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MOLECULAR THERMODYNAMICS OF GAS SOLUBILITY

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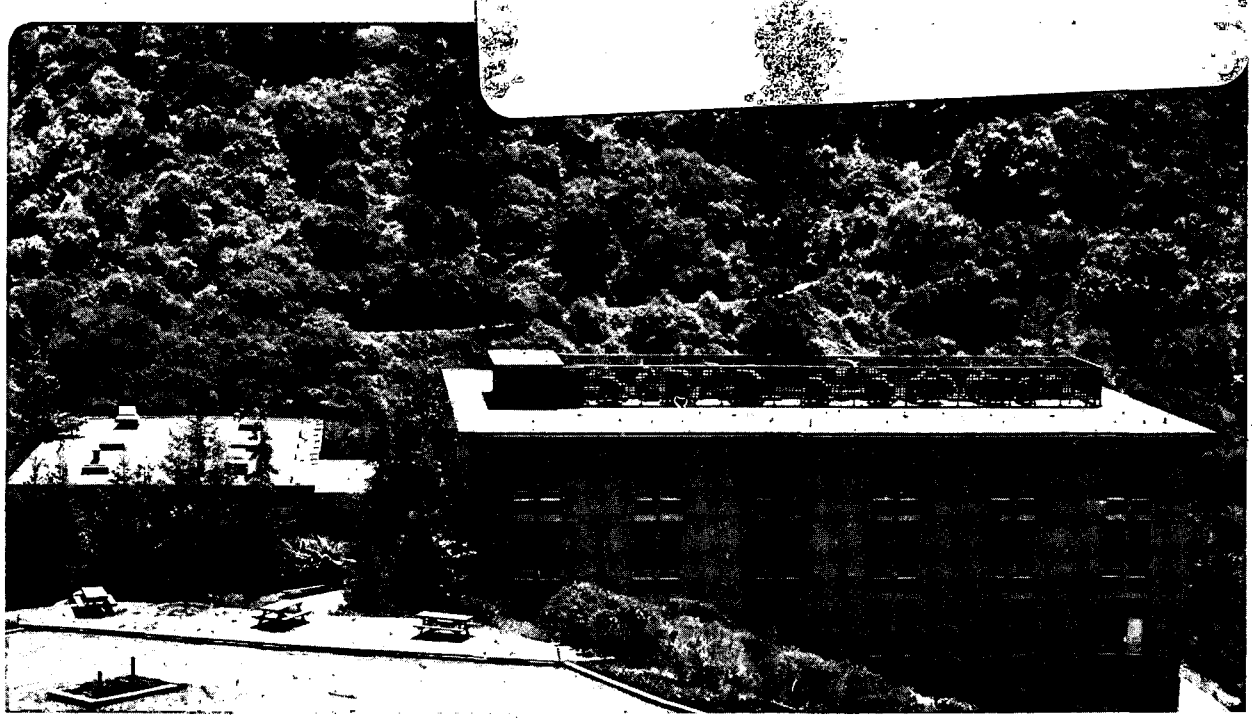

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Molecular Thermodynamics of Gas Solubility

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Abstract

A molecular-thermodynamic model has been established for the solubilities of gases in non-polar and polar solvents and in aqueous solutions of electrolytes. To obtain an expression for the Helmholz energy of the mixture, the pure components are first mixed isothermally to form an ideal gas mixture. Then each particle in the mixture is inflated into a hard sphere. Finally, all particles are charged with an appropriate potential to form a real liquid mixture; this charging step is based on an ordered first coordination shell and a random mixture beyond that first shell. This model agrees well with computer-simulation data. Calculated and observed Henry's constants are in good agreement over a wide range of temperature for various gases in benzene, cyclohexane, n-hexane, hexadecane and water, and in aqueous solutions of NaCl and KOH.

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Introduction

Numerous efforts have been made to correlate the solubilities of gases in liquids using a molecular theory of fluids. Success has been limited primarily because previous authors have given inadequate attention to the radial distribution function for a gaseous solute in a liquid solvent as a function of solvent density and temperature. In this work, we use an algebraic approximation to the radial distribution function; in our previous work on liquid mixtures, this approximation has shown good agreement with computer-simulation results and with experimental data for simple liquid mixtures[23].

Pierotti's work in 1963-1965[1,2,3] provided a pioneering step in applying a molecular theory of fluids to gas solubility. In Pierotti's theory, the process of dissolving a gas in a liquid was described by first creating in the solvent a cavity with the diameter of the solute, then charging the dissolved solute with an appropriate potential. The work required for creating a cavity was calculated using scaled-particle theory[4]. For the second step, Pierotti ignored the radial distribution function; he used a random distribution and a Lennard-Jones potential to calculate the potential energy. Pierotti's theory can be used to correlate Henry's constants for gases in non-polar solvents and water as shown by several authors, including Wilhelm, Battino and Wilcock[30] and Schulze and Prausnitz[5]. Shoor and Gubbins[6,7] and Masterton and Lee[8] applied scaled-particle theory to correlate solubilities of gases in concentrated electrolytic solutions: their results are superior to those obtained from standard electrostatic theories such as those of Debye and McAulay[9], Conway, Desnoyers and Smith[10], and from the internal-pressure theory of Long and McDevit[11]. Despite this success, some of Pierotti's basic assumptions have evoked much controversy: in particular, Pierotti used the pressure of the system instead of that of the corresponding hard-sphere mixture as required by the scaled-particle theory, and for real liquid mixtures, he ignored short-range order. Several authors have commented on these assumptions[12,13,14].

In 1967, Snider and Herrington[15] obtained results similar to those of Pierotti's by adding a van der Waals attraction term to the hard-sphere equation of state. In 1973, Neff and McQuarrie[12] derived a formula for Henry's constants using the perturbation theory of Barker and Henderson[16,17]; Tiepel and Gubbins[18,19] extended this method to electrolytic solutions by applying the WCA perturbation theory[20]. However, in that theory, it is neccessary to calculate the radial distribution functions of hard-sphere mixtures, and that requires an excessive amount of computer time. In 1981, with the use of direct correlation functions, Mathias and O'Connell[21] developed a method for calculating Henry's constants in several solvents from that in a fixed solvent.

With increasing availability of large computers, it has become possible to calculate thermodynamic properties of mixtures by computer simulation using Monte Carlo or molecular-dynamic techniques[22]. On the basis of these computer-simulation results, Hu, Lüdecke and Prausnitz[23] proposed an algebraic expression for the Helmholtz energy of a mixture which gives results in good agreement with Monte Carlo data reported by Shing and Gubbins[24]. In this work, we extend that expression to calculate Henry's constants in non-polar or polar solvents, including aqueous solutions of electrolytes.

Molecular-Thermodynamic Framework

Based on our previous work[23], we first establish an expression for the Helmholtz energy A of the liquid mixture as a function of volume V, temperature T and mole numbers $n_1, n_2, \ldots, n_K$ of all species including neutral molecules and ions. We begin with pure components in the standard state (ideal gas at 1 bar). We then calculate the isothermal change in Helmholtz energy produced by three steps.

In the first step, the pure ideal gases are mixed to form an ideal-gas mixture at system volume. The corresponding change in Helmholtz energy is

$$\Delta A_{I} = \sum_{i=1}^{K} n_i RT \ln (n_i RT/V) \qquad (1)$$

In the second step, the ideal-gas mixture is changed isometrically to a hard-sphere mixture by inflating each particle i to diameter σ_i . For this step we use the Boublik[28]-Mansoori-Carnahan-Starling-Leland[25] equation.

$$\Delta A_{II} = \frac{\frac{3DE}{F}\xi - \frac{E^3}{F^2}}{(1-\xi)} + \frac{\frac{E^3}{F^2}}{(1-\xi)^2} + \left(\frac{E^3}{F^2} - 1\right) \ln(1-\xi) \qquad (2)$$

where

$$D = \sum_{i=1}^{K} x_i \sigma_i$$

$$E = \sum_{i=1}^{K} x_i \sigma_i^2$$

$$F = \sum_{i=1}^{K} x_i \sigma_i^3$$

Here N_{Av} is Avogadro number.

