complex formation between the solute and solvent can be detected and the association constant can be approximately evaluated.

(6) DeVoe[78] has used the approach to consider the thermodynamics of transfer properties in such manner as to define a molar structural entropy change and relates this to structural ordering of the solvent. He uses a hybrid between the scaled particle work term and the Carnahan–Starling equation of state for the pressure of a hard-sphere fluid and calculates the entropy change for introducing a hard sphere into a hard-sphere fluid whose molar volume is that of the solvent. In essence he divides the term $\overline{S}_c$ into two parts, $\overline{S}_{HS} + \overline{S}_{st}$, where $\overline{S}_{SH}$ is the entropy change for cavity formation in a truly hard-sphere solvent and $\overline{S}_{st}$ is the structural term. The results obtained are quite interesting, and the approach is related to the discussion earlier on the use of experimental volumes, etc., and hard-sphere fluid properties.

## *V. Glossary of Symbols*

| | |
|---|---|
| $\alpha$ | molecular polarizability |
| $\alpha_P$ | thermal expansion coefficient |
| $\beta_T$ | isothermal compressibility coefficient |
| $B_{2\ell}$ | second solute–solvent virial coefficient |

| | |
|---|---|
| $B_{3\ell}$ | third solute–solvent virial coefficient |
| $c$ | velocity of light |
| $C_i$ | interaction energy coefficient for the designated type energy, where i is dis, ind, dip, rep, etc. |
| $\underline{C}_c$ | partial molar heat capacity of cavity formation |
| $C_i$ | partial molar heat capacity of interaction |
| $\gamma$ | surface tension |
| $\delta$ | thickness of the surface of tension |
| $\epsilon/k$ | Lennard-Jones energy parameter |
| $\epsilon_i^*$ | integrated interaction energy, where i is dis, ind, dip, and rep |
| $f$ | fugacity |
| $\underline{\boldsymbol{G}}$ | conditional probability |
| $\underline{G}_c$ | partial molar Gibbs free energy of cavity formation |
| $G_i$ | partial molar Gibbs free energy of interaction |
| $\underline{\Delta} G_s$ | molar Gibbs free energy of solution |
| $\underline{H}_c$ | partial molar enthalpy of cavify formation |
| $H_i$ | partial molar enthalpy of interaction |
| $\Delta H_s$ | molar enthalpy of solution |
| $k$ | Boltzmann constant |
| $K_i$ | where *i* is 0, 1, or 3 are coefficients of the cavity radius to the *i*th power in the work of cavity formation expression |
| $K_H$ | Henry law constant |
| $m$ | mass of an electron |
| $\mu$ | chemical potential or dipole moment |
| $\boldsymbol{N}$ | Avogadro's number |
| $N$ | number of molecules |
| $p_0(r)$ | probability of finding a cavity of radius $r$ |
| $P$ | pressure |
| $\rho$ | number density ($N/V$) |
| $\tilde{r}$ | position of a molecular center |
| $r$ | radius of a cavity |
| $R$ | gas constant |
| $\boldsymbol{R}$ | ratio of hard sphere diameters $\sigma_2/\sigma_1$ |
| $\underline{\sigma}$ | hard-sphere diameter |
| $\underline{S}_c$ | partial molar entropy of cavity formation |
| $S_i$ | partial molar entropy of interaction |
| $\Delta S_s$ | molar entropy of solution |
| $\underline{T}$ | absolute temperature |
| $\underline{V}_1$ | molar volume of the solvent |
| $\underline{V}_2$ | partial molar number of the solute |
| $V_c$ | partial molar volume of cavity formation |
| $W$ | reversible work of cavity formation |
| $y$ | reduced density ($\pi\rho\sigma^3/6$) |
| $\chi$ | molecular diamagnetic susceptibility |
| $X$ | mole fraction |

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