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FACTORS DETERMINING SOLUBILITY AMONG NON-ELECTROLYTES*

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This address has been prepared with the purpose of giving to non-specialists, so far as possible within the allotted time of fifteen minutes, a large-scale survey of the present status of the theory of solubility of non-electrolytes, with emphasis upon the methods used in attacking the various phases of the problem.   That the problem is indeed a complex one is well illustrated by a system of seven liquid phases, a photograph of which I recently published.[1]   Its components are heptane, aniline, water, "perfluorokerosene" (approximately $C_{12}F_{26}$), phosphorus, gallium and mercury. These molecular species differ so strongly among themselves as to resist more or less completely the mixing effect of thermal agitation.   The differences are in part qualitative, and include metallic character, dipole moment and hydrogen bridging, but in part, also, quantitative, differences in the strength of the "van der Waals" or, more appropriately designated, "London" forces.   Professor F. London explained these forces as the consequence of quantum mechanical interaction between the molecular electron clouds.   The strength of the attraction depends upon the number and what we may crudely call the "looseness" of the electrons.   It is expressed in terms of polarizability, α, and "zero point energy," $h\nu_0$, the energy of electrons in their ground states, an energy which persists even at absolute zero.   The expression for the potential energy between molecules of two species, 1 and 2, at distance, r, is

$$\epsilon = \frac{3\alpha_1\alpha_2}{2r^6} \cdot \frac{h\nu_{0,1} \cdot h\nu_{0,2}}{h\nu_{0,1} + h\nu_{0,2}}. \tag{1}$$

Higher terms for second order effects have been added as a result of more refined analysis but these are hardly significant for our purpose, particularly

because there is evidence[2] that the molecular fields of *polyatomic* molecules are not best described as radial from their geometrical centers but as extending, rather, from peripheral atoms or "orbitals." We find, fortunately, that such uncertainties are at least partly cancelled by the process, presently to be described, upon which our general theory is based. There are, however, three corollaries of the theory which are to be noted as most significant to our purposes: (1) the attraction is very short in range, (2) the attractive potential between pairs of unlike molecules is simply related to that between pairs of the like molecules and (3) these interactions, unlike those we call "chemical," do not saturate each other, and therefore the potential energy of a mass of liquid may be expressed as an integral of all the pair potentials.

The process we have adopted to serve as the basis for our theory of solubility is the mixing of two pure liquid components by isothermal distillation to form a solution in which their mole fractions are x_1 and x_2, respectively. The present exposition will, however, appear simpler if we think of distilling one mole of either component (let us select no. 2) into a very large amount of solution in which its mole fraction is x_2. The change in free energy accompanying such a transfer is

$$\bar{F}_2 - F_2{}^0 = RT \ln (f_2/f_2{}^0) = RT \ln a_2, \qquad (2)$$

where f_2 denotes its fugacity (a corrected vapor pressure) in the solution and $f_2{}^0$ its fugacity in its pure liquid. We shall henceforth use activity, defined as $a_2 = f_2/f_2{}^0$. When one forms a saturated solution, he applies the "solute" at an activity which he can control, by pressure, in case of a gas or vapor, or calculate, in case of a solid, from its melting point and heat of fusion.

Now the change in free energy in this process may be regarded as the resultant of the accompanying changes in heat constant, $\bar{H}_2 - H_2{}^0$ and in entropy, $\bar{S}_2 - S_2{}^0$, as given by the pure thermodynamic equation,

$$\bar{F}_2 - F_2{}^0 = \bar{H}_2 - H_2{}^0 - T(\bar{S}_2 - S_2{}^0). \qquad (3)$$

Ideal Solutions.—Let us begin with an ideal case, which, like all ideals, can be only rarely approached and never quite realized, *i.e.*, a solution of two molecular species having equal intermolecular attractions and equal molal volumes. The energy and heat of transferring any molecule from its own pure liquid into the solution is then zero, hence

$$\bar{F}_2 - F_2{}^0 = -T(\bar{S}_2 - S_2{}^0). \qquad (4_1)$$

Now the change in entropy accompanying our process is a logarithmic function of the ratio of the respective "probabilities" of finding a molecule of species 2 in its pure liquid and in its solution. (I need not take time to explain why it is logarithmic, because many in my audience already know

and the others can easily find out if they wish.)   In our ideal solution, since the molecules are of equal size, and since thermal agitation keeps them mixed with maximum randomness, the ratio of probabilities is $1/x_2$ and this, translated into entropy, gives

$$\bar{s}_2 - s_2{}^0 = -R \ln x_2. \qquad (4_2)$$

Substituting this and equation 2 into 3, gives $RT \ln a_2 = RT \ln x_2$ or $a_2 = x_2$, which is Raoult's law; a relation used in all modern texts on physical chemistry to derive the various ideal solution laws.

