

A CRITIQUE OF THE THEORY OF SOLUBILITY OF NON-ELECTROLYTES¹

JOEL H. HILDEBRAND

Department of Chemistry, University of California, Berkeley, California

Received October 25, 1948

The present state of theory is indicated by a classification of solution types based upon deviations from ideal (zero) heat of mixing, ideal entropy of mixing due to unequal molal volumes, and excess attraction between like molecules (association) or unlike molecules (solvation). The quantitative formulation of the effects of unequal molecular attractions and sizes has been made by the aid of simplified models, and sources of error and uncertainty include: (1) the assumption that intermolecular forces are radial from molecular centers, (2) the neglect of dipole interactions, which are especially large in cases of hydrogen bonding, (3) oversimplification of repulsive forces, (4) the Berthelot relation between attraction constants, (5) the assumption that thermal agitation is sufficient to give completely random distribution despite unequal attractive forces, (6) neglect of volume changes on mixing liquids, (7) uncertainty regarding the values of heat of vaporization at various temperatures, (8) in the case of solid solutes, the extrapolation of liquid properties below the melting point, (9) uncertainty regarding the entropy of mixing molecules of different sizes and shapes, and (10) chemical interactions.

The magnitude of the net uncertainty attending solubility calculations for regular solutions is appraised by calculating solubility parameters from actual measurements for a number of interrelated systems and noting their mutual consistence.

The present state of the theory of solubility of non-electrolytes may perhaps be best appreciated by the aid of the scheme in table 1. This represents a classification of the main essential factors rather than of solutions themselves, because scarcely any actual solution can be said to behave solely in any one of the several ways designated by such terms as "ideal" or "regular."

Solubilities express the composition of phases in equilibrium, and hence are to be calculated as free energies. Recent attacks upon the theoretical problem have split it into its two natural components, heat and entropy. The "ideal" or "perfect" solution is formed from its pure component liquids with zero heat of mixing at all temperatures and its components must accordingly have a partial molal entropy of transfer from pure liquid to solution of $\bar{s}_2 - s_2^0 = -R \ln x_2$, for component 2 and similarly for component 1. Such a solution obeys Raoult's law, which is that the activity of a component equals its mole fraction, $a_2 = x_2$. It has only recently been fully recognized that the components must have substantially equal molal volumes in order for Raoult's law to hold strictly,

¹ Presented at the Symposium on Thermodynamics and Molecular Structure of Solutions, which was held under the auspices of the Division of Physical and Inorganic Chemistry at the 114th Meeting of the American Chemical Society, Portland, Oregon, September 13 and 14, 1948.

except in the special case of molecules such as two normal paraffins of different lengths in parallel array (3, 10). However, there can be considerable difference between the molal volumes of the pure components without causing serious departures from Raoult's law, because the radii of two molecules will be much more nearly equal than their volumes and therefore a considerable volume discrepancy can exist without greatly affecting the structure of the solution.

The possibility of designating many non-ideal solutions as "regular" was pointed out by me many years ago (2). These are solutions in which thermal agitation is sufficient to overcome the segregating effect of unequal molecular attraction and give a structure with maximum disorder or randomness, and a

TABLE 1

Classification of solutions upon basis of enthalpy and entropy involved in transferring 1 mole of component 2 from its pure liquid to a solution in which its mole fraction is x_2

DESIGNATION	$\bar{H}_2 - H_2^0$	$\bar{s}_2 - s_2^0$	REMARKS
1. Athermal, ideal	0	$-R \ln x_2$	$a_2 = x_2$, Raoult's law, $v_1 = v_2$
2. Regular	$v_2 \phi_1 (\delta_1 - \delta_2)^2$	$-R \ln x_2$	$a_2 > x_2$, $v_1 \cong v_2$, $a_{12} = \sqrt{a_{11} a_{22}}$
3. Athermal, non-ideal	0	$-R \left[\ln \phi_2 + \phi_1 \left(1 - \frac{v_2}{v_1} \right) \right]$	$a_2 < x_2$, $v_1 \neq v_2$, $a_{12} = \sqrt{a_{11} a_{22}}$
4. General, no specific interaction	0	$-R \left[\ln \phi_2 + \phi_1 \left(1 - \frac{v_2}{v_1} \right) \right]$	$a_{12} = \sqrt{a_{11} a_{22}}$
5. One component associated	Positive	$> (-R \ln x_2)$	$a_{12} < \sqrt{a_{11} a_{22}}$
6. Solvated	Negative	$< (-R \ln x_2)$	$a_{12} > \sqrt{a_{11} a_{22}}$

