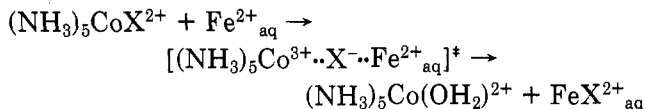


An inner-sphere mechanism involves electron-transfer via a bridging ligand, as exemplified by the system



Should such a reaction proceed by an outer-sphere mechanism a negative ΔV^{\ddagger} is predicted. Observed values of +11 ($\text{X} = \text{F}^-$), +8 ($\text{X} = \text{Cl}^-$, Br^-), and +14 ($\text{X} = \text{N}_3^-$) $\text{cm}^3 \text{mol}^{-1}$ have been interpreted in terms of an inner-sphere mechanism with appreciable desolvation of the charged species in the transition state contributing positively to the experimental ΔV^{\ddagger} .⁴⁹ Recently, activation volumes for reduction of $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ by iron(II) in the presence of sulfate ion show the influence of an iron(II) sulfate pre-equilibrium with a significant variation of ΔV^{\ddagger} observed for varying $\text{Fe}(\text{SO}_4)_{\text{aq}}/\text{Fe}^{2+}_{\text{aq}}$ ratios.⁵⁰ This variation is consistent with inner-sphere reduction by two separate pathways with $\text{Fe}^{2+}_{\text{aq}}$ or $\text{Fe}(\text{SO}_4)_{\text{aq}}$.

Concluding Remarks

While the topics discussed above encompass recent research endeavors within our laboratories for the application of activation volumes to mechanistic elucidation in reactions of octahedral metal complexes, we can expect the technique to continue to be applied to new areas of mechanistic interest in the future. Although definitive mechanistic evidence will not always be

forthcoming from activation volumes, there is now a sufficient body of experimental data accumulating to allow useful mechanistic information to be gleaned from most studies. Certainly activation volume is proving superior to activation entropy as a general mechanistic guide, since ΔV^{\ddagger} is usually determined with good precision, and the concept of a volume difference between initial and transition state is amenable to simple mechanistic modelling.

The principal and sometimes severe difficulty in interpretation or prediction of ΔV^{\ddagger} lies in an assessment of the size of any electrostrictive component. Since we are usually dealing with ionic species and often with motion of charged ligands in the activation step, electrostrictive components can dominate intrinsic components. It is likely future investigations of the role of the nonleaving groups in series of complexes with common leaving group and metal ion may aid our understanding of electrostrictive effects. Further, studies in a range of both protic and aprotic solvents, where solvation effects should vary considerably, should be of value. Few applications in reactions of organometallic compounds have been reported, and some expansion in this area would be welcome.

The increasing body of experimentally determined activation volumes and reaction volumes, combined with their value in mechanistic elucidation, presage a continued expansion in the study of reactions at elevated pressures in the area of conventional kinetics which is our prime interest. The investigations of activation volumes for octahedral coordination complexes offer more detailed insights into the actual molecular rearrangements occurring during their reactions.

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A Modern Approach to Nonelectrolyte Solubility Theory

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Received July 16, 1979

People get interested in solubility theory for one of two reasons. Engineers and applied scientists see it as a means of predicting solubilities in those systems for which data are wanted, but do not exist, and are impractical to obtain. Those among us with more theoretical inclinations would like to know, from the basis of intermolecular forces, why, at any specified temperature and pressure, one substance dissolves in another to exactly the extent that is observed. In this Account we deal with the theoretical aspects of solubility theory;

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in particular, after a preliminary comment we do four main things. First we will go through a bit of history, and in the process point out those early ideas that have found a lasting place in solubility theory. Then we show how recent advances in the theory of liquids has made it possible to quantitatively predict solubilities and related functions from intermolecular forces without using *any* adjustable parameters. Calculations of this kind, even for the very simple systems we describe, were not possible prior to about a decade ago. Following this we show how these calculations can be used both in an approximate way to interpret solubility data in complex systems and in a rigorous way to intercompare theories and to elucidate the influence on solubility made by previously neglected phenomena such as quantum effects and nonadditive intermolecular forces. Finally, we outline some of the remaining problems in the field

and indicate a possible direction of future research.

The distinguishing feature of modern solubility theory is that it is based on calculations that explicitly include a function called the radial distribution function. This function, given the symbol $g(r, \rho, T)$ (r = interparticle distance, ρ = number density, T = absolute temperature), is the factor that multiplies the bulk or macroscopic density of a liquid ρ to give the time-averaged microscopic or local density, $\rho g(r, \rho, T)$, around some fixed molecule. The gross characteristics of this function are more or less obvious; i.e. $g(r) \rightarrow 0$ as $r \rightarrow 0$ since the intermolecular forces through which atoms or molecules interact become increasingly repulsive as the electron clouds around the species begin to overlap. Also, since we are not dealing with solids, which are characterized by long-range order, it should be clear that $g(r) \rightarrow 1$ as $r \rightarrow \infty$. That is, the capacity of a selected molecule to influence the time-averaged microscopic density diminishes as the distance away from the selected molecule becomes large. At intermediate distances this function goes through a number of extrema, the details of which depend on the intermolecular forces in question. As will be shown later, the reason the radial distribution function is so important is that it is always intimately involved in any statistical mechanical theory whose purpose is to calculate the thermodynamic properties of solutions from intermolecular forces.

