THE THERMODYNAMIC PROPERTIES OF GASES IN SOLUTION. I. THE PARTIAL MOLAL VOLUME

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An understanding of the partial molal volume of gases in solution is of considerable importance in the study of the thermodynamic properties of such solutions. The available experimental data for gases in non-polar solvents are summarized and the applicability of various theories is examined. An inconsistency in the predictions of regular solution theory is observed. Finally, a simple free volume model is presented which enables the partial molal volume of dissolved gases to be predicted in a satisfactory manner.

Largely as a result of the research of Professor J. H. Hildebrand over the last half-century, a general understanding of the properties of solutions is now possible. Regular solution theory has provided a basis by which solubility can be predicted with a remarkable over-all success. Many details remain to be filled in and we may be confident that Professor Hildebrand will, in future years, be active in their solution as he has been in the past.

The more recent research of Professor Hildebrand and co-workers on the properties of gases dissolved in non-polar solvents has shown that the development of an adequate theory for these systems remains one of the outstanding problems of solution theory. Progress in this field long has been hampered by a lack of reliable data, but the recent research of Hildebrand,[1] of Clever,[2] and of Gjaldbaek[3] now has produced accurate solubility data extending over a wide range of solvent and solute molecules. These workers confirm, in general, the earlier data of Lannung[4] and of Horiuti.[5] As yet no detailed theoretical analysis has been made for gases in solution though several workers[2,3] have applied regular solution theory to their experimental results. In all cases, however, the actual prediction of gas solubility has involved the use of most unrealistic parameters which, as will be discussed later, lead to completely unacceptable values when used in the prediction of other relevant data.

The volume change on mixing for a dissolved gas is a most important thermodynamic property, yet only a few workers have produced experimental values for the partial molal volumes of gases dissolved in non-polar solvents (Table I), and these of limited accuracy.[1b,5-7] No attempt has been made to interpret such data on the basis of an acceptable model using fundamental gas and solvent parameters.

TABLE I
EXPERIMENTAL PARTIAL MOLAL VOLUME AT 25° (CM.³)

	δ	Ar	N₂	CH₄	CF₄	H₂	D₂
C₇F₁₆	6.0	54	66.1	68.4		54.4	52.9
C₇F₁₄	6.1	51					
i-C₈H₁₈	6.9	50		56.6	85.4		
C₇H₁₆	7.5			55.4	86.4		
CCl₄	8.6	44	52.5	52.4	79.7	38	
C₆H₆	9.2	43	53	52	83.2	35.2	32.7
CS₂	10.0	45		56.1	85.4		

	δ	CO	O₂	C₂H₄	CO₂	N₂O
CCl₄	8.6	52.5	45.3	61	48	47

Regular Solution Theory.—In the case of liquid and solid solutes considerable success in the understanding of solubility has been obtained by the use of the regular solution theory.[8-10]

This theory gives for the solubility of a gas[11]

$$-\log X_2 = -\log X_2^{id} + V_2(\delta_1 - \delta_2)^2/4.575T \quad (1)$$

where X_2 is the mole fraction of a gas in a saturated solution, X_2^{id} is the ideal solubility, V_2 is the molal volume of the gas in its reference state (the pure liquid), and δ_1 and δ_2 are the solubility parameters of the solvent and solute, respectively. The main difficulty in the application of eq. 1 is the choice of a suitable value for V_2. Clever[2] selected the critical volume of the gas and was able to find a solubility parameter for each gas which gave a reasonable prediction of the solubility in a series of solvents, using a comparative method to eliminate X_2^{id}. Gjaldbaek[3] took V_2 to be equal to the partial molal volume of the gas in CCl₄ solvent and evaluated δ_2 directly, since X_2^{id} can be estimated for the gases he examined. For a gas in a series of solvents a reasonably consistent value of δ_2 was obtained. Table II gives a list of the values obtained by the above mentioned workers.

Using the assumptions of regular solution theory it is possible to evaluate the excess volume change on mixing.[12] In terms of solubility parameters the

(1) (a) L. W. Reeves and J. H. Hildebrand, *J. Am. Chem. Soc.*, **79**, 1313 (1957); (b) J. E. Jolley and J. H. Hildebrand, *ibid.*, **80**, 1050 (1958); (c) Y. Kobatake and J. H. Hildebrand, *J. Phys. Chem.*, **65**, 331 (1961).

