THERMODYNAMIC PARAMETERS FOR DISSOLVED GASES*

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Abstract.—In 1958 and subsequently we correlated properties of solutions of gases in liquids by using the “force constants,” ϵ/k , and collision diameters, σ , which serve as parameters in equations for molecular pair potential energy such as that of Lennard-Jones or its variants. Unfortunately, however, the figures for these parameters that have been published are so scattered for the same gas as to make it difficult to select “best” values; in 1967, therefore, I substituted for these indirectly determined molecular parameters the directly and accurately known molal energy of vaporization, ΔE_b^v , and the molal volume, v_b , of the liquefied gas, both at its boiling point. A plot of values of ΔE_2^v against the most trustworthy values of ϵ/k reveals direct proportionality. The same is true for $v_b^{1/3}$ versus σ .

Recent examples will be shown of excellent linear correlations with these parameters of thermodynamic properties of different gases in the same solvent.

It is no less “scientific” and far more practical to regard molecules of a solute as immersed in the potential energy field of its solvent than it is to split this field into imperfectly known pair potentials of questionable additivity and to try to integrate them over an undetermined distribution function.

In 1958 J. E. Jolley and I¹ published a paper on Solubility, Entropy, and Partial Molal Volumes in Solutions of Gases in Non-Polar Solvents in which, among other things, we showed a plot of the solubility of ten gases in iso-octane, carbon tetrachloride, and benzene, expressed as logarithm of the mole fraction of the gas, x_2 , against force constants of the gases, ϵ/k . k is the Boltzmann constant, which changes 10^{-16} ergs per molecule into degrees Kelvin (a rather strange unit for force constants). ϵ is the depth of the “potential well” between repulsive and attractive branches of a curve of potential energy, $u(r)$, versus distance of separation, r , of a pair of molecules. The form of the function most widely used has been the “Lennard-Jones 6-12 potential,”

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

σ represents molecular diameter. Kobatake and I² later extended this method of plotting to 12 gases in nine solvents.

These parameters are widely used in theories of liquids and solutions, and a vast amount of labor has been devoted to their evaluation. Unfortunately, however, there is considerable scatter in the values reported for any one gas, and a person who wishes to use them is puzzled to select “best” values. It is intolerable to have to depend upon fuzzy parameters for handling precise data such as we now have for the solubility and entropy of solutions of a number of gases.

I published a paper³ in these PROCEEDINGS in 1967 on Solutions of Gases in Normal Liquids in which I substituted for the above *molecular* parameters the corresponding *molal* parameters: energy of vaporization and volume per mole of a gas at its boiling point, ΔE_b^v and v_b . The present paper is a sequel and an extension of that one.

The relation between the two pairs of parameters is implicit in an equation that Wood⁴ and I published in 1933 for the potential energy of a mole of liquid in terms of the Avogadro number, N_0 , the pair potential, $u(r)$, and the distribution function of liquid structure, $\rho(r)$,

$$E = \frac{2\pi N_0^2}{v} \int u(r) \rho(r) r^2 dr \quad (2)$$

We assumed that $E = -\Delta E^v$. Figures 1 and 2 are plots of ϵ/k versus ΔE_b^v and of σ versus $v^{1/3}$ for most of the light gases. The values of ϵ/k and σ are from two tabulations of data in the monumental book by Hirschfelder, Curtiss, and Byrd.⁵ The points for Ne, Ar, Kr, Xe, designated by open circles, are from an exceptionally competent source, W. G. Schneider and his associates.⁶ An open circle marks also four virtually identical values for CH_4 . The values of ΔE_b^v are obtained from concordant values of heats of vaporization by subtracting RT . Corrections for vapor imperfections would be nearly the same for all within limits of error. Molal volumes are reliably obtained from liquid densities.⁷

I offer the following comments on these plots. The straight lines through the open circles indicate proportionality between the corresponding parameters, therefore the easily accessible values of ΔE_b^v and $v^{1/3}$ can serve to determine values of ϵ/k and σ with little uncertainty and far less labor.