Almost half a century ago, Sisskind and Kasarnowski¹ published a paper that contained what turned out to be a very clever and insightful idea. They suggested that the energetics involved in the transfer of a molecule from the gas phase to a liquid solution be mathematically decomposed into two terms. One of these terms, they suggested, originates from the work that has to be done against the intermolecular forces in the solvent in order to create a cavity that will accommodate the solute about to be transferred. This term represents an energy requirement. A second term, representing an energy gain, arises due to the interaction of the solute molecule in the cavity with the surrounding solvent molecules. A few years after its publication, Uhlig² and Eley³ pursued this idea in their work on solubility. Uhlig correlated the surface tensions of a variety of pure liquids with the solubilities of gases in these liquids. Uhlig used the macroscopic surface tension of a liquid to calculate the work required to create a cavity. Eley's approach differed from Uhlig's principally in the way in which he calculated the cavity term. Eley used macroscopic solvent compressibilities for this calculation. For a number of reasons, neither Uhlig nor Eley could come up with quantitative predictions of solubility. These include the inappropriateness of macroscopic surface tensions or compressibilities in the calculation of the work required to make microscopic cavities and the unavailability (at the time) of accurate pair potentials and radial distribution functions, both of which are needed to calculate the second of the two terms—the solute–solvent interaction term.

The next major advance was made about 25 years later by Robert Pierotti,⁴ who took the same general

approach as Sisskind, Kasarnowski, Uhlig, and Eley, but Pierotti used a newly developed statistical-mechanical theory called the scaled particle theory⁵ (SPT) in order to calculate the cavity term. Pierotti equated the cavity term in a real solution to the reversible work required to create a cavity in the dense assembly of hard spheres. The scaled particle theory provides explicit expressions for the thermodynamic functions that characterize dense hard-sphere or hard convex-like molecule assemblies. But there still remained two fundamental problems with Pierotti's approach. First, a real solution is not comprised of hard spheres, so that Pierotti's estimate of the cavity term is only an estimate. Second, and perhaps more serious, was the fact that theoretical expressions for the distribution functions were unavailable when Pierotti did his work. Thus Pierotti was forced to approximate $g(r, \rho, T)$ by unity, and therefore he was unable to calculate the contribution made by the solute–solvent interaction term in a fundamental way. Further on in this Account we show how the cavity and interaction terms can be accounted for in a rigorous way.

By the early 1970s, all the ingredients needed for a truly fundamental solubility theory (applicable to isotropic systems) had become available. These ingredients included: (1) accurate intermolecular pair potentials obtained from the gas phase by using molecular beams, gas viscosities, and virial coefficients and from solid-state studies; (2) detailed knowledge of the radial distribution function in some prototype of a dense isotropic fluid (The development of Monte Carlo simulations, molecular dynamics calculations, and the solution of integral equations such as the Percus–Yevick equation for dense fluids provided this information. The prototype fluid was the dense hard-sphere fluid and the above methods provided the needed distribution functions, both for pure hard-sphere assemblies and for hard-sphere mixtures); (3) a procedure for connecting the properties of a hard-sphere system to those of the system of interest. This connection was provided in a rigorous way by a procedure called either thermodynamic perturbation theory or liquid-state perturbation theory, the salient features of which are outlined below.

Thermodynamic Perturbation Theory

In the late 1960s Verlet, using computer simulations of hard-sphere assemblies, showed that the structure of a hard-sphere fluid was quite similar to that of a real isotropic fluid in which attractive forces exist.⁶ This result and others like it led to the view that the structure, i.e., $g(r, \rho, t)$, of dense isotropic liquids is determined primarily by the repulsive part of the pair potential. Consequently, the influence of the attractive part of the potential on the thermodynamic properties of a fluid can be obtained by a perturbation expansion around a hard-sphere reference state. The required formalism had been previously provided by Zwanzig.⁷ The first-order result provided by this theory is given by eq 1,

$$A = A_0 + 2\pi N\rho \int_0^\infty r^2 u_p(r) g_0(r) dr + \dots \quad (1)$$

(1) B. Sisskind and I. Kasarnowsky, *Z. Anorg. Allgem. Chem.*, **214**, 385 (1933).

(2) H. H. Uhlig, *J. Phys. Chem.*, **41**, 1215 (1937).

(3) D. D. Eley, *Trans. Faraday Soc.*, **35**, 1281 (1939).

(4) R. A. Pierotti, *J. Phys. Chem.*, **67**, 1840 (1963).

(5) H. Reiss, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.*, **31**, 369 (1959); H. Reiss, H. L. Frisch, E. Helfand, and J. L. Lebowitz, *ibid.*, **32**, 119 (1960); E. Helfand, H. Reiss, H. L. Frisch, and J. L. Lebowitz, *ibid.*, **33**, 1379 (1960); H. Reiss, *Adv. Chem. Phys.*, **9**, 1 (1965).