(2) (a) H. L. Clever, R. Battino, J. H. Saylor, and P. M. Gross, *ibid.*, **61**, 1078 (1957); (b) H. L. Clever, J. H. Saylor, and P. M. Gross, *ibid.*, **62**, 89 (1958); (c) H. L. Clever, *ibid.*, **62**, 375 (1958).

(3) (a) J. C. Gjaldbaek and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 3147 (1949); (b) J. C. Gjaldbaek, *Acta Chem. Scand.*, **8**, 1398 (1952).

(4) A. Lannung, *J. Am. Chem. Soc.*, **52**, 68 (1930).

(5) J. Horiuti, *Sci. Papers Inst. Phys. Chem. Research Tokyo*, **17**, 125, No. 341 (1931).

(6) R. H. Schumm and O. L. I. Brown, *J. Am. Chem. Soc.*, **75**, 2520 (1953).

(7) J. Walkley and J. H. Hildebrand, *ibid.*, **81**, 4439 (1959).

(8) J. E. Jolley and J. H. Hildebrand, *J. Phys. Chem.*, **61**, 791 (1957).

(9) K. Shinoda and J. H. Hildebrand, *ibid.*, **61**, 789 (1957).

(10) E. B. Smith and J. Walkley, *Trans. Faraday Soc.*, **56**, 220 (1960).

(11) Hildebrand and Scott, "Solubility of Non-electrolytes," Reinhold Publishing Corporation, New York, N. Y., 1950, p. 224.

(12) Reference 11, p. 138.

TABLE II

(Gas)	H_2	O_2	CO_2	CO	He	Ne	Ar	Kr	Xe
δ	5.1	5.7	5.7	5.8	3.2	4.9	7.0	7.5	8.0
Ref.	3	3	3	3	2	2	2	2	2

partial molal volume of a solute in dilute solution, $\bar{V}_2$, is given by

$$(\bar{V}_2 - V_2) = n\beta_1\phi_1^2 V_2 (\delta_1 - \delta_2)^2 \qquad (2)$$

where V_2 is the volume of the solute in the pure liquid state, β_1 is the compressibility of the pure solvent, and ϕ_1 the volume fraction of the solvent n is the ratio $(\partial E/\partial V)_T/(E/V)$, which for most non-polar liquids is approximately equal to unity. For solid and liquid solutes eq. 2 has been used with success in the prediction of the partial molal volume.[13,14] The application of this equation to gases leads to anomalous results when used in conjunction with the solubility parameters given in Table II. For most of the gases the calculated partial molal volume is less in solvents of low solubility parameter, such as the fluorocarbons, than in carbon tetrachloride or benzene, a trend in direct contradiction to the experimental results. For nitrogen, with an estimated solubility parameter of 5.8, we calculate the partial molal volume to be (in cm.^{3})

C_7F_{16}	C_7H_{16}	CCl_4	C_6H_6	CS_2
52	53	54	55	55

V_2 was taken to be 52 cm.^{3}, in keeping with Gjaldback's assumption. For hydrogen the predicted partial molal volume is 2 cm.^{3} less in C_7F_{16} than in CCl_4, while for argon the estimated solubility parameter lies between those of the liquids considered and thus the variation in the calculated partial molal volume is very small (Table IV).

Simple Free Volume Theory.—An evaluation of the partial molal volume of the dissolved gas at what is virtually infinite dilution requires a treatment in which the properties of the solution are evaluated explicitly for a cell with the gas molecule at the center and the solvent molecules as the surrounding neighbors.[15] Certain regularities in the experimental data suggest, however, that the values of the partial molal volumes of gases in solution depend mainly upon two simple parameters: (a) the size of the gas (solute) molecule, and (b) the solubility parameter, or internal pressure of the solvent. Uhlig[16] and Eley[17] both have developed theories for gases in solution and have evaluated the energy required to make a "cavity" in solution from the surface tension and the internal pressure of the solvent. The success of these approaches and the regularities mentioned above suggest that it is appropriate to consider a simple cell model in which the gas molecule at the center of the cell, treated as a hard sphere, generates a pressure equal to the internal pressure of the solvent in which the gas will be dissolved. Having evaluated the molal volume of the gas at the internal pressure of the