In the third step, the hard spheres are charged with an appropriate potential ε to form a real mixture. For this step, we introduce a simplified but physically realistic picture for a liquid mixture as shown in Fig. 1 for a binary mixture. The essential idea of this picture is

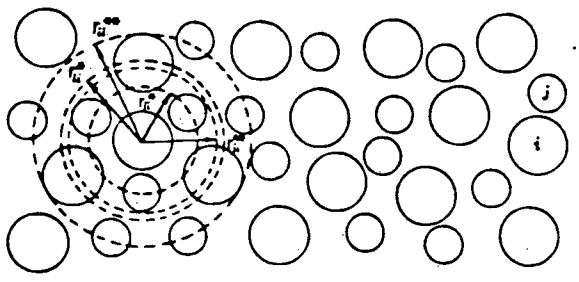

Fig. 1 Short-range order and long-range disorder. After first coordination shell, the fluid is random.

that the radial distribution in a real liquid mixture can be described effectively through a short-order first coordination shell followed by a random environment. As discussed previously [23], the radius of the first shell r^{**} and the location of the particle centers within this shell r^{*} are proportional to the collision diameter σ_{ij} ,

$$r_{ij}^{*} = K^{*}\sigma_{ij} \quad , \quad r_{ij}^{**} = K^{**}\sigma_{ij} \tag{3}$$

Proportionality constants K^{*} and K^{**} are taken from our previous work[23]; they are 1.150 and 1.575 respectively. The change in Helmholtz energy in the third step can then be written as:

$$\Delta A_{III} = \frac{N_{Av}}{2}\sum_{i=1}^{K}\sum_{j=1}^{K}\left[n_i \frac{4}{3}\pi\left(r_{ji}^{**3} - \sigma_{ji}^{3}\right)\rho_j \varepsilon_{ji}(r_{ji}^{*}) + n_i \int_{r_{ji}^{**}}^{\infty} \rho_j \varepsilon_{ji}(r) 4\pi r^2 dr\right] \tag{4}$$

Where ρ_j is the number density of species j. In deriving this equation, we have neglected the density-dependent local compositions within the first coordination shell. This simplification is reasonable because we are here concerned only with dilute solutions.

The Helmholtz energy of the liquid mixture is expressed as:

$$A = \sum_{i=1}^{K} n_i A_i^{o} + \Delta A_{I} + \Delta A_{II} + \Delta A_{III} \tag{5}$$

Where A_i^{o} is the molar Helmholtz energy of species i in the standard state. The chemical potential can be found from

$$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j(i)}} \tag{6}$$

Henry's constant is then obtained from

$$K_{Hi} = \lim_{x_i \to 0} \left[p \exp\left(\frac{\mu_i^{r}}{RT} - \ln Z\right)\right] \tag{7}$$

Where Z is the compressibility factor and μ_i^{r} is the residual chemical potential defined by:

$$\mu_i^{r} = \mu_i(T,V,x) - \mu_i^{ideal\ gas}(T,V,x) \tag{8}$$

Differential heat of solution, entropy of solution and partial molar volume of solute i can be calculated from thermodynamics:

$$\Delta \bar{H}_{si} = \left(\frac{\partial \ln K_{Hi}}{\partial (1/RT)} \right)_P \qquad (9)$$

$$\Delta \bar{S}_{si} = (\Delta \bar{H}_{si} - RT \ln K_{Hi})/T \qquad (10)$$

$$\bar{V}_i = \left(\frac{\partial \mu_i}{\partial p} \right)_{T, n_j} \qquad (11)$$

To apply these relations, it is neccessary to adopt an expression for the potential energy. For molecule-molecule interactions, we use the Lennard-Jones potential with dipole-dipole and dipole-induced dipole contributions,

$$\varepsilon_{ji}(r) = 4\epsilon_{ji}\left[\left(\frac{\sigma_{ji}}{r}\right)^{12} - \left(\frac{\sigma_{ji}}{r}\right)^{6}\right] - \frac{\alpha_i \bar{\mu}_j^2 + \alpha_j \bar{\mu}_i^2}{r^6} - \frac{2}{3kT}\frac{\bar{\mu}_i^2 \bar{\mu}_j^2}{r^6} \qquad (12)$$

Where $\bar{\mu}_i$ and α_i are dipole moment and polarizability of molecule i respectively. For molecle-ion interactions, we also use a Lennard-Jones potential with additional ion-induced dipole and ion-dipole contributions,

$$\varepsilon_{ji}(r) = 4\epsilon_{ji}\left[\left(\frac{\sigma_{ji}}{r}\right)^{12} - \left(\frac{\sigma_{ji}}{r}\right)^{6}\right] - \frac{Z_j^2 e^2 \alpha_i}{2 r^4 D} - \frac{1}{3kT}\frac{Z_j^2 e^2 \bar{\mu}_i^2}{r^4 D} \qquad (13)$$

where e is unit charge, D is dielectric constant and Z_j is charge number of ion j. Because of the compensation effect caused by ions of different signs surrounding the central neutral molecule, the last two terms in Eq. (13) may overestimate the contributions of ion-induced dipole and ion-dipole interactions; therefore we omit the long-range contribution in Eq.(4) as an approximation. Appendix I gives equations for calculating Henry's constants and other thermodynamic functions from Eq. (5).

Comparison with Computer-Simulation Results

Results from computer simulation studies provide a strict standard to test anv theory for predicting fluid properties. In 1983, using an umbrella sampling technique, Shing and Gubbins[24] presented systematic results of Monte Carlo simulation for Lennard-Jones fluid mixtures. The Henry's constants they obtained are plotted against energy parameters and size parameters in Fig.2 and 3. Henry's constants from our model and from

Pierotti's theory are also presented using model parameters identical to those used in the computer simulation. These figures indicate that our model gives results in good agreement with those from computer simulation. The figures also show that Pierotti's model is unsatisfactory, especially when the size difference between the solvent and the solute is appreciable, no matter whether calculations use the pressure of the system (curve 2) or the pressure of the corresponding hard-sphere mixture (curve 3). The success of Pierotti's model in correlating experimental Henry's constants may follow from cancellation of errors.

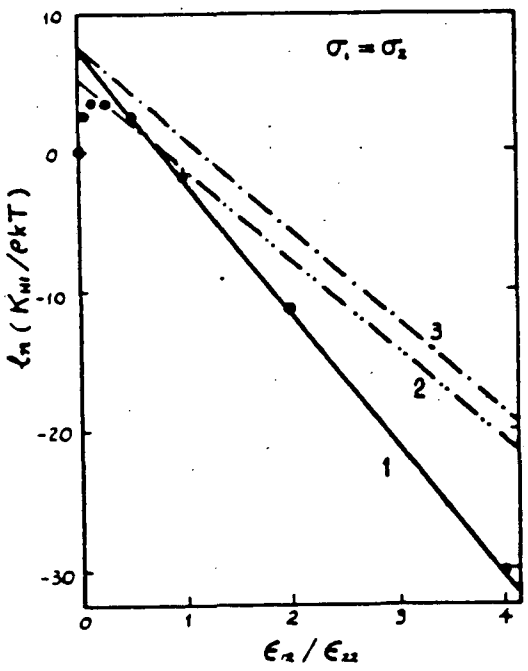

Fig.2 Henry's constants for Lennard-Jones mixtures with various energy ratios $\epsilon_{12}/\epsilon_{22}$
$\epsilon_{22}/k=100K, T=120K, \sigma_{22}=3.405Å, \rho\sigma_{22}^3=0.7$
• -- computer simulation data
1 -- present work
2 -- Pierotti's model using p_{system}
3 -- Pierotti's model using p_{hs}