(6) L. Verlet, *Phys. Rev.*, **165**, 201 (1968).

(7) R. Zwanzig, *J. Chem. Phys.*, **22**, 1420 (1954).

where A and A_0 are the Helmholtz free energy in the real and reference system respectively, $g_0(r)$ is the radial distribution function in the reference state, and $u_p(r)$, the perturbing pair potential, is given by eq 2. In eq

$$u_p(r) = u(r) - u_0(r) \quad (2)$$

$2 u(r)$ and $u_0(r)$ are the actual and reference state intermolecular pair potentials, respectively.

The infinite series represented by eq 1 will converge rapidly (i.e., the first two terms shown in the series will accurately approximate A) if $\beta u_p(r)$ is small, i.e., if the temperature is high relative to the perturbing potential. It can also be made to converge rapidly at low temperatures and high densities if the division of $u(r)$ into $u_p(r)$ and $u_0(r)$ be such that $g_0(r)$ closely approximates $g(r)$. Since, as already mentioned, the structure of a dense isotropic liquid is determined primarily by the repulsive part of the pair potential, $g_0(r)$ will closely approximate $g(r)$ at high densities if $u_0(r)$ is based on the repulsive part of the pair potential. We will return to this point further on in this Account. The higher order terms in the series are complicated and difficult to evaluate accurately because they involve integrals over higher order reference-state distribution functions (e.g., triplet, quadruplet . . . distribution functions) about which little is known. This is one of the problems encountered in the direct application of Zwanzig's theory to liquids. Another is the problem of how to separate $u(r)$ into $u_0(r)$ and $u_p(r)$.

For these reasons three different perturbation theories, similar in spirit but different in detail from Zwanzig's, have been developed.⁸⁻¹³ They all provide an objective basis for the separation discussed above, and also they were formulated to ensure rapid convergence of the series shown in eq 1.

Before describing these theories it is worthwhile to mention one additional problem that occurs when perturbation theory is applied to mixtures as opposed to pure fluids. If we consider a binary solution in which the solute has a significantly deeper well depth than the solvent, then the solute may tend to form clusters or aggregates because of the attractive part of its pair potential, so that for this situation the first two terms in eq 1 will provide an inadequate approximation for A , and higher order terms have to be included.^{14,15} Fortunately this problem is not strongly relevant to the present application wherein the solute is always at infinite dilution and so cannot form clusters.

The first-order expressions for binary mixtures that obey classical statistics with pairwise additive intermolecular potentials are given by eq 3-5 for the Leonard-

$$\beta f = \beta f^0 - 4\pi\rho x_1 x_2 d_{12}^2 g_{12}^0(d_{12})[d_{12} - \delta_{12}] + 2\pi\rho\beta \sum_{i,j=1}^2 x_i x_j \int_{\sigma_{ij}}^{\infty} u_{ij}^p(r) g_{ij}^0(r) r^2 dr \quad (3)$$

(8) J. A. Barker and D. Henderson, *J. Chem. Phys.*, **47**, 4714 (1967).

(9) P. J. Leonard, D. Henderson, and J. A. Barker, *Trans. Faraday Soc.*, **66**, 2439 (1970).

(10) G. A. Mansoori and F. B. Canfield, *J. Chem. Phys.*, **51**, 4958 (1969).

(11) G. A. Mansoori and T. W. Leland, Jr., *J. Chem. Phys.*, **53**, 1931 (1970).

(12) J. D. Weeks, D. Chandler, and H. C. Andersen, *J. Chem. Phys.*, **54**, 5237 (1971).

(13) L. L. Lee and D. Levesque, *Mol. Phys.*, **26**, 1351 (1973).

(14) D. Henderson, *J. Chem. Phys.*, **61**, 926 (1974).

(15) S. H. Sung, D. Chandler, and B. G. Alder, *J. Chem. Phys.*, **61**, 932 (1974).

$$\beta f = \beta f^0 + 2\pi\rho\beta \sum_{i,j=1}^2 x_i x_j \int_{d_{ij}}^{\infty} u_{ij}^p(r) g_{ij}^0(r) r^2 dr \quad (4)$$

$$\beta f = \beta f^0 + 2\pi\rho\beta \sum_{i,j=1}^2 x_i x_j \int_0^{\infty} u_{ij}^p(r) e^{-\beta u_{ij}^0(r)} y_{ij}^{\text{HS}}(r) r^2 dr \quad (5)$$

Henderson-Barker,^{8,9} variational or Mansoori-Canfield,^{10,11} and Weeks-Chandler-Andersen^{12,13} theories, respectively. In each of these equations the division of $u(r)$ into $u_p(r)$ and $u_0(r)$ is different (see below), so that the terms βf^0 , $u_{ij}^p(r)$, and $g_{ij}^0(r)$ are all different. Hereafter we will use the abbreviations LHB, MC, and WCA for these theories. In these equations

$$\beta f = \frac{A(N_1, N_2, V, T) - A^{\text{ig}}(N_1, N_2, V, T)}{(N_1 + N_2)KT}$$

is the reduced Helmholtz free energy per particle relative to this quantity in an ideal gas mixture at the same N_1 , N_2 , V , and T as the solution of interest. βf^0 is this quantity for the reference state mixture. Also x is mole fraction, ρ is total number density = $(N_1 + N_2)/V$, the superscripts 0, p, and HS mean reference state, perturbation, and hard sphere, respectively, d_{ij} is the hard-sphere reference-state diameter between particles i and j , and $y_{ij}^{\text{HS}}(r)$ is the hard-sphere radial distribution function, smoothly extrapolated to $r = 0$. The term δ_{12} in eq 3 is similar in magnitude to d_{12} .