partial molal entropy considered originally to be ideal, i.e., $-R \ln x_2$. If the structure can be assumed to be thus random, it is possible to integrate the intermolecular potentials of all the like and unlike molecular pairs over the whole solution and, invoking the Berthelot relation, $a_{12} = \sqrt{a_{11} a_{22}}$, for the constants of attraction between the two species, to express the heat of mixing in terms of the molal volumes and energies of vaporization of the pure components. The expression for the partial molal heat of mixing of component 2 is given in table 1, where ϕ_1 denotes the volume fraction of component 1 and δ_1 and δ_2 are what I shall call the "solubility parameters" of the pure liquids; they are the square roots of their energies of vaporization per cubic centimeter, i.e., $\delta_1 = (\Delta E_1^v / v_1)^{1/2}$, where ΔE^v and v are molal quantities. The solubility equation

for a regular solution is obtained by combining the heat and entropy terms to give²

$$RT \ln (a_2/x_2) = v_2 \phi_1^2 (\delta_1 - \delta_2)^2 \quad (1)$$

I shall return to this equation after discussing briefly the other types referred to in table 1.

The question of the entropy of mixing molecules of different sizes and shapes has recently received much attention, stimulated immensely by the developments in the field of high polymers. It has led to the equation derived inde-

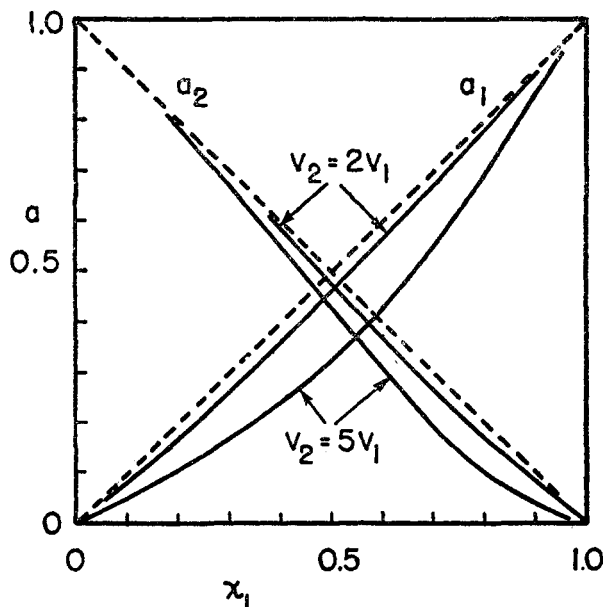


FIG. 1. Effect of inequality in molal volumes of the components of a binary solution upon their activities.

pendently by Flory and Huggins according to which the partial molal entropy of mixing is (5)³

$$\bar{s}_2 - s_2^0 = -R[\ln \phi_2 + \phi_1 \left(1 - \frac{v_2}{v_1}\right)] \quad (2)$$

The difference between this and $R \ln x_2$ is small for volume ratios of the order of 2:1, which are seldom exceeded by non-polar liquids with which we ordinarily deal. For example $v = 61$ cc. for carbon disulfide and 132 cc. for *n*-hexane at 25°C. The sign and magnitude of the deviations from Raoult's law given by

² For an account of the development of this equation and its underlying theory see reference 9.

³ For a résumé of the development of this theory see Hildebrand (5).

equation 2 for volume ratios of 2 and 5 are illustrated in figure 1. There is some reason to believe that the equation overdoes the correction. It is to be noted that whereas the positive heat of mixing of regular solutions corresponds to positive deviations from Raoult's law, i.e., $a_2 > x_2$, the effect of inequality in molal volumes is to produce negative deviations, i.e., $a_2 < x_2$.

