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Solutions of Inert Gases in Water

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Abstract: Data for the solubility in water of gases ranging from Ne to n-C_4H_{10} are reviewed and compared with their solubilities in c-C_6H_{12}. Entropies in the two solvents are very different in amount and origin. A variety of explanations have been offered to account for the losses of entropy caused by dissolving neutral molecules in this already highly structured solvent. Most of them assume either that water molecules form more rigid structures around solute molecules, or else that water is a labile mixture of different structures. We regard such models as open to question and propose instead an explanation based upon the Pople model of water molecules all bonded together by the maximum number of flexible hydrogen bonds all participating equally in thermal energy. When inert molecules are introduced, we suggest that H bonds are deactivated or destroyed to an extent depending upon the total surface of the solute. The entropy of solution of nine gases to the same mole fraction accordingly varies linearly with the two-thirds power of their molal volumes at their boiling points. The losses of entropy that occur when equal surfaces of water and liquid higher alkanes unite to form interfaces show virtually the same dependence upon the molal surfaces of the alkanes as is shown by the gaseous alkanes.

The junior author,[1] while working with E. B. Smith at Oxford, reviewed the data available on the solubility of inert gases in water. This material afforded means for a reconsideration of models that have been proposed for such solutions and for the related still live problem of the structure of water itself. We devote attention especially to the entropy, the function most closely related to structure.

The data gathered in the survey vary in precision, and those from different sources differ, in some cases to an appreciable extent. The selected data are plotted in Figure 1 as log x_2, where x_2 is the mole fraction of the gas at 1 atm partial pressure, *vs.* log T. The entropy of solution of a gas from 1 atm at any temperature is obtained from a tangent by $\bar{s}_2(x_2) - s_2^g = R(\mathrm{d} \log x_2/\mathrm{d} \log T)$. Our figures thus obtained for 25° are given in the first two columns of Table I. We include gases not listed among similar collections such as the valuable study by Himmelblau.[2] Discrepancies are large in the cases of the two sparingly soluble gases, CF_4 and SF_6, as seen in the two discordant data for each in Table I.

Because each figure for $\bar{s}_2(x_2) - s_2^g$ is for a different mole fraction, we add values of $R \ln 10^5 x_2$ in order to obtain the entropy of transferring each gas to the same mole fraction, 10^{-5}. The third-column figures are those for $\bar{s}_2(10^{-5}) - s_2^g$. We see that these do not at all follow the order of solubility that is found for these gases in nonpolar solvents reported first by Jolley and Hildebrand[3] and confirmed subsequently by other collaborators with the senior author.[4] The contrast is well illustrated by the difference between the curved, crossing lines in Figure 1 and the straight, fan-like spacing of the lines in Figure 2 for a representative number of these gases in cyclohexane, from measurements by Dymond.[5]

The contrast is revealed again in Figure 3, where solubility expressed by $RT \ln x_2$ is plotted against ΔE_2^{vap}, the energy of vaporization of a gas at its boiling point, the parameter recently introduced by the senior author[6] to replace the "force constant,"

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[1] K. W. Miller, Thesis, Oxford, 1965.

[2] D. M. Himmelblau, *J. Phys. Chem.*, **63**, 1803 (1959).

[3] J. E. Jolley and J. H. Hildebrand, *J. Am. Chem. Soc.*, **80**, 1050 (1958).

[4] (a) Y. Kobatake and J. H. Hildebrand, *J. Phys. Chem.*, **65**, 331 (1961); (b) G. Archer and J. H. Hildebrand, *ibid.*, **67**, 1830 (1963); (c) H. Hiraoka and J. H. Hildebrand, *ibid.*, **68**, 213 (1964).

[5] J. H. Dymond, *J. Phys. Chem.*, 71, 1829 (1967).