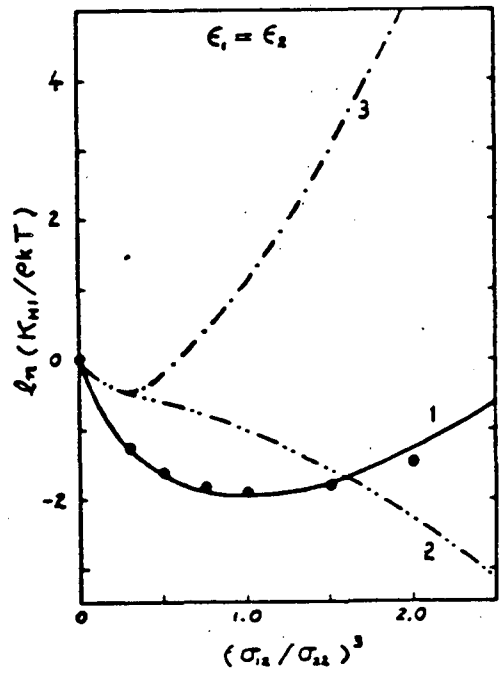

Fig.3 Henry's constants for Lennard-Jones mixtures with various size ratios σ_{12}/σ_{22}
$\epsilon_{22}/k=100K, T=120K, \sigma_{22}=3.405Å, \rho\sigma^3=0.7$
(for symbols, see caption to Fig.2)

In Fig. 2, the apparent disagreement for very small values of $\epsilon_{12}/\epsilon_{22}$ follows from different limits: When $\epsilon_{12}\to 0$, our theory is that for a hard-sphere solute whereas for Shing and Gubbins it is an ideal-gas solute

Henry's Constants for Gases in Non-polar Solvents

When we apply a molecular theoryof fluids to real systems,the first problem is to obtain model parameters. For Henry's constants in a binary mixture, the parameters needed are σ_1 and σ_2 for solute and solvent respectively, and interaction energy parameter ϵ_{12}. In this work, we obtain σ_1 from experimental second virial coefficients for various solutes (except for quantum gases). To obtain σ_2 for solvents, we follow Pierotti's procedure: we first calculate σ_2 at 25°C from Henry's constant for a hard-sphere solute; we obtain that by extrapolating Henry's constants for He and Ne with respect to solute polarizability. We then determine the temperature dependence of σ_2 by using Henry's constants for Ar in that solvent at various temperatures. The only adjustable parameter ϵ_{12} is then estimated by fitting experimental data for Henry's constants. For quantum gases H_2, He and Ne, we first estimate ϵ_{12} using the geometric mean of ϵ_1 and ϵ_2 (taken from second virial coefficients); we then obtain an effective σ_1 by fitting experimental data for Henry's constants.

Tables 1,2 and 3 show Henry's constants for various gases in benzene, cyclohexane and n-hexane, respectively; Henry's constants for a hard-sphere solute are obtained from extrapolation using solubility data for Ne and He. These tables show that with only one adjustable parameter (ϵ_{12} or σ_{1eff}), the correlation is satisfactory. Appendix II gives all parameters used here.

To examine the model for a wider temperature range and for larger differences in size and energy parameters, we examine Henry's constants for various gases in hexadecane. The results are shown in Table 4 and Fig. 4. In these calculations, ϵ_{12} is set equal to $\sqrt{\epsilon_{1eff}\epsilon_2}$; here ϵ_2 of the solvent is determined as a function of temperature using Henry's constants for N_2 as reference while ϵ_{1eff} for N_2 is taken from second-virial-coefficient data. Because of the orientation effect caused by the long chain of hexadecane, it is neccessary to introduce a temperature dependence for ϵ_2. For other gases, ϵ_{1eff} is then estimated by fitting experimental data for Henry's constants. Table 4 and Fig. 4 indicate that for some systems, Henry's

Tab. 1 Henry's constants for gases in benzene

	ln (K_H/bar)									
	hard sphere		Ar		He		Ne		N_2O	
T/K	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.
283.15			7.080	7.081			9.307	9.269	4.115	4.207
288.15	10.035	10.109	7.065	7.065	9.643	9.636	9.228	9.206	4.190	4.249
293.15	10.018	10.022	7.058	7.058	9.570	9.565	9.155	9.143	4.263	4.291
298.15	9.949	9.949	7.045	7.048	9.499	9.496	9.083	9.083	4.332	4.332
303.15	9.877	9.872	7.038	7.038	9.432	9.430	9.015	9.025	4.400	4.372
308.15	9.815	9.798	7.027	7.027	9.364	9.364	8.946	8.971	4.465	4.411
313.15	9.754	9.726	7.017	7.018	9.300	9.305	8.880	8.917	4.529	4.449
318.15			7.007	7.007	9.237	9.236				
ref.			(32)		(33)		(33)		(35)	
	H_2		N_2		O_2		C_2H_6		CH_4	
T/K	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.
283.15	8.418	8.359	7.817	7.826	7.159	7.173	4.023	4.068	6.237	6.274
288.15	8.366	8.320	7.788	7.794	7.150	7.158	4.093	4.125	6.325	6.308
293.15	8.318	8.282	7.758	7.763	7.141	7.145			6.328	6.323
298.15	8.271	8.244	7.725	7.733	7.131	7.132	4.223	4.233		
303.15	8.226	8.208	7.702	7.705	7.122	7.120				
308.15	8.183	8.174	7.676	7.676	7.111	7.107	4.343	4.335		
313.15	8.141	8.140	7.651	7.651	7.099	7.095				
318.15	8.100	8.106	7.625	7.623	7.087	7.083	4.454	4.429		
323.15	8.060	8.074	7.602	7.597	7.075	7.071				
328.15	7.994	8.041	7.579	7.571	7.061	7.059	4.557	4.517		
333.15	7.948	8.039	7.556	7.545	7.049	7.046				
338.15					7.034	7.033				
ref.	(36)		(37)		(38)		(39)		(41)	

Tab. 2 Henry's constants for gases in cyclohexane

	$\ln(K_H/bar)$							
	hard sphere		Ar		N_2		O_2	
T/K	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.
283.15			6.535	6.533	7.240	7.251	6.704	6.724
288.15	9.620	9.620	6.529	6.530	7.221	7.227		
293.15	9.543	9.545	6.529	6.527	7.201	7.205	6.701	6.708
298.15	9.471	9.472	6.522	6.524	7.185	7.183		
303.15	9.410	9.402	6.522	6.521	7.168	7.162	6.698	6.692
308.15	9.337	9.333	6.515	6.517	7.151	7.141		
313.15	9.271	9.266	6.515	6.513			6.694	6.675
318.15			6.509	6.508				
ref.			(32)		(37)		(38)	
	He		Ne		C_2H_6		H_2	
T/K	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.
283.15			8.818	8.776	3.557	3.606		
288.15	9.165	9.144	8.744	8.718	3.632	3.668		
293.15	9.092	9.080	8.675	8.663	3.706	3.730	7.837	7.832
298.15	9.024	9.018	8.611	8.600	3.785	3.788	7.803	7.800
303.15	8.961	8.959	8.545	8.558	3.867	3.846	7.767	7.770
308.15	8.894	8.900	8.484	8.507				
313.15	8.831	8.843	8.424	8.458	3.935	3.952	7.735	7.739
318.15	8.766	8.785			3.989	4.002		
323.15					4.043	4.050		
328.15					4.097	4.098		
333.15					4.150	4.145		
338.15					4.203	4.190		
343.15					4.254	4.234		
348.15					4.305	4.276		
353.15					4.353	4.317		
ref.	(33)		(33)		(39,42)		(36)	

Tab. 3 Henry's constants for gases in n-hexane

	ln (K_H/bar)									
	hard sphere		Ar		He		Ne		C_2H_6	
T/K	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc	expt.	calc
273.15									3.088	3.026
283.15									3.255	3.232
288.15	8.799	8.746	5.954	5.949	8.378	8.330	7.988	7.954		
293.15	8.725	8.701	5.977	5.977	8.323	8.298	7.951	7.936	3.409	3.425
298.15	8.652	8.657	5.997	5.998	8.268	8.260	7.912	7.910	3.484	3.509
303.15	8.582	8.605	6.013	6.017	8.215	8.223	7.878	7.884	3.557	3.583
308.15	8.509	8.559	6.033	6.034	8.162	8.187	7.842	7.858		
313.15	8.440	8.514	6.043	6.050	8.111	8.151	7.807	7.832		
318.15			6.066	6.062						
ref.			(32)		(33)		(33)		(39)	