Since most non-polar solutions in which specific or chemical interactions are absent would present both volume discrepancy and positive heat of mixing, one may combine equations 1 and 2 to give, for class 4 in table 1,

$$RT \ln (a_2/\varphi_2) = v_2\varphi_1^2(\delta_1 - \delta_2)^2 + RT \varphi_1(1 - v_2/v_1) \quad (3)$$

If one component is associated, as by hydrogen bonding, its dilution by the other causes heat absorption and we have chemical equilibria to deal with. The effect is to give positive deviations from Raoult's law (class 5). An enhanced attraction between the unlike species, on the other hand, is accompanied by positive heat, diminished entropy, and negative deviations from Raoult's law (class 6).

Actual solutions may, of course, present combinations of the above effects which may be difficult or even impossible to disentangle. The present critique is aimed at an appraisal of the adequacy of equations 1 and 3 to solutions where there is reason to believe that the highly specific chemical effects referred to in classes 5 and 6 are practically absent. Moreover, since equation 2 has not been thoroughly tested, we shall concern ourselves mainly with components for which the molal volume ratios do not exceed 2 and apply equation 1.

Let us begin by reviewing the various sources of error or uncertainty. In deriving the above equation, the following assumptions were either stated or at least implicit. I say implicit, because those of us who had a hand in it were not always conscious at the time of their precise import. (1) The intermolecular forces operating are the short-range additive "dispersion forces," for the understanding of which we are indebted to London. If the molecules possess dipoles, strict additivity can no longer be assumed. London (12), in an important paper on "Centers of van der Waals Attraction," has discussed two sources of non-radial behavior, stating that "(1) The elementary units of the dipole interactions are, in general, not at all spherically symmetrical forces. They have rather to be built up by highly *anisotropic force centers*. (2) In certain large molecules we encounter characteristic, long, extended electronic oscillators. In these molecules the *spacial extension* of the oscillators has to be accounted for, . . . and it is suggested in these cases that the molecular forces be built up by certain smaller units, which forces, however, are *no longer additive*."

(2) These force fields are considered as radial and of similar form. This is an obvious oversimplification for molecules such as paraffins, geometrically far from being spherical. Furthermore, Gilman and I (7) have presented evidence that two molecular species such as ethane and 1,2-dimethylbutane, which are closely similar except for considerable difference in size, do not conform to the theory of corresponding states, as they should if their force fields were like those of the monatomic gases.

The errors introduced by neglecting dipoles depend upon both their magnitude and their location within the molecules. If the dipole moment is not greater than about 1 Debye unit and is somewhat buried within the molecule, as it is in the cases of chloroform and ether, its effect may be mainly to alter the apparent solubility parameter, but larger or more exposed dipoles, such as hydroxyl, obviously introduce highly specific interactions which render equation 1 more or less inapplicable.

(3) Repulsive forces are simplified by assuming them to be of a uniform, radial, high-inverse-power type.

(4) The constants of attraction between unlike molecules are assumed to be the geometric mean between those for the like molecules (Berthelot relation). This is obviously violated whenever there are such interactions as hydrogen bonds, or electron donor-acceptor chemical reactions. These may be so small as to have eluded recognition by ordinary criteria and yet be sufficient to have considerable effects upon solubility relations. A striking illustration has recently been discovered by Benesi and Hildebrand (6) in the increasing solvation of iodine in benzene, toluene, xylene, and mesitylene, in that order, an apparently acid-base type of reaction that could scarcely have been predicted.

(5) The thermal agitation is assumed to be sufficient to overcome completely the segregating effect of unequal attractive forces. While this cannot be strictly true, there is a good deal of evidence that appreciable disturbance occurs only in the immediate neighborhood of a critical mixing point (4, 8, 11).