Regular Solutions.—It has been our good fortune to find that thermal agitation usually suffices to give practically complete randomness of mixing, with two non-polar species, in spite of even large differences in their molecular forces, and, therefore, if their molal volumes are not significantly different, the entropy of transfer can still be close to the ideal entropy, $-R \ln x_2$. This uniformity regarding entropy causes a regularity in solution behavior evident in the family of solubility curves illustrated in figure 3, which suggested the term, "regular solutions." But now, in order to have a solubility equation, we must express $\bar{H}_2 - H_2{}^0$ in terms of

FIGURE 1

Cross-section of structure of an ideal liquid.

the pure components. If we were dealing with pure and mixed crystal lattices of equal, known lattice dimensions, we could add all the pair potentials to give the lattice energy. We can apply equivalent reasoning to liquids, but, instead of a summation over all the discrete distances in a crystal lattice, we must integrate over a continuous "distribution function" which expresses time-average frequency for all pair distances in the highly blurred, short range order in the liquid. The meaning of this function, $\rho(r)$, is easily grasped by referring to figure 1, which represents a cross-section of the instantaneous arrangement of molecules around a central one. The volume of a spherical shell of thickness dr of large radius is simply $4\pi r^2\, dr$, and since the density of molecules in the liquid is the Avogadro number divided by the molal volume, N/v, the number of molecular centers in the large shell is $(4\pi N r^2\, dr)/v$. But when r is small, the presence of the central molecule makes the probability of molecular
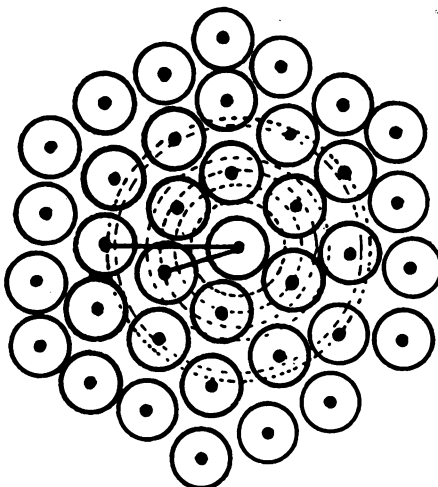
centers in such a shell much higher than unity at about $2r$, moderately higher at about $4r$, etc. This varying probability is the distribution function, $\rho(r)$. Its form is nearly the same for all equally expanded liquids if plotted as $\rho(r/r_{\max})$ as illustrated for four liquid metals in figure 2. By combining $\rho(r)$ with the pair potential function, $\epsilon(r)$, we can obtain an expression for the potential energy of a mole of liquid,

$$\mathbf{E} = \frac{2\pi N^2}{v} \int \epsilon(r)\rho(r)r^2 \, dr. \tag{5}$$

We may extend this treatment to the potential energy of a solution, where the (random) molecular distribution involves the relative molal
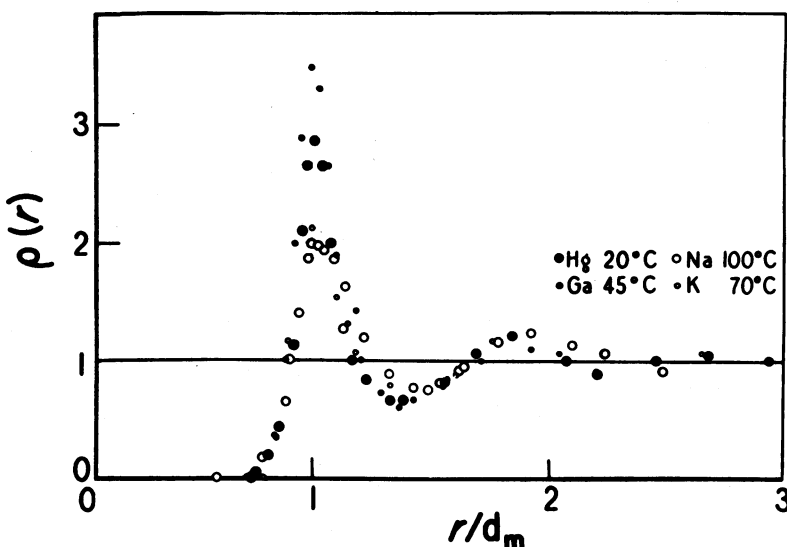