The LHB and MC theories are both based on a hard-sphere reference state, but the way in which the hard-sphere diameters are calculated differ.⁸⁻¹¹ The WCA theory is not based on hard-sphere reference state. Rather it is obtained from the following division of the potential $u(r)$

$$u_0(r) = u^{\text{LJ}}(r) + \epsilon, r < r_m \\ = 0, r \geq r_m$$

$$u_p(r) = -\epsilon, r < r_m \\ = u^{\text{LJ}}(r), r \geq r_m$$

where $u^{\text{LJ}}(r)$ is the Lennard-Jones 6-12 pair potential.¹⁶ In this particular division $u_0(r)$ is based on all the repulsive forces in the Lennard-Jones system. Consequently $g_0(r)$ will very closely resemble $g(r)$,¹⁷ so that the first two terms in eq 1 will provide a particularly good approximation for A .

Thermodynamics

We now connect the measurable quantities that arise in solubility investigations with the statistical-mechanical quantity βf which is calculable from any one of eq 3 to 5.

The most commonly used measure of solubility of a volatile solute is the Henry's law constant. For a vapor phase over a solution that is reasonably dilute (i.e., $P \lesssim 10$ atm) the solute in the vapor phase may be considered to behave as an ideal gas. Under these circumstances the Henry's law constant (K) of the solute is given by eq 6, where P is the partial pressure of the

$$K = \lim_{x_2 \rightarrow 0} (P_2/x_2) \quad (6)$$

(16) The Lennard-Jones 6-12 pair potential has the form

$$u(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$$

$u(r)$ has a minimum equal to $-\epsilon$ at $r = 2^{1/6}\sigma$; $u(r)$ is zero when $r = \sigma$.

(17) D. Chandler, *Acc. Chem. Res.*, **7**, 246 (1974).

solute over the solution and x_2 is the mole fraction of the solute in the solution. From this definition and the usual thermodynamic relations we obtain¹⁸ eq 7-9. In

$$\ln K = \ln \left(\frac{RT}{\bar{V}_1} \right) + (\beta f)^* + n^1 \left(\frac{\partial \beta f}{\partial n_2} \right)_{n,T,V}^* \quad (7)$$

$$\Delta H_s^* = -RT^2 \left(\frac{\partial \ln K}{\partial T} \right)_P \quad (8)$$

$$\bar{V}_2^* = RT \left(\frac{\partial \ln K}{\partial P} \right)_T \quad (9)$$

these equations R is the gas constant, subscripts 2 and 1 mean solute and solvent, respectively, \bar{V}_1 is the molar volume of the pure solvent, n denotes number of moles, and the superscript $*$ denotes the limit $x_2 \rightarrow 0$; ΔH_s^* and \bar{V}_2^* are respectively the molar heat of solution and the partial molar volume of the solute at infinite dilution.

Microscopic Basis of Cavity Term and Solute-Solvent Interaction Term

We have in eq 7 a connection between solubility and terms that directly involve the energetics of the solution process at a microscopic level. For example, if eq 4 from the variational theory is used for βf in eq 7, we obtain^{19,20} eq 10,

$$\ln K = \ln \left(\frac{RT}{\bar{V}_1} \right) + \beta \mu_2^* (\text{hard sphere}) + I_{11}^* + I_{12}^* \quad (10)$$

where

$$\beta \mu_2^* (\text{hard sphere}) = \beta f^* (\text{hard sphere}) + N_1 \left(\frac{\partial \beta f(\text{hard sphere})}{\partial N_2} \right)_{N_1,T,V}^*$$

$$I_{11}^* = 2\pi\rho N_1\beta \left[\frac{\partial}{\partial N_2} \left(\int_{d_{11}}^{\infty} r^2 u_{11}(r) g_{11}^{\text{HS}}(r) dr \right)_{N_1,T,V} \right]^*$$

$$I_{12}^* = 4\pi\rho_1\beta \int_{d_{12}}^{\infty} r^2 u_{12}(r) g_{12}^{\text{HS}}(r) dr$$

The $\ln(RT/\bar{V}_1)$ term arises solely because of a different choice for the solute standard state in the liquid and gas phases, so that it is not involved in either the cavity or the interaction terms. The term $\beta \mu_2^*(\text{hard sphere})$, on the other hand, comes from the reversible work required to create a cavity of diameter d_{22} in a hard-sphere system of particles with diameter d_{11} at the same density, temperature, and composition (infinite dilution with respect to the solute) as the solution of interest. Clearly, however, there has to be an additional term that corrects the hard-sphere cavity term to a cavity term for the soft-sphere system of interest. It was first pointed out by Neff and McQuarrie²¹ that the term represented by I_{11}^* provides this correction to the first order. As may be seen by examining the expression for I_{11}^* , this term arises because of a *change* in the total solvent-solvent interaction potential energy beyond that accounted for by hard-sphere potentials. This change is brought about by the creation of a cavity in

a real solvent. The presence of the cavity causes the solvent structure to be altered from what it is in the absence of a cavity, and this results in a change in the total solvent-solvent interaction potential energy. Finally, the solute-solvent interaction energy is accounted for by the term I_{12}^* . The fact that this term has the form of the integral shown has long been known. What is new is our ability to obtain accurate values of I_{12}^* because of our newly acquired knowledge of the term $g_{12}^{\text{HS}}(r)$ in the integrand of this term.