(6) Equation 1 does not take cognizance of changes of volume on mixing, although the formation of regular solutions is usually accompanied by expansion and increased entropy. The treatment can be refined by measuring and allowing for this expansion, but I propose in this critique deliberately to neglect this correction on the ground that our purpose is to predict the behavior of solutions from the properties of their pure components alone; if we must measure other properties of solutions in order to calculate solubility, we might as well measure the solubility itself. We can at least be reasonably sure of the sign and rough magnitude of the errors entailed by neglecting these volume changes. That we shall ever be able to calculate them for the wide variety of molecular types seems quite unlikely.

(7) The numerical values of the solubility parameters, δ , are often desired for temperatures far from those at which the heat of vaporization has been accurately determined, and the difference between the heat capacities of liquid and vapor, necessary for an extrapolation, are known only for comparatively few substances.

(8) In order to deal with the solubility of a solid, we refer its activity to the substance in the supercooled liquid form, to calculate which accurately we need not only the heat of fusion at the melting point but also the heat capacities of the solid and liquid forms. Even where these have both been measured, which is often not the case, the heat capacity of the liquid has to be extrapolated below the melting point.

With all the above sources of uncertainty, one might expect that equation 1, or, even where $v_1 \gg v_2$, equation 3, would yield only extremely rough figures

for solubility; hence those who have become sufficiently conversant with both theory and data to judge have doubtless come, like myself, to feel both surprised and gratified to find how well it holds. This is well illustrated by the solubilities of iodine (table 2) in liquids of widely different solvent power, selected from a more extensive study by Benesi and Hildebrand (1). It will be noted that, although the solubility of iodine ranges from 0.0185 to 7.82 mole per cent, and its activity coefficient, a_2/x_2 , in the saturated solutions ranges from 3.30 to 1400, these solubilities substituted in equation 1 yield δ_2 values for iodine agreeing within 3 per cent. Moreover, the dipoles present in chloroform, bromoform, and 1,2-dibromoethane and the large molal volume of normal perfluoroheptane appear to cause no serious disturbance. Numerous other cases of similarly good agreement have been presented.

We see, also, that the average of the δ -values for iodine calculated from its solubilities is a little larger than the value we obtain from its energy of vaporiza-

TABLE 2
Iodine solutions at 25°C.

SOLVENT	MOLECULAR VOLUME	MOLE PER CENT I ₂	a_2^s/x_2	δ_1	δ_2
	cc.				
<i>n</i> -C ₇ F ₁₆	227	0.0185	1400	5.7	14.2
SiCl ₄	115.3	0.499	51.8	7.6	13.9
CCl ₄	97.1	1.147	22.5	8.6	14.2
TiCl ₄	110.5	2.15	12.0	9.0	14.1
CHCl ₃	80.7	2.28	11.3	9.3	14.3
CS ₂	60.6	5.46	4.73	9.9	14.1
CHBr ₃	87.8	6.16	4.19	10.5	14.1
1,2-C ₂ H ₄ Br ₂	86.6	7.82	3.30	10.4	14.1
Average.....					14.1
I ₂	59.0	25.8	1.00	($\Delta E^v/v$) ^{1/2} = 13.6	

tion per cubic centimeter. It is evident, therefore, that 14.1 would be a better figure than 13.6 to use for calculating its solubility in a new solvent, and this is not an isolated case. It seems worth while, therefore, to study the interrelations of a group of substances to see whether it is possible to derive a consistent set of δ -values from solubility data. It is, of course, desirable for this purpose to select solutions with large values of $\delta_2 - \delta_1$.

We have data for the solubilities at 25°C. in a more or less common group of solvents of the following solutes of comparatively high internal pressures, or δ -values: phosphorus (P₄), iodine (I₂), sulfur (S₈), stannic iodide, *p*-dibromobenzene, naphthalene, anthracene, and phenanthrene. The data are nearly all given, with references, in the third edition of *Solubility of Non-Electrolytes* (9) and need not be repeated here. The values of $\delta_2 - \delta_1$ in equation 1 calculated from these data are represented in figure 2. The vertical scales for the solutes have been displaced so as to make the line connecting the points for carbon