solvent we may consider mixing to occur with no further volume change. The internal pressure of a liquid is defined by

$$(\partial E/\partial V)_T = T(\partial P/\partial T)_V - P$$

The external pressure term P may be ignored in comparison to $T(\partial P/\partial T)_V$. The free volume of a system of hard sphere molecules is given by

$$V_f = \int_0^{a-\sigma} 4\pi r^2 \, dr = 4\pi(a - \sigma)^3/3$$

where σ is the collision diameter of the molecule and a the nearest neighbor distance.[18] The pressure generated may be evaluated

$$P = RT \, \partial \ln V_f/\partial V = (RT/V)(1 - \sigma/a)^{-1}$$

Equating this pressure to the internal pressure of the solvent we may obtain an estimate of the molal volume of the gas, V_2, under these conditions

$$\frac{V_2}{V_0} = \left[1 - \frac{R}{V_2} \left(\frac{\partial P}{\partial T}\right)_V^{-1} \right]^{-3} \qquad (3)$$

where $V_0 = \gamma N\sigma^3$ and $V_2 = \gamma Na^3$. γ is a constant depending on the geometry of the lattice and V_0 is equal to the volume of the gas at absolute zero. From a knowledge of the collision diameter of the gas and the $(\partial P/\partial T)_V$ of the solvent, V_2 may be evaluated numerically from eq. 3. The values of $(\partial P/\partial T)_V$ for most common solvents are readily available.[19] The choice of σ for each gas is more difficult as in certain cases the reported values show considerable variation. Three sources have been used. The most reliable are the values of σ obtained from gas imperfection and transport data,[20] the third source is the volume of the solid at low temperatures. For Ar, N_2, CO, and CH_4 there is substantial agreement between all three methods if the packing parameter γ is taken as unity. For N_2O and C_2H_4, however, a wide discrepancy exists between the gas imperfection and transport values, but in both cases the values from the transport data were in agreement with the volume of the solids at low temperatures and thus were used in the theory. For H_2 and D_2 the volume of the solids were used. Values of the molal volume of the various gases at 25° obtained from this simple model are given in Table III. A comparison with the experimental partial molal volume data in Table I shows that the agreement between the two sets of data is good, except in the case of CO_2. This confirms the original supposition that on going into solution there will be no further change in volume of this hypothetical hard sphere (pure solute) liquid and the molal volume thus is equal to the partial molal volume of the dissolved gas. Further, for every gas the correct trend of the experimental data is reproduced.

Discussion

The application of regular solution theory to solutions of gases is illustrated in Table IV where

(13) E. B. Smith and J. Walkley, *Trans. Faraday Soc.*, **56**, 1276 (1960).

(14) E. B. Smith, J. Walkley, and J. H. Hildebrand, *J. Phys. Chem.*, **63**, 703 (1959).

(15) J. Walkley, *Trans. Faraday Soc*, in press.

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

(17) D. D. Eley, *Trans. Faraday Soc.*, **35**, 1281 (1939); **35**, 1421 (1939).

(18) Reference 11, p. 75.

(19) (a) J. H. Hildebrand and J. M. Carter, *J. Am. Chem. Soc.*, **54**, 3592 (1932); (b) B. J. Alder, E. W. Haycock, J. H. Hildebrand, and H. Watts, *J. Chem. Phys.*, **22**, 1060 (1954); (c) E. B. Smith and J. H. Hildebrand, *ibid.*, **31**, 145 (1959).

(20) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "The Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 1100.