	H_2			CH_4		N_2O		O_2	
T/K	expt.	calc	T/K	expt.	calc.	expt.	calc.	expt.	calc
213.15	7.899	7.549	273.15						
223.15	7.810	7.568	298.15			4.012	3.972	6.238	6.358
233.15	7.728	7.579	308.15	5.269	5.259				
243.15	7.655	7.579	313.15	5.296	5.294	4.136	4.173	6.502	6.387
253.15	7.526	7.571	318.15	5.321	5.324				
263.15	7.522	7.555	323.15	5.343	5.351			5.502	5.506
273.15	7.482	7.533	328.15	5.363	5.371				
283.15	7.407	7.505	333.16	5.381	5.390				
288.15	7.381	7.495	338.15	5.398	5.399				
293.15	7.355	7.483	343.15	5.398	5.395				
298.15	7.332	7.466							
ref.	(36)			(42)		(35)		(38)	

Tab. 4 Henry's constants for gases in n-hexadecane

	$\ln(K_H/bar)$											
	N_2		NH_3		CO		H_2S		HCl		CO_2	
T/K	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.
300	6.685	6.685	3.837	3.869	6.301	6.302	3.248	3.128	3.820	3.743	4.321	4.486
325	6.624	6.624	4.091	4.099	6.280	6.277	3.497	3.424	4.008	3.982	4.548	4.634
350	6.566	6.566	4.309	4.297	6.257	6.252	3.724	3.683	4.200	4.190	4.732	4.764
375	6.507	6.507	4.486	4.463	6.230	6.223	3.919	3.904	4.374	4.365	4.873	4.873
400	6.439	6.439	4.618	4.600	6.191	6.182	4.089	4.099	4.521	4.509	4.987	4.954
425	6.369	6.369	4.732	4.709	6.146	6.134	4.232	4.237	4.638	4.622	5.059	5.017
450	6.316	6.316	4.817	4.816	6.093	6.102	4.352	4.388	4.727	4.738	5.137	5.085
475	6.261	6.261	4.873	4.907	6.051	6.058	4.428	4.520	4.767	4.837	5.187	5.147
ref.	(43)		(43)		(43)		(43)		(43)		(43)	
	SO_2		CH_4		C_2H_6		C_3H_8		$n\text{-}C_4H_{10}$		H_2	
T/K	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.
300	2.728	2.884	5.149	5.163	3.313	3.429	2.134	2.624	0.969	1.257	7.828	8.942
325	3.118	3.192	5.255	5.251	3.619	3.687	2.570	2.862	1.447	1.685	8.925	8.854
350	3.441	3.463	5.331	5.326	3.884	3.914	2.938	3.087	1.970	2.070	8.825	8.797
375	3.707	3.696	5.400	5.385	4.111	4.107	3.047	3.285	2.395	2.485	8.729	8.712
400	3.927	3.890	5.442	5.424	4.301	4.255	3.516	3.449	2.747	2.892	8.672	8.673
425	4.105	4.046	5.468	5.443	4.451	4.390	3.741	3.577	3.048	2.928	8.577	8.525
450	4.253	4.210	5.471	5.479	4.567	4.524	3.927	3.745	3.301	3.182	8.442	8.497
475	4.358	4.356	5.471	5.505	4.640	4.641	4.050	3.902	3.513	3.413	8.350	8.411
ref.	(43)		(45)		(39)		(44)		(44)		(36)	

constant increases, while for others, Henry's constant decreases as the temperature rises from 300 to 475 K. The correlation for most gases is satisfactory; however, those for long-chain molecules and those for molecules with a significant quadrupole moment are not as good. For these molecules, the correlation is much improved if a small temperature dependence for $\epsilon_{i,eff}$ is introduced, as shown in Fig. 5.

Table 5 compares calculated with experimental differential heats of solution, entropies of solution and partial molar volumes for gases in benzene. The predictions are in good agreement with experiment. In these

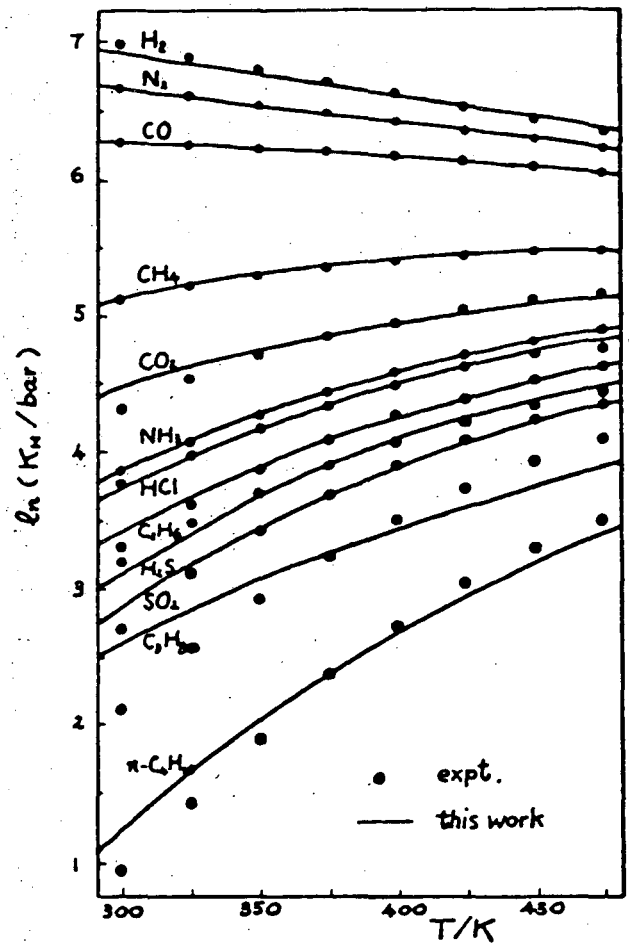

Fig. 4 Henry's constants for various gases in n-hexadecane

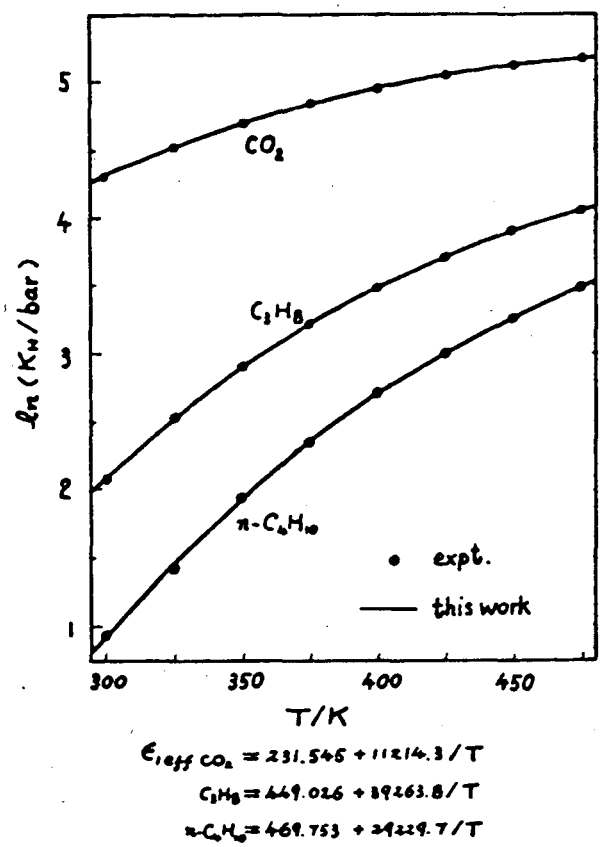

Fig. 5 Henry's constants for CO_2 C_3H_8 and n-C_4H_{10} in n-hexadecane (ϵ_{1eff} =a+b/T)

calculations, since the density dependences of r^* and r^{**} have not been considered, only the hard-sphere contributions are used to calculate partial molar volumes. (We neglect the very small contribution from the solvent's compressibility.)