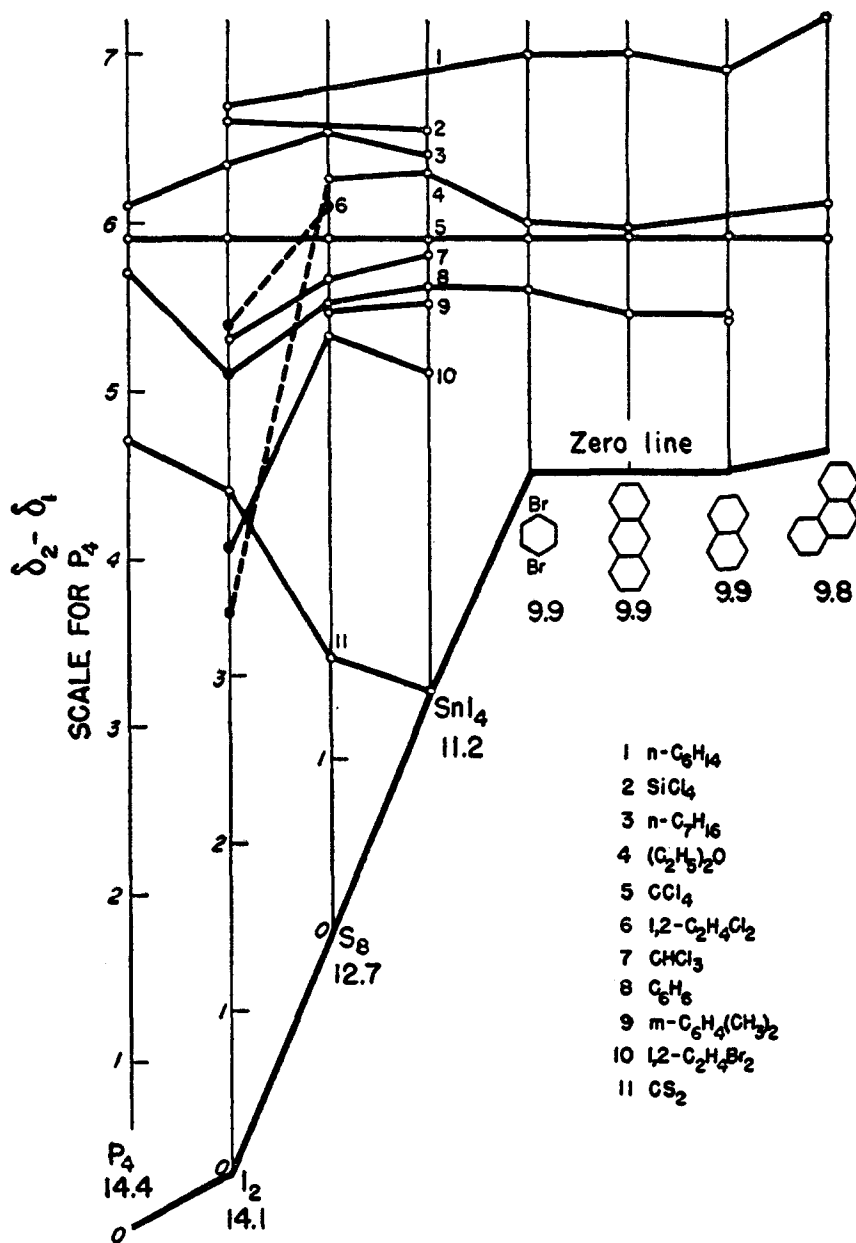


Fig. 2. A test of the internal consistence of solubility parameters

tetrachloride horizontal. If the equation applied rigidly to all the solutions represented, the other lines would also all be horizontal. The departures represent the various degrees of inadequacy of equation 1. The discrepancies are seen to be greatest for (a) iodine in ether, (b) 1,2-dichloroethane and 1,2-

dibromoethane, and (c) carbon disulfide. The first of these is explained by the evidence of strong solvation furnished by the brown color of the solution. The second pair of solvents have two strong dipoles each; hence some irregularity is to be expected. Carbon disulfide has the smallest molal volume of all the solvents represented, and some, at least, of the drop in its line in going from P_4 and I_2 to S_8 and SnI_4 may be explained by the increased difference in molal volumes. The line would be more nearly horizontal if the partial molal entropy of the solute were calculated by the aid of equation 2, instead of $-R \ln x_2$. The neglect of this factor is intentional.

