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ORDER AND DISORDER IN PURE LIQUIDS AND SOLUTIONS[1]

By Professor JOEL H. HILDEBRAND

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THE only fault I can find with an occasion such as this is its effect upon my character; I shall doubtless emerge shorn of every shred of modesty I may have possessed on arrival. You will hardly expect me, however, not to feel, and therefore to express, several sources of satisfaction. I am, of course, greatly honored, not only by the action of the Jury of Award, but also by the presence this evening of so many fellow chemists, former students and old friends. Again, my heart is warmed by the kind things that have been said of me by Dr. Harned and Dr. Eyring. Harned was my first research student, and we did together the first work published in this country on the use of the hydrogen electrode to follow the course of a chemical reaction. I can claim only this credit for his subsequent notable scientific career that I did not spoil his natural instinct for research. As for Eyring, I claim a little credit for having helped to create the bracing atmosphere which he breathed as a graduate student in Berkeley and much more credit for having urged him to take the plunge into the liquid state which has resulted in his bringing up some brilliant results.

Further satisfaction is lent by the fact that the award of the Nichols medal is based upon having stimulated research. The problems involved in the theory of solubility are so numerous and complex that it became evident long ago that to catalyze their solution on a broad scale would be a finer achievement than to cultivate only a little of the large field which, years

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[1] William H. Nichols Medal Address before the New York Section of the American Chemical Society, March 10, 1939.

ago, only a few of us occupied. I have endeavored, therefore, to analyze the problems, to point out the main hurdles that I was not equipped, myself, to surmount, and to gather the kind of data which would provide honest and crucial tests for any theories, whether my own or those of others.

It is highly gratifying, therefore, to see to-day a wide-spread interest in the liquid state and a number of brilliant investigators devoting attention to it. Symposia on liquids and solutions held recently by the Faraday Society and by our own division of physical and inorganic chemistry have been truly exciting. In my discussion this evening of "Order and Disorder in Pure Liquids and Solutions," I am presenting ideas credit for which I am pleased to share with a number of others, including Bernal, Butler, Debye, Eyring, Fowler, Guggenheim, Kirkwood, Lennard-Jones, London, Menke, Prins, O. K. Rice, Scatchard, G. W. Stewart and, I am eager to add, my own young collaborators.

In discussing order and disorder we shall find it convenient to make frequent use of the term "entropy," a word which is sometimes a bit terrifying. A student once asked me, "What is entropy?," saying that his instructor in engineering thermodynamics had answered that question by saying that "nobody understands entropy, you just use it." Now as a matter of fact, that is rather a gloomy view, and I should like, for my purposes, to review the background of this concept in a very elementary way. Entropy is a term occurring, as you know, in certain thermodynamic equations to account for the fact that heat can not be transformed quantitatively into work, and kinetic theory indicates that it is rather simply related to molecular disorder. The amount of disorder depends upon the number of possible arrangements. In a pure, monatomic, crystalline solid at absolute zero there is no disorder, and therefore no entropy. The molecules are in the position of checkers on a board whose spaces just fit them. However, a solid solution, say of two isotopes, would have entropy, due to the fact that there are a great many ways in which molecules of the two species might be arranged. It comes out that the entropy change in forming a mole of solution from its pure crystalline components is

$$-R(\mathrm{N}_1 \ln \mathrm{N}_1 + \mathrm{N}_2 \ln \mathrm{N}_2),$$

where N_1 and N_2 are their respective mole fractions in the solution.

As a pure solid is heated, it is as if the squares on the checkerboard increased in size, and the pieces, although remaining within the squares, could acquire a certain degree of disorder. Melting would correspond roughly to abolishing the squares, so that a given piece could be anywhere on the board where it could find space with, consequently, a considerable increase in the possibilities of disorder. Vaporization would correspond to spilling the checkers over a large floor space, where a given piece could be almost anywhere within the area, and the possible disorder dependent on the available area, diminished only by the relatively insignificant space occupied by the pieces themselves. The change of entropy of a dilute gas in expanding from V_1 to V_2 is $R \ln \frac{V_2}{V_1}$, *i.e.*, it is a function of volume only.

Let us return now to a closer examination of the degree of order existing in liquids, and begin with the simplest cases—those liquids whose molecules are effectively spherical. A crude model for such liquids could be a number of tennis balls in a box about 25 per cent. larger than the minimum that would hold them, and violently agitated by vibrating walls. Such an assemblage may be assumed to be in the maximum permitted state of disorder.