Tab. 5 Thermodynamic properties of gases in benzene (25°C)

gas	$\Delta\bar{H}_{s1}$ / kJ·mol^{-1}		$\Delta\bar{S}_{s1}$ / J·mol^{-1}K^{-1}		$\bar{V}_1$ / ml·mol^{-1}	
	calc.	expt. (ref)	calc.	expt.	calc.	expt. (ref)
He	9.903	10.321 (33)	-45.75	-44.25	31.7	
Ne	10.490	10.210 (33)	-40.21	-41.86	59.9	
Ar	1.531	1.535 (32)	-53.46	-53.33	47.5	43.0 (50) 44.6 (51)
H_2	5.385	6.767 (36)	-50.49	-45.97	38.8	35.2 (50) 35.4 (51) 35.3 (54)
N_2	4.345	4.100 (34)	-49.73	-50.60	56.2	53.0 (50)
O_2	-1.905	-1.566 (38)	-52.93	-53.88	49.1	
CH_4	-0.535	-1.500 (34)	-54.34	--	59.9	52.0 (50) 53.3 (51) 54.8 (53) 56.1 (52)
N_2O	-5.971	-9.941 (35)	-56.06	-67.45	88.9	
C_2H_6	-7.748	-9.234 (39)	-61.19	-65.97	64.5	72.0 (52)

Henry's Constants in Water

A severe test of the theory is provided by Henry's constants in water over a wide temperature range. For typical gases, a plot of Henry's constants in water versus temperature shows a strong maximum.

The temperature dependence of σ_2 for water is again obtained using Henry's constants for Ar as reference, as in non-polar solvents. For other gases, ϵ_{12} (or σ_{1eff} for quantum gases) are estimated by fitting experimental data for Henry's constants. Figures 6,7 and 8 show Henry's constants for various gases. Agreement between calculated and experimental values is satisfactory in view of experimental uncertainties. For plots of Henry's constants versus temperature, the maxima are predicted well. If a slight temperature dependence is introduced for ϵ_{12} or σ_{1eff} , the results can be improved further. Appendix II gives all parameters used here.

Table 6 compares calculated and experimental differential heats of solution, entropies of solution and partial molar volumes. Agreement is good, considering experimental uncertainties.

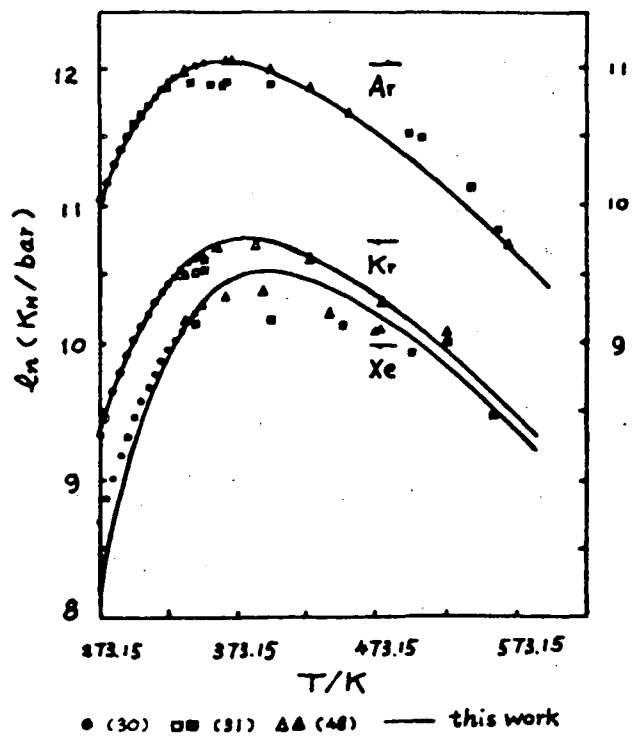

Fig. 6 Henry's constants for Ar, Kr and Xe in water

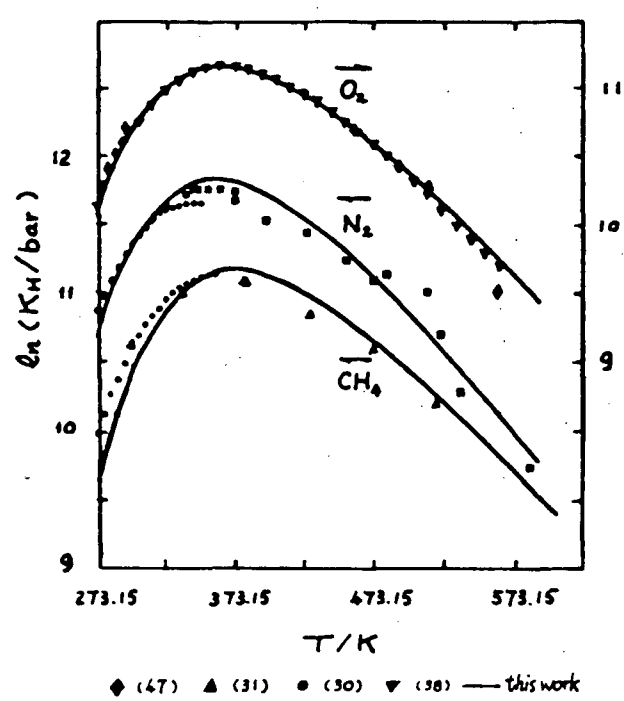

Fig. 7 Henry's constants for O_2, N_2 and CH_4 in water

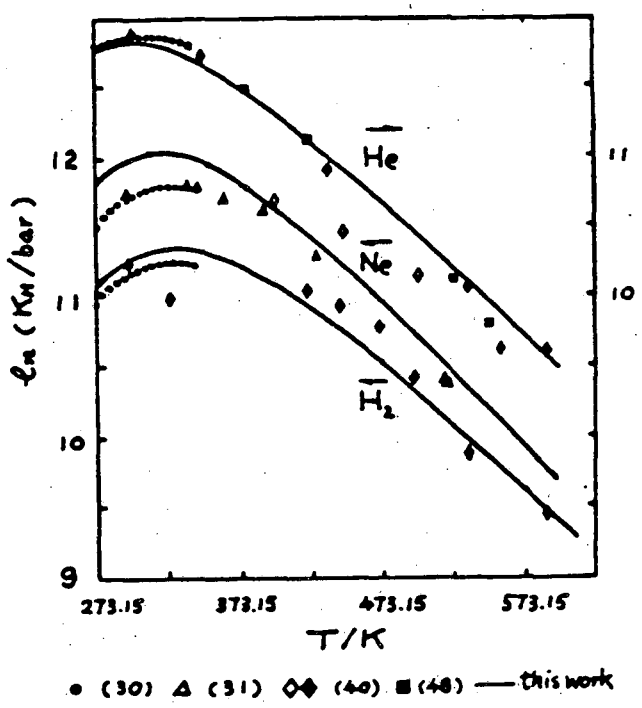

Fig. 8 Henry's constants for H_2, He and Ne in water

Tab. 6 Thermodynamic properties of gases in water (25°C)

gas	$\Delta\bar{H}_{sl}$ / kJ·mol⁻¹		$\Delta\bar{S}_{sl}$ / J·mol⁻¹·K⁻¹		$\bar{V}_i$ / ml·mol⁻¹	
	calc.	expt. (ref)	calc.	expt.	calc.	expt. (ref)
He	-8.34	8.69 (33)	97.3	101.0	15.1	15.5 (57)
Ne	2.98	3.87 (33)	109.6	110.4	21.2	
Ar	12.44	12.24 (32)	130.1	129.1	31.2	31.7 (18) 32.2 (58)
Kr	16.25	15.69 (30)	138.3	135.9	35.4	
Xe	25.13	18.41 (30)	161.4	140.4	47.7	
H_2	3.46	4.07 (36)	105.6	106.6	19.0	25.2 (18) 18.9 (57) 26.0 (56) 26.0 (28)
N_2	14.02	13.39 (37)	141.5	140.0	37.7	32.5 (57) 40.0 (56)
O_2	12.95	12.06 (38)	132.4	129.5	32.4	30.4 (18) 32.1 (58) 31.0 (28) 31.0 (56) 25.8 (57)
CH_4	18.04	13.79 (30)	147.3	134.3	40.4	37.4 (18) 37.1 (59) 35.9 (55) 31.0 (28) 25.8 (56)

Henry's Constants in Aqueous Solutions of Electrolytes.