Results

The results given below are grouped into four categories which result from the different types of problems to which the theoretically derived equations were applied. As will be seen, the applications differ in degree of rigor from somewhat ad hoc to fundamental. The computational details will of course not be given here. They can be obtained from ref 18, 20-26.

(a) Preferential Solvation in Mixed Solvents.^{22,23}

This application, which is in the ad hoc category, was undertaken because of the importance of this subject to chemists and because a truly microscopic theory had never before been applied to a phenomenon that so obviously is microscopic in origin.

We call this application ad hoc because it was necessary to approximate the solvent-solvent and solvent-water pair potentials by "effective" isotropic potentials and because it proved necessary to obtain the effective water-solvent pair potentials by fitting to experimental solubility data in the unmixed solvents. The idea is really quite simple. Water is known to obey Henry's law up to saturation in each of pure benzene, carbon tetrachloride, and cyclohexane.²² Also the solubility of water in benzene, carbon tetrachloride, and cyclohexane is in the ratio of about 10:4:1. Therefore, we might expect that water may be preferentially solvated by benzene when dissolved in the binary mixtures benzene-cyclohexane or benzene-carbon tetrachloride and by carbon tetrachloride when dissolved in binary mixtures of carbon tetrachloride and cyclohexane. The Henry's law constants of water in the pure and mixed solvents were experimentally determined,^{22,23} and all that remained was to devise a theory that would quantitatively predict the Henry's law constants of water in the mixed solvents, under the assumption of *no* preferential solvation of the water. Then a comparison of theory and experiment would provide a basis for deciding whether preferential solvation of the water occurred in any of the systems. The theoretical expression for the Henry's law constant was a modified, three-component version of eq 10.²³ The condition of no preferential solvation of the water in the mixed solvent systems was incorporated into the theoretical expression for $\ln K$ by using hard-sphere radial distribution functions to characterize the water-solvent and solvent-solvent distribution functions.

Some of the results obtained are displayed in Figure 1 from which it is seen that in the benzene-cyclohexane mixed solvents the experimental points (open circles) fall systematically below the theoretical curve, but that

(18) S. Goldman, *J. Solution Chem.*, **6**, 461 (1977).

(19) D. A. McQuarrie, "Statistical Mechanics", Harper and Row, New York, 1976, pp 324-325.

(20) S. Goldman, *J. Phys. Chem.*, **81**, 608 (1977).

(21) R. O. Neff and D. A. McQuarrie, *J. Phys. Chem.*, **77**, 413 (1973).

(22) S. Goldman, *Can J. Chem.*, **52**, 1668 (1974).

(23) S. Goldman and T. R. Krishnan, *J. Solution Chem.*, **5**, 693 (1976).

(24) S. Goldman, *J. Chem. Phys.*, **67**, 727 (1977).

(25) D. Henderson, *Annu. Rev. Phys. Chem.*, **25**, 461 (1974).

(26) S. Goldman, *J. Chem. Phys.*, **69**, 3775 (1978).

Table I
Deviations between the Classically Calculated Values of K , \bar{V}_2^* , and ΔH_s^* (cal/mol) and the Corresponding Quantum-Corrected Values for H_2 , He, and Ne in C_6H_6

$t, ^\circ C$	$K(\text{quantum})/K(\text{classical})^a$			$\bar{V}^*(\text{quantum})/\bar{V}_2^*(\text{classical})^a$			$\frac{\Delta H_s^*(\text{quantum}) - \Delta H_s^*(\text{classical})^a}{\Delta H_s^*(\text{classical})^a}$		
	H_2	He	Ne	H_2	He	Ne	H_2	He	Ne
20	1.066	1.021	1.008	1.022	1.008	1.003	90	29	12
60	1.047	1.015	1.006	1.018	1.007	1.003	77	25	10
100	1.035	1.012	1.004	1.016	1.006	1.002	68	22	8.7
150	1.024	1.008	1.003	1.013	1.005	1.002	62	20	7.9
200	1.017	1.006	1.002	1.011	1.004	1.001	59	19	7.4

^a The experimental values of K , \bar{V}_2^* , and ΔH_s^* for H_2 in C_6H_6 at 25 $^\circ C$ are 3.38×10^3 atm, 35 cm^3/mol , and 1520 cal/mol, respectively; see E. B. Smith and J. Walkley, *J. Phys. Chem.*, **66**, 597 (1962), and J. H. Hildebrand and R. L. Scott, "Regular Solutions", Prentice-Hall, Edgcliff, NJ, 1962. ^b The results for the quantum effect on ΔH_s^* are expressed as a difference rather than a ratio, since ΔH_s^* for the H_2 in C_6H_6 system goes through zero in the range 20–200 $^\circ C$.