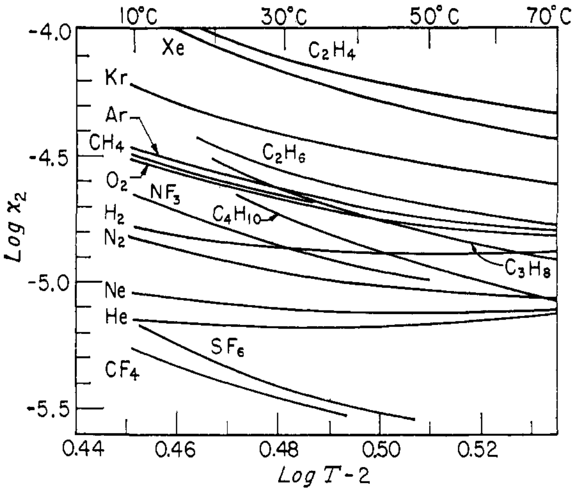

Figure 1. The temperature dependence of the measured solubility of gases at 1 atm in water. The entropy of solution is $R(\mathrm{d}\log x_2/\mathrm{d}\log T) = \bar{s}_2(x) - s_2^g$.

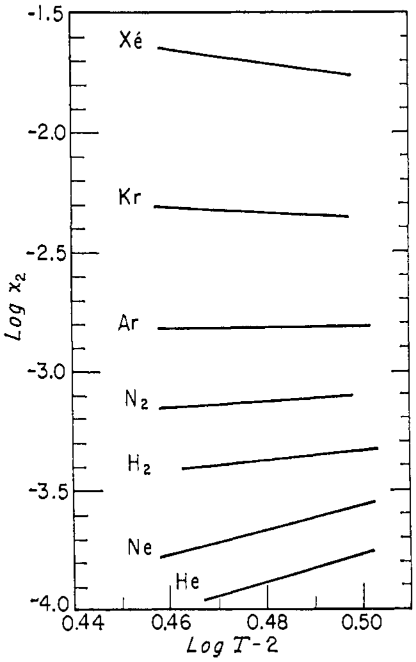

Figure 2. The temperature dependence of the solubility of gases in cyclohexane on the same scales as in Figure 1.

ϵ/k, calculated from gas imperfections on the basis of an assumed pair-potential function. The large role of entropy in the case of water solutions is illustrated again by plotting the figures for 15 and 40°. The same shift in temperature for the gases in cyclohexane would cause merely a rotation of the line of 3° 40′ toward the vertical around the point for Ar, where $\Delta s = 0$. One sees in this energy relation considerable departures of the points for paraffins and nitrogen. CF_4 is a law unto itself.

The senior author drew attention further to a close parallelism between (a) the percentage excess of the partial molal volume of a dissolved gas over its molal volume at its own boiling point and (b) the part of the partial molal entropy of solution attributable to expansion. We have long regarded this "configuration entropy" as an effect of "increased freedom of motion of solvent molecules in the neighborhood of a solute gas molecule resulting from the weakening of molecular attraction and its attendant expansion."[3,7] The situation in water is very different, as can be seen from the figures in Table II, which compares partial molal volumes of four gases in water and in benzene with their

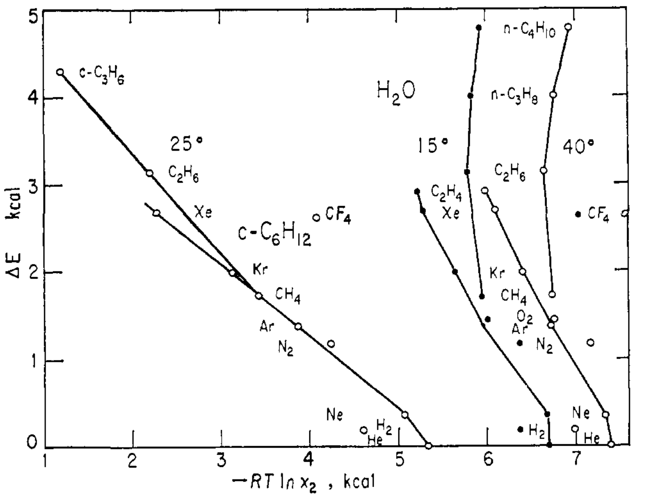

Figure 3. A comparison of the solubility of gases in c-C_6H_{12} and H_2O using as gas parameters their energy of vaporization at their boiling points.