To apply our theory to aqueous solutions containing electrolytes, we require ion parameters. Toward the end, we use Mavroyannis-Stephen's dispersion theory[26] to estimate energy parameters for ions:

$$\epsilon_i = 3.146 \times 10^{-24} \alpha_i^{3/2} Z_i^{*1/2} / \sigma_i^6 \quad (erg) \qquad (14)$$

Here Z_i^* is number of electrons and α_i denotes polarizability for ion i. For size parameter σ_i, Masterton et al[8] used twice the crystal radius of Pauling[27]. Tiepel and Gubbins[19] suggested the relation

$$\sigma = 1.04\ \sigma^{crystal} \qquad (15)$$

In this work, we use

$$\sigma = \eta\ \sigma^{crystal} \qquad (16)$$

Where η is a temperature-dependent constant obtained by fitting Henry's constants for Ar in ten aqueous solutions of electrolytes as shown in Fig. 9. Table 7 gives η at different temperatures. In Fig. 9, data for LiCl were not included.

Table 8 and Figures 10 and 11 compare calculated and experimental Henry's constants for Ar in aqueous KOH and NaCl solutions at various electrolyte concentrations and various temperatures. Table 9 shows calculated Henry's constants for other gases in aqueous KOH solutions; also shown are calculated results reported by Shoor and Gubbins[6,7]. In general, our calculated Henry's constants are somewhat better than those of Shoor and Gubbins, but they are appreciably better for high electrolyte concentrations and for systems with a large size difference such those where neopentane is the solute.

Fig. 12 shows the temperature dependence of Henry's constants for O_2 in aqueous NaCl solutions: the maximum of the curves is predicted well. The results shown in Table 9 and Fig. 12 are truly predicted (not fitted) results.

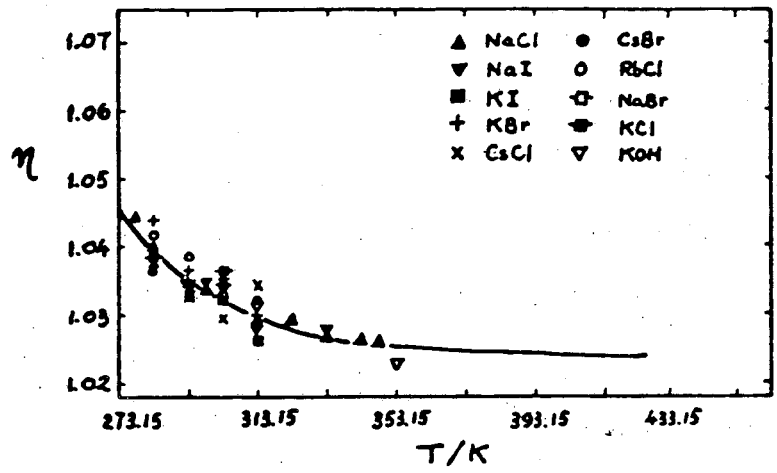

Fig. 9 η for various electrolytic solutions

Tab. 7 Temperature dependence of η

T/K	η	T/K	η
273.15	1.0465	328.15	1.0276
278.15	1.0425	333.15	1.0264
283.15	1.0394	338.15	1.0258
288.15	1.0366	343.15	1.0252
293.15	1.0349	348.15	1.0246
298.15	1.0345	353.15	1.0242
298.15	1.0340	363.15	1.0236
303.15	1.0328	373.15	1.0231
308.15	1.0314	398.15	1.0221
313.15	1.0323	423.15	1.0219
318.15	1.0290	448.15	1.0218
323.15	1.0282		

Tab 8 Henry's constants for Ar in aqueous solutions of KOH and NaCl

KOH	ln (K_H/bar)								ref. (7)	
	298.15 K		313.15 K			333.15 K			353.15 K	
C/M	expt.	calc.	C/M	expt.	calc.	C/M	expt.	calc.	C/M	expt.	calc.
0.0000	10.598	10.624	0.0000	10.833	10.838	0.0000	11.007	11.007	0.0000	11.187	11.081
0.9283	11.043	10.961	0.9236	11.225	11.164	0.9153	11.344	11.324	0.9053	11.385	11.419
2.6853	11.755	11.519	2.6695	11.866	11.681	2.6453	11.959	11.817	2.6324	12.016	12.007
4.9784	12.637	12.564	4.9453	12.769	12.652	4.9017	12.774	12.738	4.8866	12.825	12.963
7.5694	13.725	13.651				7.2295	13.681	13.623	7.1666	13.783	13.640
10.3989	14.851	14.971	10.3363	14.897	14.921	10.2498	14.838	14.861	9.9238	14.505	14.685

NaCl	ln (K_H/bar)								ref. (32)	
	278.15 K		293.15 K		298.15 K		323.15 K		348.15 K	
C/M	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.
0.0000	10.160	10.202	10.537	10.534	10.623	10.624	10.922	10.937	11.077	11.071
0.5000	10.354	10.366	10.695	10.664	10.778	10.756	11.063	11.024	11.212	11.183
1.0000	10.550	10.549	10.851	10.822	10.931	10.914	11.200	11.162	11.340	11.312
1.5000	10.746	10.724	11.010	10.972	11.083	11.052	11.344	11.301	11.477	11.421
2.0000	10.939	10.894	11.164	11.122	11.232	11.190	11.481	11.430	11.584	11.558
2.5000	11.134	11.066	11.320	11.263	11.387	11.352	11.621	11.557	11.744	11.690
3.0000	11.325	11.266	11.475	11.437	11.537	11.501	11.765	11.718	11.873	11.821
3.5000	11.518	11.446	11.631	11.600	11.684	11.662	11.895	11.841	11.996	11.961
4.0000	11.709	11.639	11.795	11.775	11.837	11.850	12.047	11.999	12.137	12.107
4.5000	11.899	11.841	11.942	11.992	11.989	11.993	12.178	12.169	12.265	12.252
5.0000	12.091	12.064	12.100	12.165	12.140	12.161	12.310	12.308	12.394	12.420
5.4000	12.243	12.257	12.271	12.324	12.267	12.316	12.424	12.463	12.497	12.543