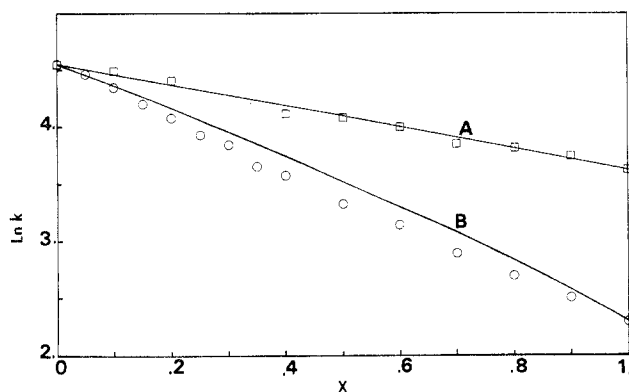


Figure 1. Variation of the Henry's law constant of water with solvent composition in the water-carbon tetrachloride-cyclohexane system (A) and the water-benzene-cyclohexane system (B). Points are experimental values. For curves A and B, X is the mole fraction of carbon tetrachloride and benzene, respectively. The curves were calculated by fitting to the end points ($X = 0$ and 1) and by assuming no preferential solvation.

no such discrepancy occurs in the cyclohexane-carbon tetrachloride mixture (open squares). The results for the benzene-carbon tetrachloride system are similar to those for the benzene-cyclohexane solvent. Since a lower K (or $\ln K$) means a higher solubility, it was concluded that water was preferentially solvated by benzene in the benzene-containing mixed solvents, but that no significant preferential solvation of the water occurred in the carbon tetrachloride-cyclohexane mixed solvent. A hydrogen-bonding-like interaction between water and the π -electron cloud in benzene seemed to be a reasonable explanation for these results. Thus the extra energy from this interaction makes possible some microscopic unmixing of the binary solvent mixture so as to provide the water with more benzene molecules in its immediate vicinity.

(b) **The Influence of Quantum Effects.**²⁰ It is easy to show, on the basis of the much smaller mean free path in liquids than in gases, that conditions which ensure the validity of classical statistical mechanics are much more readily found in the gas phase than in solution.²⁰ This difference in the degree of validity of classical statistics makes it necessary to correct the theoretical solubility expressions based on classical statistics for those systems in which the temperature is low ($T < 150$ K) or the solute is light (i.e., molecular mass < 20) or both. For systems in which the quantum deviations are not too large (e.g., excluding solutions involving H_2 or He near absolute zero) the deviations can be treated as a perturbation on the classical result. The

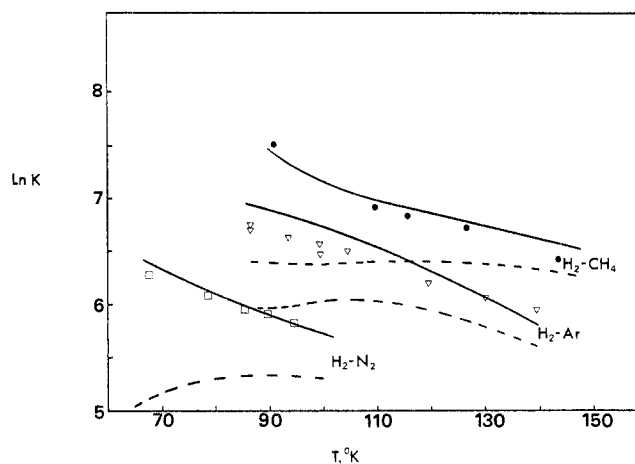


Figure 2. Calculated and experimental Henry's law constants for hydrogen. The solid and broken curves give the quantum-corrected and classical results respectively. The data source was M. Orentlicher and J. M. Prausnitz, *Chem. Eng. Sci.*, **19**, 775 (1964). (●) H_2 in CH_4 ; (▽) H_2 in Ar; (□) H_2 in N_2 .

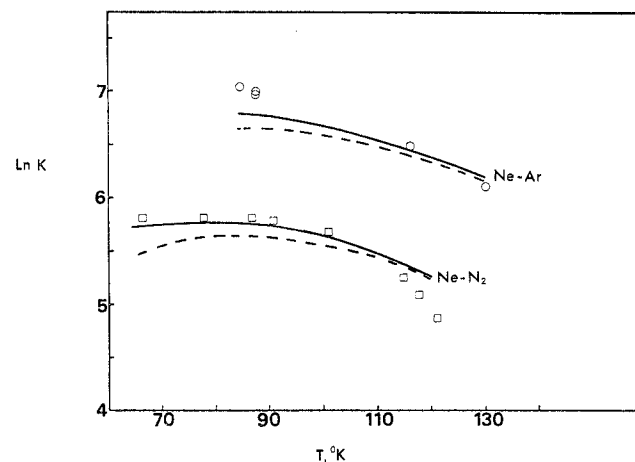


Figure 3. Calculated and experimental Henry's law constants for neon. Curves are explained in caption for Figure 2. Data sources: Ne in Ar, W. B. Streett, *J. Chem. Phys.*, **42**, 500 (1965); Ne in N_2 , W. B. Streett, *Cryogenics*, **5**, 27 (1965). (○) Ne in Ar; (□) Ne in N_2 .

detailed expressions for the first-order quantum correction to the Helmholtz free energy and the chemical potential have been given elsewhere,²⁰ and here we focus on some of the results that were found.