FIGURE 2

Distribution functions, $\rho(r)$, for liquid mercury, gallium, sodium and potassium plotted against $r \div$ molecular diameter.

volumes, and the total potential energy involves the pair potentials, ϵ_{11}, ϵ_{22}, ϵ_{12}, and the last can be eliminated by assuming the geometric mean. The model is simple but the mathematical steps in arriving at the final equation are far beyond the scope of this presentation, so I give only the result,

$$\bar{H}_2 - H_2{}^0 = v_2\phi_1{}^2(\delta_2 - \delta_1)^2, \tag{6}$$

where ϕ_1 denotes volume fraction of that component and $\delta = (\Delta E^v/v)^{1/2}$, the square root of the energy of vaporization per cc., an easily obtainable property of both pure liquids. With this expression for the heat effects, our solubility equation becomes

$$RT \ln a_2 = v_2\phi_1{}^2(\delta_2 - \delta_1)^2 + RT \ln x_2. \tag{7}$$

The δ-values play so predominant a rôle in determining solubility relations that we have designated them as "solubility parameters" and find it useful to have at hand tables of their numerical values at the standard temperature, 25°. Illustrative values for common substances are given in Table 1.

Solubility Relations of Iodine.—The high attractive field of iodine molecules, indicated by its solubility parameter, 14.1, is correlated with the great spread in the solubility curves plotted in figure 3, and the enormous deviations from ideal behavior in those solvents low in the plot. These solutions present a particularly exacting test of the theory underlying equation 7. Iodine solutions offer another important advantage in that one can easily distinguish two classes of solutions—one, the violet solutions, whose color, identical with iodine vapor, shows that chemical interaction is absent, and that they should behave "regularly"; the other class, yellow

TABLE 1

SOLUBILITY PARAMETERS OF IODINE, δ_2, CALCULATED FROM SOLUBILITY IN VARIOUS SOLVENTS AT 25°

SOLVENT	SOLUBILITY, 100 x_2	δ_1	δ_2 (CALC.)
n-C_6F_{16}	0.0182	5.7	14.2
$SiCl_4$	0.499	7.6	13.9
CCl_4	1.147	8.6	14.2
$TiCl_4$	2.15	9.0	14.1
CS_2	5.58	10.0	14.2
1,2-$C_2H_4Br_2$	7.82	10.4	14.1
Ideal	25.8		

to brown in color, indicating specific, "chemical" interactions. I invite your attention to the following features of the solid curves, all of which refer to violet solutions.

First, the parallelism in the slopes of these curves was what originally suggested applying to such solution the term "regular," and the regularity is obviously a matter of entropy, because it has to do with the temperature coefficient of a free energy relation.

Second, the positions of the curves accord remarkably well with the demands of equation 7, as seen by the small variations in the values of δ_2 for iodine calculated from the δ_1 values and the experimental solubilities, illustrated in Table 1 for several representative solvents. Reversing the procedure, calculating x_2 using $\delta_2 = 14.1$ for all, would obviously not lead to serious error. Particularly striking is the agreement in the case of fluoroheptane. When I first heard of the remarkable extremes in the solvent powers of fluorocarbons, I wondered whether they would overstrain the theory. The point for iodine in perfluoro normal heptane at 25° was the first to be determined, and when it was found to fit equation 7

so well I felt confident that all other solubility relations of fluorocarbons would fit the theory, and this expectation has since been abundantly confirmed.