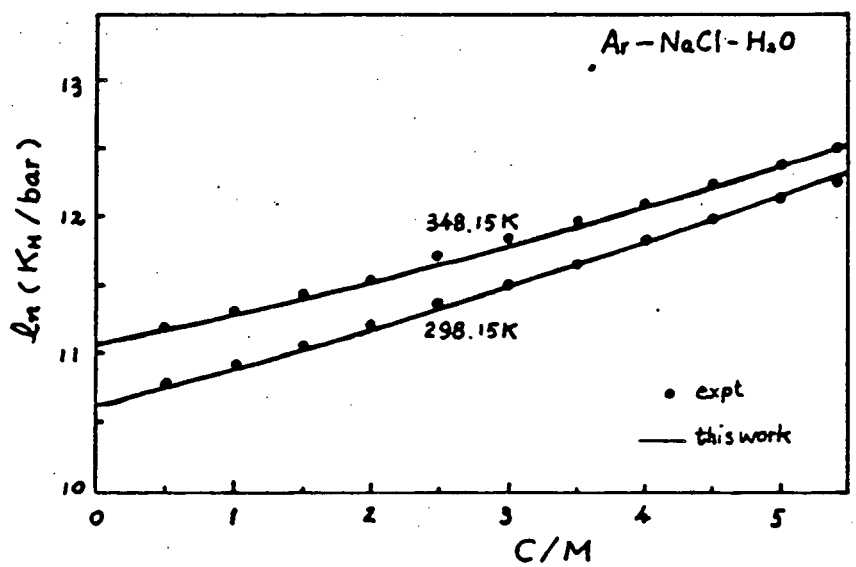

Fig. 10 Henry's constants for Ar in aqueous NaCl solutions

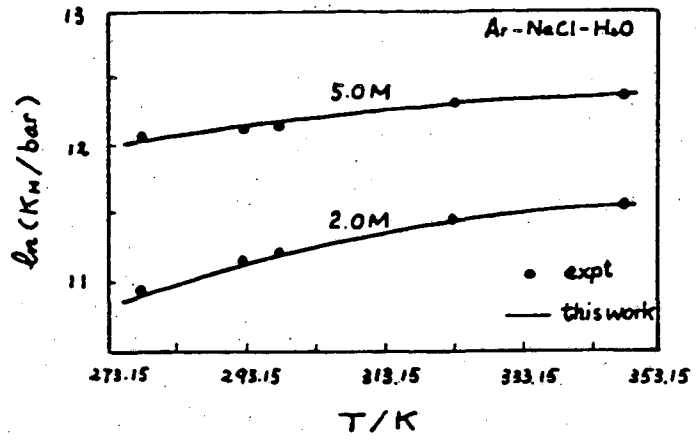

Fig. 11 Henry's constants for Ar in aqueous NaCl solutions

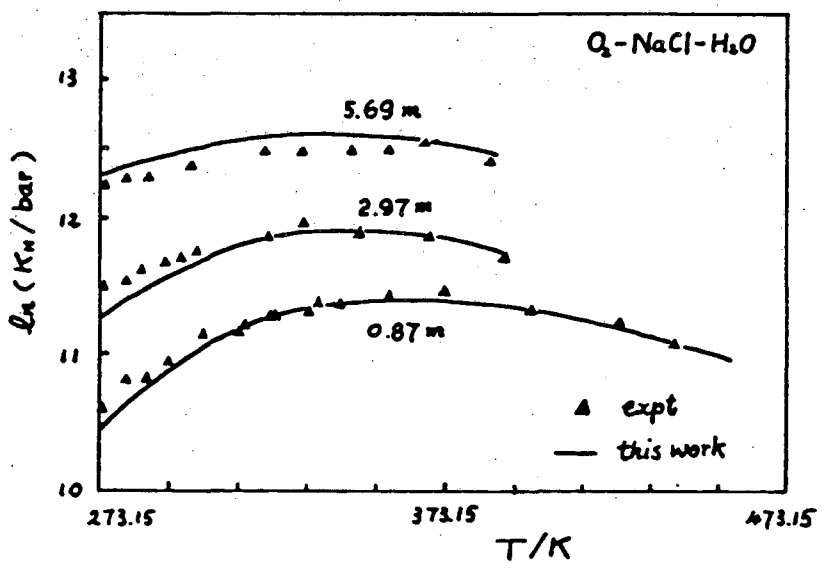

Fig. 12 Henry's constants for O_2 in aqueous NaCl solutions

Tab. 9 Henry's constants for various gases in KOH solutions

KOH wt%	ln (Kn/bar) ref.(7)								
	expt.	calc.	Shoor, Gubbins	expt.	calc.	Shoor Gubbins	expt.	calc.	Shoor Gubbins
	298.15K								
	He			H_2			Ar		
0	11.93	11.83	11.62	11.17	11.30	11.11	10.60	10.62	10.28
10	12.52	12.50	11.99	11.76	11.89	11.86	11.46	11.30	11.05
20	13.29	13.31	12.86	12.46	12.61	12.54	12.39	12.20	11.99
30	14.22	14.28	13.63	13.20	13.46	13.43	13.45	13.36	13.36
40				14.03	14.38	14.64	14.70	14.77	14.48
50				15.13	15.28	16.16			
	O_2			CH_4			$C(CH_3)_4$		
0	10.72	10.70	10.48	10.62	10.43	10.59	11.52	11.40	11.81
10	11.54	11.44	11.29	11.51	11.15	11.39	13.00	12.62	13.56
20	12.50	12.44	12.26	12.54	12.10	12.49	14.87	14.50	16.44
30	13.58	13.69	13.44	13.70	13.40	13.67	16.81	16.92	19.88
40	14.81	14.24	14.83	14.51	14.91	15.18			
50	16.08	17.11	16.60						
	353.15K								
	He			H_2			Ar		
0	11.75	11.63	11.43	11.25	11.31	10.68	11.11	11.08	10.82
10	12.40	12.18	12.12	11.88	11.84	11.90	11.71	11.70	11.61
20	13.12	12.90	12.83	12.58	12.50	12.68	12.56	12.60	12.51
30	14.10	13.77	13.72	13.33	13.20	13.63	13.53	13.50	13.55
40				14.19	14.00	14.74	14.47	14.50	14.92
50				15.30	15.01	16.04			
	O_2			CH_4			$C(CH_3)_4$		
0	11.16	11.18	11.05	11.16	11.15	11.19	12.37	13.34	11.43
10	11.80	11.80	11.73	11.79	11.77	12.06	13.61	14.37	16.44
20	12.61	12.60	12.67	12.63	12.65	13.11	15.10	15.95	19.41
30	13.63	13.62	13.84	13.69	13.53	14.36	16.98	17.98	23.11
40	14.79	14.98	15.13	15.00	14.97	15.80			
50	16.06	16.55	16.83						

Conclusion

The simple model presented here appears to be useful for describing solubilities of gases in liquids. The model is consistent with computer-simulation results; for real systems, using only one adjustable parameter ϵ_{12} (or σ_{eff}), Henry's constants for gases in non-polar or polar solvents can be correlated well over a wide range of temperature. The results for predicting Henry's constants in aqueous electrolytic solutions are also encouraging. For these solutions, no additional adjustable parameters are needed.

Because we have not considered the density dependence of r^* and r^{**}, and because we have neglected local-composition effects within the first coordination shell, our model does not satisfy the low-density limit; that is, the model does not provide an equation of state valid for all fluid densities. Nevertheless, the model appears to be applicable to liquid-like densities and therefore it is useful for correlating solubilities of sparingly-soluble gases in liquids, including aqueous solutions of electrolytes.

List of Symbols

A	Helmholtz energy
C	molar concentration
D,E,F	variables in BMCSL equation
e	charge of electron
f	fugacity
G	Gibbs energy
H	enthalpy
K	number of components
K_H	Henry's constant
N_{Av}	Avogadro number
n	number of moles
p	pressure
R	gas constant
r	distance
S	entropy
T	temperature
V	volume
$\bar{V}_i$	partial molar volume
x	mole fraction
Z	compresibility factor
Z_i	charge number of ion i
Z_i^*	number of electrons in ion i
k	Boltzmann constant
D	dielectric constant
ε	potential energy
ϵ	energy parameter
σ	size parameter
ξ	variables in BMCSL equation
μ	chemical potential
$\bar{\mu}$	dipole moment
α	polarizability
α_p	Coefficient of thermal expasion
β_T	isothermal compressibility
ρ	number density

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Appendix I Equations for Calculations