Table I. Solubility and Entropy of Solution of Gases in Water, 25°, and Molal Volumes of Gases at their Boiling Points (cc)

	10^5x_2	$\bar{s}_2(x) - s_2^g$	$\bar{s}_2(10^{-5}) - s_2^g$	V_b	Ref
CF_4	0.36	−9.8	−11.9	54.3	*a, m*
	0.38	−12.1	−14.0		*i, j*
SF_6	0.44	−16.5	−18.1	(75.5)	*i, j*
	0.44	−11.4	−13.0		*n*
He	0.68	−1.35	−2.0	...	*a–c*
Ne	0.82	−3.5	−3.9	16.7	*a, c, d*
N_2	1.19	−8.75	−8.4	34.7	*d, e, h, k, l*
H_2	1.42	−3.2	−2.5	28	*k*
NF_3	1.49	−12.8	−12.0	46	*q*
n-C_4H_{10}	2.17	−20.3	−18.8	97	*k, p*
O_2	2.31	−9.5	−7.8	28	*d, e, g, h, k*
CH_4	2.48	−10.5	−8.7	38	*g, k, o, p*
Ar	2.54	−9.1	−7.25	28.6	*a–j*
n-C_3H_8	2.73	−17.5	−15.3	75	*k, p*
C_2H_6	3.10	−13.4	−12.0	54.7	*g, k, l, p*
Kr	4.32	−10.8	−7.9	34.7	*a*
Xe	7.71	−14.5	−10.4	43	*a, g*
C_2H_4	8.74	−13.3	−9.0	49	*k*

[a] T. J. Morrison and N. B. Johnson, *J. Chem. Soc.*, 3441 (1954). [b] H. L. Friedman, *J. Am. Chem. Soc.*, **76**, 3294 (1954). [c] A. Lannung, *ibid.*, **52**, 68 (1930). [d] H. L. Clever, *et al.*, *J. Phys. Chem.*, **61**, 1078 (1958). [e] C. E. Klots and B. B. Benson, *J. Marine Res.*, **21**, 48 (1963). [f] A. Ben Naim and S. Baer, *Trans. Faraday Soc.*, **59**, 2735 (1963). [g] A. Eucken and G. Herzberg, *Z. Physik. Chem.* (Leipzig), **195**, 1 (1950). [h] E. Douglas, *J. Phys. Chem.*, **68**, 169 (1964). [i] R. A. Dawe, Thesis, Oxford, 1965. [j] B. Stickings, Thesis, Oxford, 1966. [k] T. J. Morrison and F. Billett, *J. Chem. Soc.*, 3819 (1952). [l] J. C. Gjaldbaek and H. Niemann, *Acta Chem. Scand.*, **12**, 1015 (1958). [m] H. M. Parmelee, *Refrig. Eng.*, **61**, 1341 (1953). [n] T. J. Morrison and N. B. Johnson, *J. Chem. Soc.*, 3655 (1955). [o] A. Lannung and J. C. Gjaldbaek, *Acta Chem. Scand.*, **14**, 1124 (1960). [p] W. F. Clausen and M. F. Polglase, *J. Am. Chem. Soc.*, **74**, 4817 (1952). [q] T. Ashton, Thesis, Oxford, 1967.

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(6) J. H. Hildebrand, *Proc. Natl. Acad. Sci. U. S.*, **57**, 542 (1967).

(7) J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962, p 45.