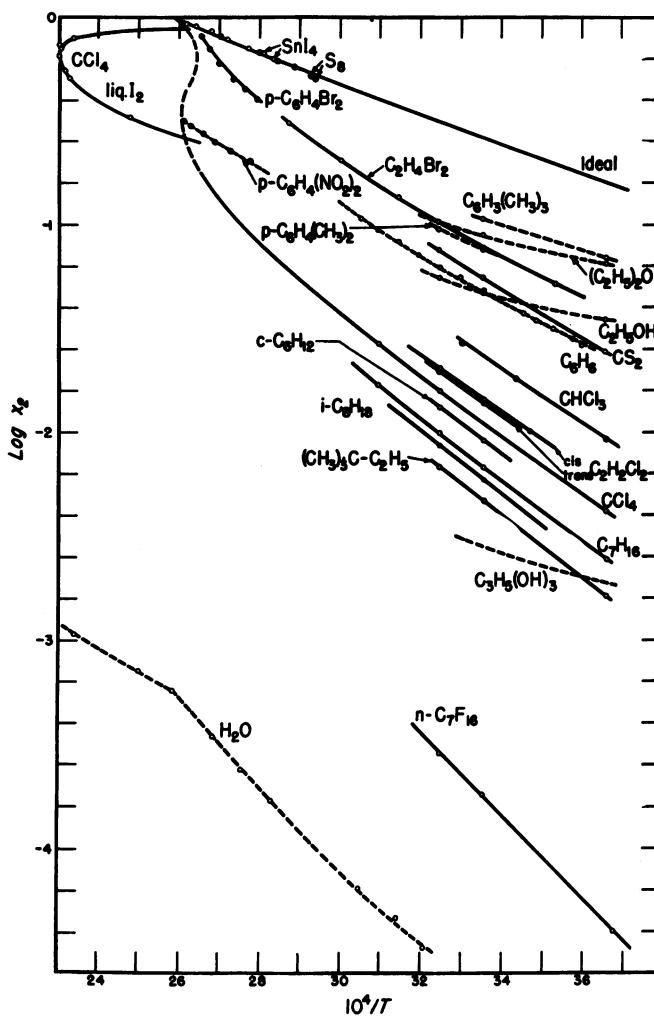Third, a particularly striking confirmation was furnished by the pre-

FIGURE 3

Solubility curves for iodine.

diction of the liquid-liquid loop for iodine and carbon tetrachloride, seen in figure 3, and this was later found close to the position predicted.

Fourth, moderate dipole moments, other than the very exposed ones leading to hydrogen bridging, may affect the δ-value slightly while not

interfering with regularity, as seen by the curve for chloroform, and the practical identity of the curves for *cis-* and *trans*-dichloroethylenes, whose dipole moments are 1.89 and 0.00 Debye units, respectively.

Solvated Solutions.—In cases where the unlike molecules react chemically, the 1–2 attraction is enhanced, and is no longer equal to the geometric mean of the 1–1 and the 2–2 attractions; the heat absorbed on dilution will be reduced over its regular solution value, and its sign may even be reversed; and the disorder and hence the entropy of the process will be less than ideal. But all these effects are more or less specific, not to be calculated by any general theory. The solutions of iodine in benzene, toluene, xylenes and mesitylene present illustrations of extraordinary interest.

Iodine dissolves in them to give solutions with brown colors increasing in the above order. They show strong absorption bands in the ultraviolet[3] whose intensities, when iodine and an aromatic are dissolved together in a "violet" solvent in varying concentrations, indicate a 1:1 solvate. We explain the interaction as that between an acid and a base; the aromatics are bases or "electron donors," whose strengths increase in the above order, and the iodine, an acid, or "electron-acceptor." The equilibrium constant for the reaction $I_2 + C_6H_6 = I \cdot C_6H_6$ in carbon tetrachloride was found to be 1.72, and the constant for the corresponding reaction with mesitylene is 7.2. (Anyone who thinks that none but "proton-acceptors" can act as bases will not be able to understand this.)

The solubility curves for these aromatics would all lie close to the curve for chloroform if there were no solvation; the curves are lifted to the positions seen in the figure[4] by the solvation, and the amount of displacement agrees remarkably well with that calculated by aid of the equilibrium constants for the acid-base interactions. It should be emphasized that the solvation is related to this displacement and not to departure from the ideal solubility curve. The common practice of interpreting inconstant partition coefficients in terms of chemical equilibria may be quite unrealistic and lead to conclusions very different from those which could be drawn from light absorption.

The Entropy of Mixing Molecules of Different Size.—It will be recalled that in deriving the term $-R \ln x_2$ for the entropy of transfer from pure liquid to solution, equality of molal volumes was not taken too seriously, however, the necessity for this limitation was not appreciated until recently because solutions are known which approximate closely to Raoult's law despite some inequality in molal volumes, but there have recently been discovered solutions of high polymers which depart strongly from Raoult's law while showing little or no heat of mixing, making it clear that it is entropy which must be held responsible. This led to efforts on the part of several investigators to formulate the entropy of mixing monomer molecules with small integral multiple polymers, but Flory and Huggins,[5]