It is seen from Figures 2 and 3 and Table I that the effect of including the correction for quantum deviations is to raise the calculated values of K , ΔH_s^* , and \bar{V}_2^* relative to what is obtained on the basis of purely

Table II
Comparisons of Calculated and Experimental Values of $\ln K$, ΔH_s° , and \bar{V}_2° for Ne in Ar

T, K	$\ln(K/\text{atm})$				ΔH_s° , cal/mol				\bar{V}_2° , cm ³ /mol			
	LHB	MC	WCA	exptl ^a	LHB	MC	WCA	exptl ^a	LHB	MC	WCA	exptl ^a
87.29	6.77	7.40	6.93	6.99	132	288	159	201	23.1	27.2	26.1	25
87.42	6.77	7.40	6.92	6.97	132	289	159	232	23.2	27.3	26.1	-
115.80	6.48	6.88	6.56	6.48	437	627	461	597	40.5	47.3	43.8	45

^a These values are from W. B. Streett, *J. Chem. Phys.*, 42, 500 (1965); the ΔH_s° have an estimated uncertainty of 150 cal/mol.⁴ ^b These values are from W. B. Streett, *J. Chem. Phys.*, 46, 3282 (1967); their uncertainty is estimated to be 5 cm³/mol.

classical statistical mechanics. More specifically, we see from Figure 2 that the inclusion of the quantum term is crucial for quantitative agreement with experiment when the solute is H₂ and the solvent is either liquid N₂, Ar, or CH₄. We see from Figure 3 that the quantum correction for Ne in either liquid N₂ or Ar is significant at the lower temperatures shown but that it becomes less important as the temperature goes up.

Table I demonstrates the result that for H₂ in benzene at ordinary temperatures the quantum term contribution to K and to ΔH_s° cannot be neglected since it contributes between 5 and 10% toward the overall value of these functions. The quantum correction to \bar{V}_2° is relatively small. Table I also demonstrates the result that quantum deviations in solubility calculations can be neglected in ordinary solvents at ordinary or high temperatures provided the solute has a molecular mass equal to or greater than that of He. This limit was never before established.

(c) Relative Accuracy of Different Perturbation Theories in Solubility Calculations.²⁴ Each of eq 3 to 5 is based on a different perturbation theory. Consequently, by using each of these equations in eq 7 to 9 and applying the result to a particular system, we can intercompare the three theories with respect to how well they predict experimental results, and we can learn how sensitive a particular solubility function (e.g., K , ΔH_s° , or \bar{V}_2°) is to the theory being used to obtain it. This was done for a variety of systems,²⁴ and a sample of the results obtained are displayed in Table II for the system Ne in Ar. In these calculations the same intermolecular pair potentials, taken from gas-phase virial coefficients, were used. We see from Table II that the LHB and WCA theories provide similar and good predictions for $\ln K$, but that the predictions from the MC theory are worse. The relatively poor performance of the MC theory is believed due to the fact that the upper bound on the free energy that this theory is based on^{10,11} is too high a bound to be useful for highly accurate solubility predictions. The closeness of the predictions of the other two theories (both to experimental results and to each other) is remarkable. The WCA theory is known to be more accurate than first-order LHB theory with respect to the prediction of total thermodynamic properties (e.g., βf).²⁵ Apparently the function

$$(\beta f)^\circ + n_1 \left(\frac{\partial \beta f}{\partial n_2} \right)_{n_1, T, V}^\circ$$

upon which solubility depends (see eq 7) entails a fair amount of cancellation among the higher order terms left out in the LHB theory.

We see from Table II that all three theories predict the functions ΔH_s° and \bar{V}_2° to within experimental error.

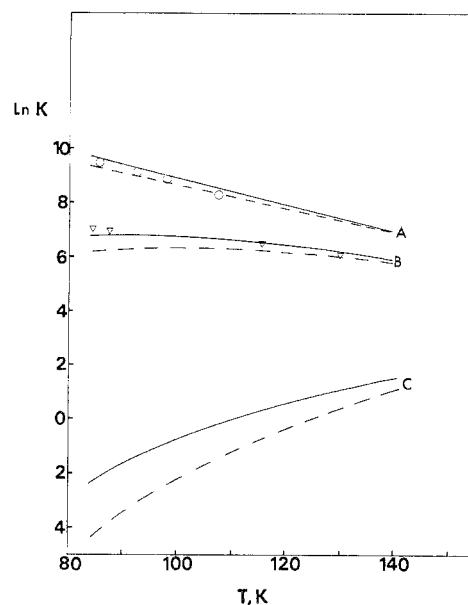


Figure 4. Calculated and experimental Henry's law constants. Labels A, B, and C refer to the systems He in Ar, Ne in Ar, and Kr in Ar, respectively. The solid curves include the three-body dispersion nonadditive term; the dashed curves do not. Data sources: Ne in Ar, W. B. Streett, *J. Chem. Phys.*, 42, 500 (1965); He in Ar, K. A. Solen, P. L. Chueh, and J. M. Prausnitz, *Ind. Eng. Chem. Process Des. Dev.*, 9, 310 (1970). (∇) Ne in Ar; (\circ) He in Ar.