TABLE III

PARTIAL MOLAL VOLUMES FROM INTERNAL PRESSURE OF THE SOLVENT AT 25° (CM.^{3})

	Ar	N$_2$	O$_2$	CO	CH$_4$	CO$_2$	C$_2$H$_4$	CF$_4$	N$_2$O	H$_2$	D$_2$
$V_0 = \gamma N \sigma^3$	25^a	32^a	28^a	32^a	35^a	40^b	40^c	63^b	33^b	23^c	20^c
C$_7$F$_{16}$	53	60	56	60	64	69	69	94	62	51	48
C$_7$F$_{14}$	51	59	55	59	63	68	68	92	61	50	47
C$_7$H$_{16}$	49	57	52	57	60	65	65	89	58	47	44
CCl$_4$	44	51	47	51	54	59	59	83	52	42	39
C$_6$H$_6$	42	49	46	49	53	58	58	81	51	40	37
CS$_2$	42	49	46	49	53	58	58	81	51	40	37
CHBr$_3$	40	47	43	47	50	55	55	78	48	38	35

^{a} From gas imperfection data: ref. 20, assuming $\gamma = 1$. ^{b} From transport properties: ref. 20, assuming $\gamma = 1$. ^{c} From the volume of the solid.

the partial molal volumes of argon in various solvents, calculated using eq. 2, are compared with the experimentally observed values. It can be seen that the well defined trend of the experimental data is not reproduced. In general it is impossible to obtain solubility parameters for gases that lead to acceptable values for both the partial molal volumes and the solubility. Also included in Table IV are the partial molal volume values for argon calculated using the Prigogine–Scott model.[21] This model, by making use of the thermodynamic properties of the pure components, gives a theory with only the minimum dependence upon the cell model. The free energy of a second liquid may be related to that of a reference liquid by expanding in a double power series in the characteristic molecular parameters of energy, ϵ, and volume, σ^3. The volume change on mixing may be obtained by a suitable differentiation of the free energy, thus

$$\frac{\Delta V^m}{x_1 x_2} = V^p\left(\eta\xi + \frac{11}{6}\xi^2\right) + T\left(\frac{\partial V}{\partial T}\right)_p [3\eta\xi + 4\xi^2 - 2\eta^2]$$

(4)

where $\xi = (\sigma_{11}^3 - \sigma_{22}^3/\sigma_{11}^3 + \sigma_{22}^3)$
and $\eta = (\epsilon_{11} - \epsilon_{22}/\epsilon_{11} + \epsilon_{22})$

As terms higher than the second power of ξ and η have been neglected, the application of this model to solutions of gases takes it beyond its range of applicability since from the large differences in the size of the molecules concerned ξ may be as high as 0.8. It may be seen that this model greatly overestimates the expansion caused by the differences in the size of the solvent and solute molecules. Higher terms in the expansion would, no doubt, tend to correct this feature but it is unlikely that a correction would be obtained to the extent necessary to give agreement with the experimental values.

(21) R. L. Scott, *J. Chem. Phys.*, **25**, 193 (1956).

TABLE IV

THE PARTIAL MOLAL VOLUME OF ARGON AT 25° (CM.^{3})

	CS$_2$	C$_6$H$_6$	CCl$_4$	C$_7$H$_{16}$	i-C$_8$H$_{18}$	C$_7$F$_{16}$
Observed	45	43	44	..	50	54
This work, eq. 3	42	42	44	49	51	53
Prigogine–Scott, eq. 4	43	91	105	165	..	250
Regular soln. theory, eq. 2	45	45	44.5	44.5	44.5	44.5

It is considered that the success of the simple free volume theory arises from its neglect of the differences in the size of the solvent and solute molecules due to its consideration of the properties of the isolated pure solute under the conditions appropriate to the solution. The model of a hypothetical pure solute at the $(\partial P/\partial T)_V$ of the solvent gives a naive explanation of the solubility "quantum differences" observed experimentally since the gas is considered not at 1 atmosphere but at an effective pressure of some 2–3000 atmospheres. The quantum differences are introduced only through the V_0 values used (those of the solid at a low temperature) and in view of the simplicity of the model the agreement between the theoretical and experimental partial molal volume values, though not as good as those for the classical gases, certainly confirms the experimentally measured differences.[7] It seems unlikely that such a simple model could be an adequate basis for the complete evaluation of the thermodynamic properties of gases in solution. Nevertheless it has a considerable predictive value in the case of partial molal volume, an area of solubility study where both theoretical and experimental investigation has been lacking.

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