simultaneously and independently, succeeded in deriving an expression for the entropy of solution of flexible, chain molecules occupying multiple sites in a quasi lattice with solvent molecules occupying single lattice sites. The same formula can be derived without the limitations of either linear polymers or lattice structure. The method used can be illustrated by the problem of properly expressing the disorder presented by blocks scattered randomly over the floor of a room, a picture with which, as a father and grandfather, I have become very familiar. It is obvious that the degree of disorder is some function of the number of blocks and also of the area of the floor, but it depends also upon the size of the blocks, since, in order to make the process of creating order truly analogous to parallel task with molecules which we cannot see, we must locate our blocks by wandering over the floor blindfold and barefoot. We will be able, of course, to locate blocks of lar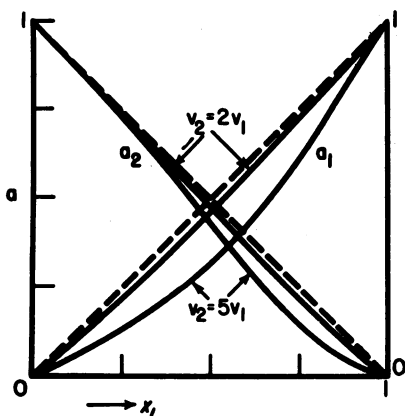ger area more easily than smaller ones. The entropy of transfer from pure liquid to solution formulated by aid of analogous probabilities for molecules, led, much to my satisfaction, to the same expression as the one obtained by Flory and Huggins. I here write it in the form

FIGURE 4

Effect upon activity of disparity in molal volumes for $v_2/v_1 = 2$ and 5.

$$\bar{s}_2 - s_2{}^0 = -R \ln \phi_2 + \phi_1\left(1 - \frac{v_2}{v_1}\right). \qquad (8)$$

When $v_1 = v_2$, the right-hand member reduces to $-R \ln x_2$, as it should if correct.

The order of magnitude of this correction is shown in figure 4 for two different ratios of v_2/v_1, 2 and 5. One sees that the departure from ideal entropy is rather small for the ratio 2, but very considerable for the ratio 5. Most pairs of ordinary organic solvents have molal volume ratios of 2 or less, but if one wishes to deal with solutions in fluorocarbons of small molecules such as nitrogen, or chlorine, the Flory-Huggins expression for entropy becomes significant. Since both heat and entropy may be nonideal, it is useful to substitute the expression in equation 8 for $-R \ln x_2$ in equation 7, giving

$$RT \ln a_2 = v_2\phi_1(\delta_2 - \delta_1)^2 + RT\left[\ln \phi_2 + \phi_1\left(1 - \frac{v_2}{v_1}\right)\right]. \quad (9)$$

Recent measurements of the solubility of nitrogen[6] and of chlorine in fluorocarbons can be better correlated by means of equation 9 than by equation 7, since the volume ratios, v_1/v_2, in these solutions run as high as 5, and the solubilities are markedly increased thereby.

The remarkably low solubility parameters for the fluorocarbons are mainly the result of their large molecular volumes. Although a pair of fluorocarbon molecules would attract each other more strongly than a pair of their hydrocarbon equivalents equally separated, the latter pair approach each other so much more closely at their equilibrium distance that, in view of the inverse sixth power of attractive potential, a cubic centimeter of liquid hydrocarbon not only contains many more molecules than the same volume of a corresponding fluorocarbon but they attract each other much more strongly.

* AUTHOR'S NOTE: The variation of this contribution from the coldly impersonal style customary in these PROCEEDINGS is the result of a remark by Professor P. Debye that it "should be published just as it was delivered." I trust that readers will feel that its purpose has been served thereby.

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[3] Benesi, H. A., and Hildebrand, J. H., *J. Am. Chem. Soc.*, **71**, 2703 (1949).
[4] Benesi, H. A., and Hildebrand, J. H., *Ibid.*, **72**, (in press) (1949).
[5] For an account of this development see *J. Chem. Phys.*, **15**, 225 (1947).
[6] J. Chr. Gjaldback and Hildebrand, J. H., *J. Am. Chem. Soc.*, **71**, 3147 (1949).

NOTE ON A RELATION IN DIRAC'S THEORY OF THE ELECTRON

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A relation in Dirac's theory of the electron will be described here which allows one to show that the hyperfine structure energy of an electron in a Coulomb field is proportional to $<r^{-2}>$, where the $< >$ denote the expectation value of the enclosed operator. This is an extension of the well-known relation of proportionality in non-relativistic theory of the hyperfine energy to $L(L + 1)<r^{-3}>$ and hence to $a_H<r^{-2}>$, where L is the azimuthal quantum number and a_H is the Bohr radius $\hbar^2/me^2$. Specifi-