As examples of practical applications, the only fluorocarbon gas for which a value of ϵ/k had been published is CF_4 , but K. W. Miller⁸ of this laboratory correlated the solubilities of CF_4 , C_2F_6 , SF_6 , C_3F_8 , and $\text{c-C}_4\text{F}_8$ in cyclohexane, obtaining a straight line in a plot of ΔE_b^v versus $RT \ln x_2$, as I had done for two other groups of gases in the 1967 papers.

FIG. 1.—The scatter of published values for "force constants" of gases compared with values of their energy of vaporization at their boiling points.

Again, R. G. Linford⁹ determined partial molal volumes of these gases in the same solvent and correlated them with entropies of expansion using values of v_b . Further examples of excellent linear correlations by means of these parameters will be found in a new book by Hildebrand, Prausnitz, and Scott.⁷

Scott and I wrote in 1962 that "Any satisfying interpretation of liquids and solutions must be a molecular theory and must involve molecular parameters." My own studies of solutions of gases since 1962 have caused me to be quite dissatisfied with supposedly molecular parameters that can be determined only approximately, with great labor, by aid of a roundabout process based upon an essentially empirical formulation of intermolecular pair-potential. I reassert what we wrote later, and rather contradictorily, in the same paragraph as the above:

"For practical purposes, the most useful theory is likely to be one which is built 'close to the ground,' and which evaluates its parameters under conditions closely approximating those where they will be applied. For this reason, we prefer to relate the properties of liquid solutions to those of pure liquids, rather than to dilute gases at very different temperatures."

A further comment on v_b is pertinent. One of the parameters of the theory of corresponding states, itself a nonmolecular theory, is the critical volume per mole, v_c . The practical difficulty with it is that to fix its value at all precisely requires the measurement of subcritical liquid and vapor densities over a range of temperature. There are probably persons who do not realize how uniform is the ratio v_b/v_c for approximately symmetrical molecules of different atomicity. Illustrations are:

Ar	0.379	CF ₄	0.373	SnCl ₄	0.377
Kr	0.377	C ₂ H ₄	0.377	c-C ₆ H ₁₂	0.376
Xe	0.377	C ₃ H ₈	0.374	C ₆ H ₆	0.374
CH ₄	0.383	n-C ₄ H ₁₀	0.374		

The variations are within the uncertainty of the values of v_c . Note that the correspondence holds even for the cyclohexane and benzene, for which meaningful values of σ would scarcely be obtainable.

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¹ Jolley, J. E., and J. H. Hildebrand, *J. Am. Chem. Soc.*, **80**, 1050 (1958).

FIG. 2.—The scatter of published values for molecular diameters compared with cube-roots of values of the molal volumes of gases at their boiling points.

- ² Kobatake, Y., and J. H. Hildebrand, *J. Phys. Chem.*, **65**, 331 (1961).
³ Hildebrand, J. H., these PROCEEDINGS, **57**, 542 (1967).
⁴ Hildebrand, J. H., and S. E. Wood, *J. Chem. Phys.*, **1**, 12 (1933).
⁵ Hirschfelder, J. O., C. F. Curtiss, and R. B. Byrd, *Molecular Theory of Gases and Liquids* (New York: John Wiley and Sons, Inc., 1954, 1964), pp. 1110, 1212.
⁶ Nicholson, G. A., and W. G. Schneider, *Can. J. Chem.*, **33**, 589 (1955); Whalley, E., and W. G. Schneider, *J. Chem. Phys.*, **23**, 1644 (1955).
⁷ Values for both quantities for a number of gases are tabulated in Appendix 7 of a book now in press: *Regular and Related Solutions*, by Hildebrand, J. H., J. M. Prausnitz, and R. L. Scott, (New York: Reinhold Van Nostrand Book Co., 1970).
⁸ Miller, K. W., *J. Phys. Chem.*, **72**, 2248 (1968).
⁹ Linford, R. G., and J. H. Hildebrand, *Trans. Faraday Soc.*, **65**, 1470 (1969).
¹⁰ Hildebrand, J. H., and R. L. Scott, *Regular Solutions*, (Englewood Cliffs, N. J.: Prentice-Hall, 1962), p. 155.