Unfortunately this is a consequence of the sizeable uncertainty in the experimental values of these functions. The spread in the predicted values of these quantities that results from the use of the different theories is certainly significant; presumably the WCA predictions are the most accurate.

(d) The Role of Nonadditivity of the Pair Potentials.²⁶ A feature shared by all previous generations of solubility theories was the assumption of perfect additivity of the intermolecular pair potentials. This obviously cannot be perfectly true because the presence of other particles around an interacting pair will, because of their interactions with the pair, alter the pair potential from what it would be in the absence of neighboring particles.

It is generally believed (at least for isotropic particles) that the most important of the higher-body nonadditive terms is that due to three-body dispersion forces, for which the potential energy is given by the Axilrod-Teller formula.²⁷ As with quantum deviations, three-body nonadditive effects can be formally dealt with by treating them as a perturbation to the two-body (i.e., pairwise additive) result. The detailed form of the first-order correction to βf due to this effect has been

(27) B. M. Axilrod and E. Teller, *J. Chem. Phys.*, 11, 299 (1943).

given elsewhere,^{26,28} and here we will concentrate on the results obtained.

Some of the results of the calculations for $\ln K$ are shown in Figure 4, from which the following principal features are apparent. (1) The effect of including the triple-body dispersion term is to raise the calculated values of K relative to the values obtained for this quantity using only two-body forces. (2) The relative influence of the three-body term on K increases in the order (He in Ar) < (Ne in Ar) < (Kr in Ar). The effect is so pronounced in the system Kr in Ar that it is unlikely that "effective" pair potentials (which are contaminated by nonadditive effects) could ever properly account for the thermodynamics of this or of any system with a large solute:solvent size ratio. (3) Inclusion of the three-body nonadditive term results in excellent agreement with experimental data in those systems for which data are available. For the system Ne in Ar, where inclusion of this term significantly alters the calculated values of K , the agreement with experiment is improved relative to what is obtained by assuming pairwise additivity. Similar conclusions are drawn by examining the effect of nonadditivity on the functions ΔH_s° and \bar{V}_2° .²⁶

What Next?

The next major challenge would seem to be the calculation, from a rigorous molecular basis, of solubilities and related functions in complex chemical systems, i.e., those in which anisotropic forces such as anisotropic overlap and dispersion forces, multipolar forces, and charge-transfer forces play a significant role. For example, a rigorous molecular interpretation of the solubility and the temperature and pressure derivatives of the

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solubility of benzene in water is still not feasible. The barriers to such a calculation are of two types. First, the relevant, full angle-dependent intermolecular potentials are not available for complex polyatomic molecules. A considerably less severe, but still significant, restriction is the absence of a statistical-mechanical formalism capable of accommodating dense fluids wherein the intermolecular interactions are strongly anisotropic. There have been a number of attempts made recently to deal with this problem,²⁹⁻³³ the most promising of which is, in the opinion of the author, one due to Gray and Gubbins,³¹⁻³³ who use perturbation theory to express the free energy of an anisotropic fluid as an expansion around that of an isotropic (e.g., Lennard-Jones) reference state. These authors have applied their theory to investigate the role of anisotropic forces in phase separations and related phenomena. While the theory is in principle applicable to molecules with any degree of anisotropy, difficulties are encountered in the evaluation of the higher order terms in the expansion, which become increasingly important as the anisotropy becomes large. For example, a molecule such as benzene, which is moderately anisotropic in its shape, or water, which manifests strong multipolar anisotropy (i.e., hydrogen bonding), can only just barely, if at all, be accommodated by this theory. More highly anisotropic molecules cannot. It seems likely that improvements in this theory, which would increase the range of its applicability, will be developed in the near future.

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Molecular Structure and Bonding in the 3d Metallocenes

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Received June 12, 1979

The accidental and independent discovery of dicyclopentadienyliron, now better known as ferrocene, was reported by two research groups in 1951 and 1952.¹ This was the first pure hydrocarbon derivative of iron to be prepared, and its exceptional stability caused considerable excitement. Ferrocene is not only unaffected by air, moisture, and heat up to 470 °C, it can be boiled in concentrated hydrochloric acid or 10% caustic soda without decomposition. Even somebody

who had not completed his secondary education at the time can feel some of this excitement when reading the literature. Within months the then novel but now well-known sandwich model had been proposed by Wilkinson, Rosenblum, Whiting, and Woodward^{2a} in the United States and independently by Fischer and Pfab^{2b} in Germany, and confirmed by X-ray crystallography.³ During the following years the dicyclo-

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