Table II. Molal Volumes of the Gases at Their Boiling Points Compared with Their Partial Molal Volumes in Water and Benzene at 25°

	H_2	N_2	CH_4	C_2H_6
V_2 at t_b	28	35	38	55
$\bar{V}_2$ in H_2O	$<28^{a,b}$	33^{b}	$37^{a,c}$	51^{c}
$\bar{V}_2$ in C_6H_6	35^{d}	58^{e}	57^{e}	73^{e}

[a] I. Kritchevsky and A. Ilunskaya, *Acta Physiochem. URSS*, **20**, 327 (1945). [b] D. D. Eley, *Trans. Faraday Soc.*, **40**, 184 (1944). [c] W. L. Masterton, *J. Chem. Phys.*, **22**, 1830 (1954). [d] J. Walkley and J. H. Hildebrand, *J. Am. Chem. Soc.*, **81**, 4439 (1959). [e] J. Horiuti, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **17**, 125 (1931).

molal volumes at their own boiling points. Reasons for the use of this parameter were given in ref 6. It is a corresponding state quantity, paralleling the cube of σ, the intrinsic molecular diameter as determined from gas imperfections but free from their considerable uncertainties. Our present purpose requires relative molecular diameters only.

Any valid explanation of the extraordinary features of the entropy of solution of inert gases in water must obviously be based upon a reasonably valid model of the structure of water itself. Concerning this there is as yet no consensus. A competent, detailed, and critical account of the various models that have been proposed has been published by Némethy and Sheraga.[8] The models differ mainly in the number of hydrogen bonds that are assumed to have been broken, and upon different molecular species and discrete clusters assumed to be present. The large losses in entropy when gases are dissolved in water have been explained by most writers by postulating that the water surrounding a solute molecule becomes more rigidly structured. The term "iceberg" has often been applied. One writer uses the terms "ice I-like" and "ice II-like." Others speak of "hydrates." We leave definite descriptions of these various concepts to their authors. We think that Némethy and Sheraga have done it very well. Our purpose is not to "prove" that any of them are "wrong," but rather to throw into the ring an alternative model for consideration. We think that the more popular models are still not satisfactory despite all the labor that has been expended to construct formulas to fit the facts. An equation is not "proof," particularly if it contains parameters that are adjustable or not operational.

We are influenced by the deduction of Wall and Hornig[9] from Raman intensities of HDO that "a mixture model with well structured lattice regions must be discarded. The contribution of ice-like regions can be no more than about 5% of the total." Also, "the contribution of vapor-like molecules is limited...to about 5% of the total."

Stevenson[10] concluded from the uv absorption spectrum of water that "the concentration of nonhydrogen-bonded water monomer between 0 and 100° is less than 1% of the molecules of the liquid."

Mysels[11] found no light scattering such as would be expected in "compact structures separated by liquid."

The assumption that an inert gas molecule can attach to itself a "cage" of water molecules sufficiently rigid to reduce entropy sufficiently to form a real "hydrate" seems to us negated by the following facts. The solid hydrate, "$Xe \cdot 6H_2O$," reported by de Forcrand,[12] has a dissociation pressure at 0° of 1.15 atm. The solubility of Xe in H_2O at 0° and 1.15 atm is only 0.0178 mol %. The solid would seem to be only a very unstable clathrate.

We propose a model for the loss of entropy upon solution of gases in water that does not postulate the formation of rigid structures of any sort. It is based upon the model of water proposed by Lennard-Jones and Pople[13] and elaborated by Pople in considerable detail. In this model, the hydrogen bonds of ice become subject to bending upon melting instead of being broken. He calculated that much less energy is required for bending H bonds than for breaking them. He accounted successfully for the radial distribution function obtained from X-ray scattering, for the change in density upon melting ice, and for the temperature dependence of the dielectric constant. His treatment of the dielectric constant was further refined by Harris and Alder.[14]

We are encouraged by the fact that so keen a critic in such matters as Scatchard,[15] in a recent review of theories of the structure of water, concluded by saying: "Since I learned of the Lennard-Jones and Pople model...I have not been able to accept any other."