If instead of tennis balls we should use sausage-shaped balloons, a certain amount of order would be imposed solely by the fact that the balloons would tend to arrange themselves in parallel array. Again, if each ball or balloon, as the case might be, had a magnet somewhere just beneath the surface, these magnets would encourage some degree of order, however small. Since there are many substances whose molecules are linear, such as carbon dioxide and pentane, or flat, like benzene, we may suspect their liquids of some degree of order. The presence of electric dipoles in molecules such as ethyl iodide should have a similar orienting effect. Any chemical combination should likewise reduce the amount of disorder.

Now there are at least two distinct kinds of evidence available concerning orderly arrangement in the liquid state, one, the well-known diffraction of x-rays, the other, which I am presenting here for the first time, the change in entropy on vaporization. I shall deal first with the latter. All chemists are doubtless familiar with a useful rule discovered long ago by Trouton, which states that the heat of vaporization per mole divided by the boiling point on the absolute scale has the same value, about 21 cals. per degree, for a large number of liquids which we have come to distinguish as "normal." This quotient turned out to be not a constant but to have a slow upward drift with increasing boiling point. Several investigators published empirical formulas to take this into account. In 1915 I noted that a graphic plot of the logarithm of vapor pressure against the logarithm of absolute temperature, as in Fig. 1, indicated that the entropy of vaporization, which is given by the slope of the tangent to such a curve, is approximately the same if the liquids are compared, not at their boiling points, where the pressures are the same, but at temperatures so selected that the final volume of vapor is always the same. This substitute for Trouton's rule is a rather good approximation for normal liquids all the way from nitrogen to silver. We can perhaps see why equal volumes rather than equal pressures should be chosen simply by inspecting the thermodynamic equation, $\Delta S = \Delta V(dp/dT)$. The value of ΔS depends in part upon ΔV, which in turn depends mainly upon the volume of the vapor.

Since all normal vapor pressure curves, when plotted as in Fig. 1, can be superimposed by sliding along a line of unit slope, we need only a single point, such as the boiling point, to enable us to draw a good approximation to the entire vapor pressure curve.

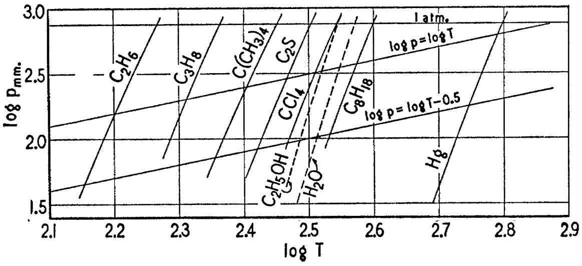

FIG. 1. Uniformity of entropy of vaporization of normal liquids at identical vapor concentration.

This rule should, of course, be true only for liquids in which there is the same amount of disorder. One way to insure this is to compare liquids in which the disorder is a maximum, which should be the case with liquids whose molecules are spherically symmetrical. Such molecules, however, are in the minority. More numerous are those which, as suggested above, have geometrical shapes tending to pack in some sort of ordered array. Still others are electrically polar and this also gives rise to more or less orientation. Now both of these effects show up quite clearly in increasing the entropy of vaporization to constant volume. Table 1 gives the entropy of vaporization at a concentration arbitrarily chosen as 0.0153 moles per liter, corresponding to log $Rc = 0.1$, together with the excess of each over the value for neopentane, a substance whose structure is so symmetrical that it has been selected as a standard of reference for all the others. Let us notice first the figures for the three isomeric pentanes. The isopentane, with its branched chain, shows a slight excess, while the linear normal pentane shows a much larger excess, 0.6. Going to longer hydrocarbons, with their greater orienting effect, we see a still further increase, while comparing hexane with its much more symmetrical isomer, di-isopropyl, we see a drop from 1.4 to 0.2.