The fluctuations of the lines for the various solvents from the horizontal seldom exceed 0.3 unit, if we exclude the cases of strong dipoles and solvation mentioned above, and we may regard this as determining the uncertainty in calculated values of solubility. In the case of iodine in carbon tetrachloride, for example, the measured values are: $v_1 = 97.1$ cc., $v_2 = 59.0$ cc., $a_2^s = 0.258$ (the activity of solid iodine referred to supercooled liquid), and $x_2 = 0.01147$. These give $\delta_2 - \delta_1 = 5.6$. Reversing the calculation and taking $\delta_2 - \delta_1 = 5.9$, one obtains $x_2 = 0.0094$, an error of 18 per cent. The logarithmic relation between x_2 and $(\delta_2 - \delta_1)^2$ naturally enhances the percentage error in calculating x_2 .

It is noteworthy, next, that all the solubility data agree in assigning to chloroform a δ -value of about 9.0, less than that of benzene, 9.16, whereas its $(\Delta E^Y/v)^{1/2} = 9.3$. It might be expected that its dipole moment would have some such effect, and it is our good fortune that it is so nearly the same with different solutes.

This study appears to me to justify the following general conclusions. Equation 1, or equation 2 if a volume ratio far from unity appears to make it worth the extra computation, applied to solutions in which specific interactions are absent, can yield figures for solubility of moderate reliability with uncertainties corresponding to 0.2–0.3 unit in δ -values. It can predict relative solubilities in different solvents with much smaller uncertainties. The direction and rough magnitude of departures from values which may be caused by association and solvation can often be fairly well estimated.

The quantitative limitations set forth in this paper are not so serious as to prevent the theory from being qualitatively very serviceable. We seek qualitative and relative solubility data far more often than exact figures. We seek the best or sometimes the poorest solvent for a certain solute. We seldom want to know a solubility to, say, 1 per cent and, indeed, we seldom control temperature or purity to a corresponding degree. If we do need a solubility to that accuracy we must rely upon measurement, better measurement, indeed, than many in the literature. All theory can do for us in that case is to select, out of the scores of solvents upon our shelves, the few likely to serve our purpose.

REFERENCES

- (1) BENESI, H. A., AND HILDEBRAND, J. H.: *J. Am. Chem. Soc.*, in press.
- (2) HILDEBRAND, J. H.: *Proc. Natl. Acad. Sci. (U. S.)* **13**, 267 (1927); *J. Am. Chem. Soc.* **51**, 66 (1929).

- (3) HILDEBRAND, J. H.: J. Am. Chem. Soc. **59**, 794 (1937).
- (4) HILDEBRAND, J. H.: Science **90**, 1 (1939).
- (5) HILDEBRAND, J. H.: J. Chem. Phys. **15**, 225 (1947).
- (6) HILDEBRAND, J. H., AND BENESI, H. A.: J. Am. Chem. Soc. **70**, 2832 (1948).
- (7) HILDEBRAND, J. H., AND GILMAN, T. S.: J. Chem. Phys. **15**, 229 (1947).
- (8) HILDEBRAND, J. H., AND NEGISHI, G. R.: J. Am. Chem. Soc. **59**, 339 (1937).
- (9) HILDEBRAND, J. H., AND SCOTT, ROBERT L.: *Solubility of Non-Electrolytes*, 3rd edition. Reinhold Publishing Corporation, New York (1949).
- (10) HILDEBRAND, J. H., AND SWENY, J. W.: J. Phys. Chem. **43**, 297 (1939).
- (11) KIRKWOOD, J. G.: J. Phys. Chem. **43**, 97 (1939).
- (12) LONDON, F.: J. Chem. Phys. **46**, 305 (1942).