The extraordinarily large heat capacity of water results from the capacity of these H bonds to absorb thermal energy. This necessarily becomes less with water molecules that are in contact with a nonwetting surface of Teflon or paraffin, and likewise, we propose, with molecules of an inert gas. The loss of entropy of this water may be expected to be related to the total inert surface area exposed to the water. The surface areas per mole of dissolved gases we assume to be proportional to $V_b^{2/3}$ for the gases at their boiling points.

Figure 4 presents evidence for this hypothesis in a plot of the values of $s_2(10^{-5}) - s_2^g$, from Table I, against $V_b^{2/3}$. In the case of SF_6, which melts at 222.5°K with a pressure of 1700 mm, we have calculated a value for its molal volume as liquid at 760 mm from its critical molal volume, 200 cc.[16] The ratio of V_c to V_b is close to 2.65 for many liquids of symmetrical molecules: *e.g.*, Ar 2.63, Xe 2.65, CF_4 2.68, $SnCl_4$ 2.65. Assuming 2.65 for SF_6 gives $V_b = 75.5$ cc.

The two widely divergent values of $s_2(10^{-5}) - s_2^g$ given in Table I for CF_4 as well as for SF_6 are plotted in Figure 1. The lower points, which fall on a different line with the point for NF_3, were all three determined at Oxford in the laboratory of E. B. Smith. In view of what we know of the abnormally weak interactions between paraffins and perfluoro chemicals,[17] it seems reasonable that the latter should fall on a line somewhat lower than the line for the other inert gases.

The departure of the point for C_2H_4 is consistent with

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(8) G. Némethy and H. A. Sheraga, *J. Chem. Phys.*, **36**, 3382 (1962).

(9) T. T. Wall and D. F. Hornig, *ibid.*, **43**, 2079 (1965).

(10) D. P. Stevenson, *J. Phys. Chem.*, **69**, 2145 (1965).

(11) K. J. Mysels, *J. Am. Chem. Soc.*, **86**, 3503 (1964).

(12) R. de Forcrand, *Compt. Rend.*, **181**, 15 (1925).

(13) J. Lennard-Jones and J. A. Pople, *Proc. Roy. Soc.* (London), **A205**, 155 (1951); J. A. Pople, *ibid.*, 163 (1951).

(14) F. E. Harris and B. J. Alder, *J. Chem. Phys.*, **21**, 1031 (1953).

(15) G. Scatchard, *Federation Proc.*, **25**, 954 (1966).

(16) H. P. Clegg, J. S. Rowlinson, and J. R. Sutton, *Trans. Faraday Soc.*, **51**, 1327 (1955).

(17) J. H. Dymond and J. H. Hildebrand, *J. Phys. Chem.*, **71**, 1145 (1967).

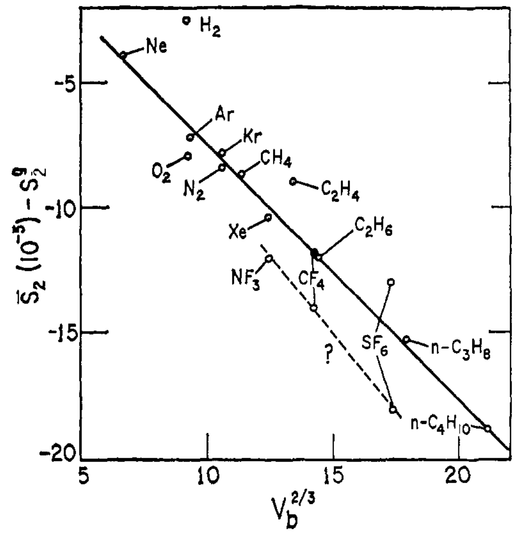

Figure 4. Relation between the entropy of transferring at 25° gas at 1 atm to solutions in water at the same mole fraction, $x_2 = 10^{-5}$, and the relative total surfaces of the gas molecules from their molal volumes at their boiling points.

its π electrons and relatively high solubility. Hydrogen is a law unto itself in all of its solubility relations.