TABLE I

STRUCTURAL ENTROPY OF LIQUIDS

Hg	0.0	CCl_4	0.6
$C(CH_3)_4$	0.0	$SiCl_4$	1.1
$i\text{–}C_5H_{12}$	0.1	$SnCl_4$	1.7
$n\text{–}C_5H_{12}$	0.6	$C(NO_2)_4$	2.5
$n\text{–}C_6H_{14}$	1.4	C_6H_6	1.1
$n\text{–}C_7H_{16}$	1.4	C_6H_{12}	1.0
$n\text{–}C_8H_{18}$	1.1	$(C_2H_5)_2O$	1.7
$i\text{–}C_6H_{14}$	0.2	$(CH_3)_2CO$	2.4
(Di-isopropyl)		C_2H_5OH	6.9

Carbon tetrachloride, although tetrahedral and rotating, has been shown by Menke through x-ray scattering to have some slight degree of structure and in harmony with this we find an excess entropy of 0.6 unit. Silicon and tin tetrachlorides, with their progressively larger, more open structures, show further increases to 1.1 and 1.7, respectively. Tetra-nitro-methane, with distortable nitro groups, shows evidence of still more structure.

Benzene and cyclohexane are free from dipole moment, but their flat rings are doubtless responsible for a marked degree of structure. Their rather high freezing points may be regarded as contributory evidence. Ether has a moderate dipole, but this is fairly well buried, as shown by the fact that its electric polarization in solution varies only slightly with concentration. In harmony with this, its entropy of vaporization gives evidence of only moderate structure, for which its geometrical form is doubtless to a large degree responsible. To vaporize acetone, which has a larger and more exposed dipole, involves a much greater increase in entropy. Ethyl alcohol shows a greatly enhanced value due to the hydrogen bonds which give the liquid a pronounced structure, confirmed by x-ray scattering. We shall see later that each of these three sources of structure may influence the entropy changes occurring when different liquids are mixed.

The evidence then for the non-polar liquids in Table I indicates that most of them possess some degree of structure and are, therefore, not completely normal in the sense of possessing the most complete randomness of molecular distribution. It is true that if we omit neopentane and mercury, a number of others would differ but to a small extent from their mean value. It is only when we select the comparatively rare substances possessing complete symmetry that we bring to light the different degrees of approach to so-called normal behavior. My colleague, Dr. Pitzer, proposes, quite appropriately, to call liquids such as neopentane "perfect liquids." The fact that perfect liquids are rare does not destroy the usefulness of the concept. Ideal cases are almost as rare in physical science as in human behavior, but whenever a number of instances occur in which the departure from the ideal are small, as with normal liquids, it pays to analyze the implications of the ideal and thus approach more or less closely to an understanding of the actual cases.

What we have called completely random liquid structure does indeed possess a certain kind of structure, due to the fact that no two molecules can occupy the same space simultaneously. Their centers must always remain about one molecule diameter apart. If, therefore, we consider the distribution of molecular centers around any one molecule selected as an origin for polar coordinates, we may imagine a series of thin concentric shells of thickness *dr* and radius *r* from the central molecule, as in Fig. 2. It is evident that no such shell could contain any molecular centers until *r* equaled the molecular collision diameter, which would, of course, vary slightly with the force of the collision and therefore with the temperature. As *r* increases, the number of molecular centers in a shell would go through a minimum and reach a second maximum when a second layer of molecules is reached. This maximum would, of course, be less pronounced than the first, and so on for successive maxima. When *r* is large compared to the molecular diameter, the ordering effect of the central molecular disappears and the number of molecular centers in the shell is simply the product of the volume of the shell, $2\pi r^2 dr$, by the molecular density, N/v, where N is Avogadro's number and v, the volume per mole. For small values of r this must be corrected by the factor, W, which is a function of r, as previously explained, whose form is represented in Fig. 3 and which expresses in a most useful way the structure of such a liquid. The form of this function was first determined by Menke for mercury and gallium, and more recently by Gingrich and coworkers for sodium and potassium. As might be expected, the form of the function, expressed in terms of molecular diameter, is essentially the same for these four substances; *cf.* Fig. 4. It varies slightly with the temperature, as one might expect, since thermal agitation and expansion tend to smooth it out to approach unity. My coworker, Dr. W. E. Morrell, was able to construct a model liquid with gelatin balls for molecules, which gave a distribution function of the same form, with a similar temperature dependence.

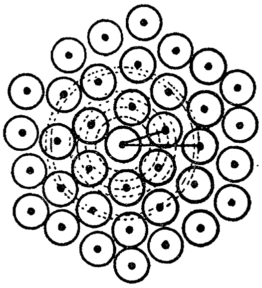

FIG. 2. Structure of a "perfect" liquid.