For solute 1 ,

$$\ln K_{H1} = \ln\left(kT\sum_{i=2}^{K}\rho_i\right) + G_{II1}/RT + G_{III1}/RT \tag{a}$$

$$G_{III}/RT = -\frac{\pi}{kT}\Big[5.14025\sum_{i=2}^{K}\rho_i\epsilon_{i1}\sigma_{i1}^3 + 2.01696\sum_{i=2}^{K}\Big(\frac{2}{3kT}\bar{\mu}_1^2\bar{\mu}_i^2 + \alpha_1\bar{\mu}_1^2 + \alpha_i\bar{\mu}_i^2\Big) + 2.21611\sum_{i=2}^{K}\frac{\rho_i Z_i^2 e^2}{2\sigma_{i1}D}\Big(\alpha_1 + \frac{\bar{\mu}_1^2}{3kT}\Big)\Big] \tag{b}$$

$$G_{II1}/RT = -\ln(1-y_3) + p^{hs}\sigma_1^3 + \frac{3y_2\sigma_1}{1-y_3} + \frac{3y_1\sigma_1^2}{1-y_3} + \frac{9y_2^2\sigma_1^2}{2(1-y_3)^2} + 3\Big(\frac{y_2\sigma_1}{y_3}\Big)^2\Big[\ln(1-y_3) + \frac{y_3}{1-y_3} - \frac{y_3^2}{2(1-y_3)^2}\Big] - \Big(\frac{y_2\sigma_1}{y_3}\Big)^3\Big[2\ln(1-y_3) + \frac{y_3(2-y_3)}{1-y_3}\Big] \tag{c}$$

$$y_l = \frac{\pi}{6}\sum_{i=2}^{K}\rho_i\sigma_i^l \tag{d}$$

$$p^{hs} = \frac{y_0}{1-y_3} + \frac{3y_1y_2}{(1-y_3)^2} + \frac{3y_2^3}{(1-y_3)^3} - \frac{y_3y_2^2}{(1-y_3)^3} \tag{e}$$

$$\Delta\bar{H}_{S1} = \alpha_p RT^2 - RT + H_{II1} + H_{III1} \tag{f}$$

α_p : coefficient of thermal expansion

$$H_{III1} = \Big[\frac{\partial(G_{III1}/RT)}{\partial(1/RT)}\Big]_p \tag{g}$$

$$H_{II1} = \Big[\frac{\partial(G_{II1}/RT)}{\partial(1/RT)}\Big]_p \tag{h}$$

$$\bar{V}_1 = \beta_T RT + V_{II1} + V_{III1} \simeq \beta_T RT + V_{II1} \tag{i}$$

β_T : isothermal compressibility

$$V_{II1} = \Big[\frac{\partial(G_{II1}/RT)}{\partial p}\Big]_T \tag{j}$$

Appendix II Parameters

Tab. A Molecular parameters

(σ and ϵ from second virial coefficients)

gas	σ/Å	ϵ/k/K	$10^{24}\alpha$/ml	gas	σ/Å	ϵ/k/K	$10^{24}\alpha$/ml
hard sphere	2.55	0.00	0.000	HCl	3.34	344.70	2.56
He	2.63	6.03	0.204	SO_2	4.11	335.40	3.77
Ne	2.78	34.90	0.393	N_2O	3.83	232.40	2.92
Ar	3.40	122.00	1.630	CH_4	3.82	70.16	2.70
Kr	3.60	171.00	2.460	C_2H_6	3.95	76.00	4.30
Xe	4.10	221.00	4.000	C_3H_8	5.04	226.00	-
H_2	2.87	29.20	0.802	n-C_4H_{10}	4.97	155.00	
N_2	3.70	95.00	1.730	C_6H_6	5.26	440.00	10.32
O_2	3.46	118.00	1.560	n-C_6H_{14}	5.91	413.00	11.70
CO	3.76	100.00	1.930	C_6H_{12}	6.09	324.00	10.70
CO_2	4.07	205.00	2.590	H_2O			1.47
H_2S	3.62	301.10	3.640			(dipole moment)	1.84

ref. Hirschfelder, J.O., Curtiss, C.F., Bird, R.B., "Molecular Theory of gases and Liquids". John Wiley and Sons Inc. New York. N.Y., 1945. p.852

Reid, R.C., Prausnitz, J.M., Sherwood, T.K., "The Properties of gases and Liquids". 3rd.ed., McGraw-Hill Book Company, 1977.

Tab. B Parameters for solvents in this work with temperatures

C_6H_6		cyclo-C_6H_{12}		n-C_6H_{14}		n-$C_{16}H_{34}$		H_2O	
T/K	σ/Å	T/K	σ/Å	T/K	σ/Å	T	ϵ/k/K	T/K	σ/Å
283.15	5.1831	283.15	5.5602	213.15	5.8353	300.00	542.84	273.15	2.7823
288.15	5.1789	288.15	5.5551	223.15	5.8354	325.00	539.80	298.15	2.7703
293.15	5.1746	293.15	5.5510	233.15	5.8354	350.00	532.82	323.15	2.7591
298.15	5.1705	298.15	5.5462	243.15	5.8355	375.00	523.74	348.15	2.7482
303.15	5.1666	303.15	5.5424	253.15	5.8355	400.00	512.44	373.15	2.7318
308.15	5.1632	308.15	5.5380	263.15	5.8355	425.00	502.02	398.15	2.7171
313.15	5.1595	313.15	5.5348	273.15	5.8356	450.00	496.23	423.15	2.7026
318.15	5.1560	318.15	5.5307	283.15	5.8351	475.00	488.37	448.15	2.6885
323.15	5.1526	323.15	5.5270	288.15	5.8356			473.15	2.6755
328.15	5.1493	328.15	5.5234	293.15	5.8356			498.15	2.6646
333.15	5.1461	333.15	5.5199	298.15	5.8356			523.15	2.6570
338.15	5.1430	338.15	5.5166	303.15	5.8357			548.15	2.6530
343.15	5.1400	343.15	5.5133	308.15	5.8357			573.15	2.6511
		348.15	5.5102	313.15	5.8357				
		353.15	5.5071	318.15	5.8357				
				323.15	5.8357				
				328.15	5.8357				
				333.15	5.8357				
				338.15	5.8357				
				343.15	5.8357				

Tab. C Parameter for gases in several solvents

Solvent	H_2O		C_6H_6		n-C_6H_{14}		cyclo-C_6H_{12}			n-$C_{16}H_{34}$	
gas	σ/Å	ϵ/k/K	σ/Å	ϵ/k/K	σ/Å	ϵ/k/K	σ/Å	ϵ/k/K	gas	σ/Å	ϵ/k/K
He	2.3856	29.58	2.7410	42.80	2.7960	41.32	2.7502	44.00	N_2	3.7000	122.50
Ne	2.8347	71.16	3.8135	102.97	3.3766	99.40	3.2261	105.85	H_2	2.5452	29.20
Ar	3.4000	133.05	3.4000	192.51	3.4200	185.85	3.4000	197.90	NH_3	2.9000	186.83
Kr	3.6000	148.99							CO	3.7630	143.97
Xe	4.1000	121.33							H_2S	3.6230	292.73
H_2	2.6883	65.09	2.6941	94.18	2.7738	90.92	2.7000	96.82	HCl	3.3390	230.34
N_2	3.7000	140.88	3.7000	224.88			3.7000	215.39	CO_2	4.0700	261.14
O_2	3.4600	136.77	3.4600	193.06	3.4600	163.45	3.4600	194.74	SO_2	4.1120	355.14
CH_4	3.8170	155.95	3.8170	238.11	3.8170	219.15			CH_4	3.8170	200.58
C_2H_6			3.9540	304.72	3.9540	277.49	3.9540	312.12	C_2H_6	3.9540	306.89
N_2O			4.5900	319.74	4.5900	275.23			C_3H_8	5.6370	226.00
									nC_6H_{14}	4.9710	306.88
										$\sigma_2 = 8.4106$ Å	

Tab. D Parameters for ions

ion	Z_i^*	$10^{24}\alpha$/ml	σ_i/Å
Li^+	2	0.075	1.200
Na^+	10	0.210	1.900
K^+	18	0.870	2.660
Rb^+	36	1.400	2.960
Cs^+	54	2.420	3.380
OH^-	10	1.830	2.947
Cl^-	18	3.020	3.620
Br^-	36	4.170	3.900
I^-	54	6.280	4.320

ref. (6)(8)

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