The linear relation between loss of entropy and molar surface area seen in Figure 4 holds also for higher alkanes as can be deduced from the entropy of their liquid–liquid interfaces with water. We use for illustration the following data for surface tensions and entropies for normal octane and water at 25°.

	n-C_8H_{18}	H_2O	Interface
γ, ergs/cm^2	21.3	72.0	51.2
$-\partial\gamma/\partial T$, erg/(deg cm^2)	0.097	0.157	0.089

Values of γ for n-C_8H_{18} over a range of temperature were measured by Harkins and Cheng;[18] those for H_2O are from the American Institute of Physics Handbook, and for the interface by Aveyard and Haydon.[19] The interfacial entropy is virtually the same for all alkanes from hexane to tetradecane, and surface entropies vary but little.

We begin by forming a drop of octane under water to a surface of 1 cm^2. This involves an increase of entropy of $\Delta S_i = 0.089$ erg/deg. The formation of a drop of the same size in air would involve $\Delta S_0 = 0.097$ erg/deg, and, similarly, for a bubble of this size in water, $\Delta S_w = 0.157$ erg/deg. The difference, $\Delta S_i - (\Delta S_0 + \Delta S_w) = 0.089 - (0.097 + 0.157) = -0.165$ erg/deg, may be regarded as the loss of entropy that would occur if 1 cm^2 each of octane and water are brought into contact.

If we introduce into water a mole of octane divided into N drops, the volume of 1 drop is V/N; its surface is $4.84(V/N)^{2/3}$ (since the surface area of any sphere is $(4\pi)^{1/3}3^{2/3}v^{2/3}$) and the total surface area of N drops is then $4.84N^{1/3}V^{2/3}$. If N is the Avogadro number, the total surface per mole of octane would be $41 \times 10^7V^{2/3}$. The experimental net entropy per mole of surface cannot remain constant at -0.165 as the radius of a drop approaches the range of molecular forces, but since all three components of entropy would be similarly affected we can neglect it without serious error in an approximate treatment such as this. Using the figure -0.165 erg/(deg cm^2), the loss of entropy per mole becomes $6.8 \times 10^7V^{2/3}$ erg/(deg mole) or $1.65V^{2/3}$ cal/(deg mole). The difference in the entropy of solution in the case of two alkanes, A and B, would be $-1.65(V_A^{2/3} - V_B^{2/3})$ as compared with the slope of the long line in Figure 4, $-1.0(V_A^{2/3} - V_B^{2/3})$.

In view of the approximate nature of the foregoing analysis, the agreement of this theoretical proportionality constant with the experimental one for much smaller molecules is closer than could be expected. We believe it clearly shows that the differences in entropy of solution of inert gases in water to the same mole fraction is a matter of surface rather than of volume. Molecules and drops of varying sizes could hardly lose entropy in any consistent fashion by surrounding themselves with any reasonable sort of "icebergs."

Our findings do not unequivocally "prove" that our explanation based upon the Pople model is the only one possible. We adopted it as a basis for this study because it seemed reasonable that water molecules forced against a paraffin surface would not possess the full quota of four hydrogen bonds that contribute heavily to its exceptionally large heat capacity. We have no other explanation that is consistent with the quite evident dependence of the entropy upon surface rather than volume, and the small solvent power of water for alkanes. We are not the first to suggest that inert solutes can cause reduction in the number of hydrogen bonds; Rowlinson,[20] in 1959, wrote, "The addition to water of any molecules containing inert groups must reduce the total number of hydrogen bonds. . . ."

Acknowledgment. We thank Berni J. Alder, Robert L. Scott, John M. Prausnitz, and John A. Pople for helpful discussions, and the National Science Foundation for its support.

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(18) W. D. Harkins and Y. C. Cheng, *J. Am. Chem. Soc.*, **43**, 35 (1921).

(19) R. Aveyard and D. A. Haydon, *Trans. Faraday Soc.*, **61**, 2255 (1965).

(20) J. S. Rowlinson, "Liquids and Liquid Mixtures," Butterworths & Co. (Publishers), Ltd., London, 1959, p 183.