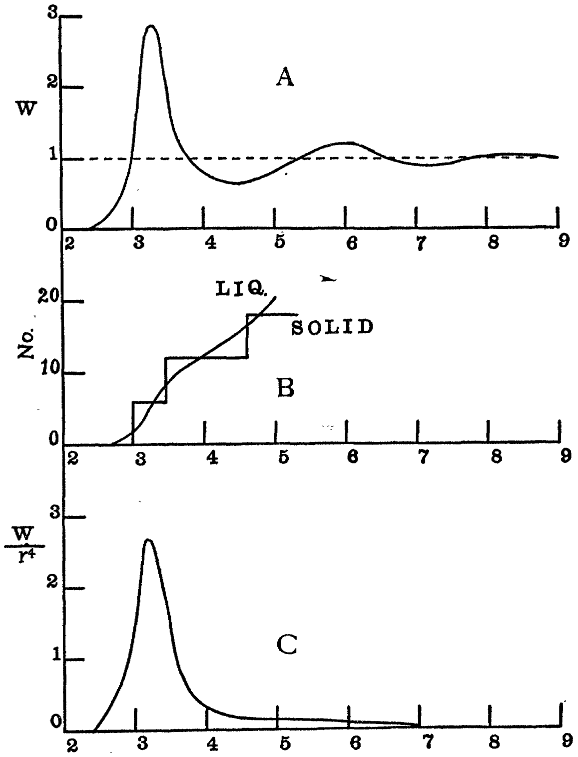

FIG. 3. A. Distribution function for mercury. B. Number of molecules around a central one at distance *r*. C. Potential function, area under which indicates small contribution by molecules beyond first layer to heat of vaporization.

Having at hand such an expression to describe the structure of a perfect liquid it has been possible to solve an important problem, which is to connect the potential energy between pairs of molecules with the potential energy of a mass of liquid E. This equation is

$$\mathrm{E} = \frac{2\pi N^2}{\mathrm{v}} \int \varepsilon W r^2 dr. \qquad (1)$$

The important theoretical study by London of the forces between non-polar molecules which result from

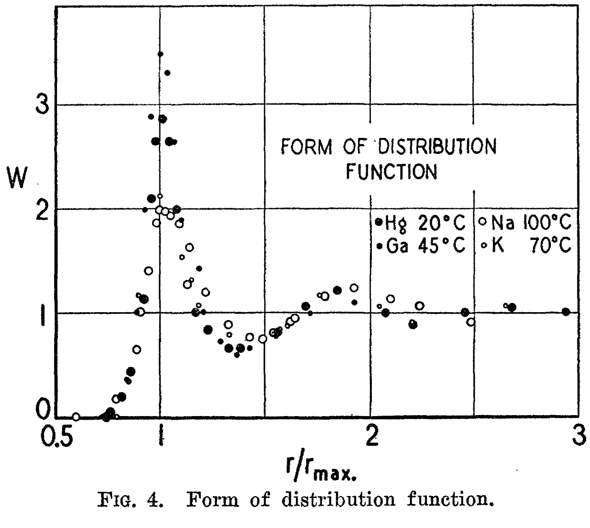

FIG. 4. Form of distribution function.

an interaction between their moving electrons shows that this potential varies inversely with sixth power of the distance, *i.e.*, $\varepsilon = -k/r^6$. If we substitute this expression for attractive potential in the preceding equation and neglect the repulsion we obtain the following expression, which throws light upon the energy of vaporization of a liquid.

$$\Delta E = \frac{-2\pi N^2 k}{V} \int \frac{W}{r^4} dr \qquad (2)$$

The value of the integral can be obtained by the aid of the curve in Fig. 3A and is represented by the area under the curve in Fig. 3C. (Curve B compares the structures of liquid and solid.) This curve shows what a small proportion of the energy of vaporization of a liquid is contributed by the molecules more than one diameter apart.

Again, the function plotted in Fig. 3A varies but slightly with temperature. The value of the integral determined graphically in the case of potassium drops off by some 5 per cent. in this range of temperature. We have known for some time that the energy of vaporization in a normal liquid is almost, but not quite, inversely proportional to its molal volume. We can see from equation (2) that it would be exactly proportional if the value of the integral were constant. As a matter of fact, I have shown recently that the drop of 5 per cent. in the value of the integral, together with the increase in molal volume for potassium when heated from 70° to 395°, accounts quite accurately for the decrease in the energy of vaporization of potassium in going from the lower to the higher temperature. Their ratio was calculated to be 1.154, while the measured values were in the ratio of 1.155. Moreover, I found that when benzene is expanded by the same amount, which in this case occurs between 0 and 72.5°, its energy of vaporization falls off in the same proportion as for potassium through the much longer temperature interval.

Turning now to solutions, let us begin again with the simplest conceivable cases, which will be solutions of spherical molecules of the same size and same molecular field strength. When such species are mixed an individual molecule has the same tendency to escape into a vapor phase as if it were surrounded entirely by its own kind. The number of molecules which so escape into a given vapor space will therefore be proportional to their percentage in the solution, and the solution obeys Raoult's law, the law of an ideal or perfect solution. The increase in free energy is $-RT \ln N_1$ and the increase in entropy is $R \ln N_1$, when one mole of component 1 is transferred from the pure liquid state to a large amount of solution in which the mole fraction is N_1.

If the molecules of the second species have not the same size but consist, say, of two normal paraffins of different length, we may expect them to be arranged in some approach to parallel array. An analysis of the number of arrangements possible in such a case shows it to be identical with the number in the preceding case, where molecules were spherical. In both cases, therefore, the degree of disorder is unchanged on mixing the two species, and hence the increase of entropy is the same, *i.e.*, $-R \ln N_1$ for each component. If the two species were as alike as two paraffins, we should expect little or no change in energy on mixing, *i.e.*, there should be no heat of mixing and therefore the free energy of mixing, which determines the vapor pressure, is dependent only on the entropy, hence the solution of long paraffin molecules, like the solution of spherical molecules, should obey Raoult's law, which is indeed the case, even for molecules of such different length as hexane and hexadecane.

Let us next consider spherical molecules of the same size but differing in strength of molecular field, as indicated by different energies of vaporization. In spite of the fact that the molecules with the larger attractive forces tend to squeeze out the molecules of the other component, we may choose temperatures sufficiently high so that thermal agitation may frequently overcome this tendency to segregation and give the same sort of random arrangement as exists in a pure liquid. For such a solution, the entropy of mixing will be the same as for an ideal solution; however, since the different attractive forces give rise to a heat or energy of mixing, the free energy change in forming the solution will not be ideal and the solution will not obey Raoult's law. Nevertheless, the fact that the entropy is ideal yields certain regularities in behavior which induced me to designate such solutions as "regular." If we can discover a satisfactory method for calculating the energy of mixing we can then get the free energy and hence vapor pressures and all other solubility relations. An extension of equation (2) to the case of a solution of two components of identical size, aided by the assumption, which is approximately true in the majority of cases, that the attractive constant between unlike molecules is the geometrical mean of the constants for the like species, gives the equation,

$$\bar{E}_1 - E_1^0 = [(\Delta E_1^0)^{1/2} - (\Delta E_2^0)^{1/2}]^2 N_2^2, \qquad (3)$$

for the energy of transferring a mole of component 1 from the pure state to a solution in which component 2 has a mole fraction, N_2. From this we can calculate the free energy and hence vapor pressures and solubilities.

When the molecules of the two species differ in size, the energy of mixing n_1 and n_2 moles of the components is

$$E = \frac{2\pi N^2}{V}\left[n_1^2 \int (11) + n_2^2 \int (22) + 2n_1 n_2 \int (12) \right],$$

where $\int (11)$ is an abbreviation for $\varepsilon_{11} W_{11} r^2 dr$, etc. We have to make certain approximations in order to derive from this an equation containing nothing but terms easily accessible to experiment. The resulting approximate equation for regular solutions in general is

$$RT \ln (a_2/N_2 = V_2 \left(\frac{N_1V_1}{N_1V_1 + N_2V_2}\right)^2 \left[\left(\frac{\Delta E_1}{V_1}\right)^{1/2} \left(\frac{\Delta E_2}{V_2}\right)^{1/2}\right]^2 \quad (4)$$

This equation is extremely useful and makes it possible to calculate with a fair degree of accuracy solubilities of substances even in cases where the deviation from Raoult's law is enormous.

A number of the factors discussed above, as well as others, are illustrated strikingly by the solubilities of iodine plotted in Fig. 5. The ordinates are logarithms of the mole fraction of iodine in solution and abscissas the reciprocal of the absolute temperature. The solid lines represent solutions whose color is violet, like iodine vapor; the broken lines represent red or brown solutions. The former obviously constitute a family of curves and indicate that these solutions are more or less regular; the latter are irregular. The ideal solubility is calculated by aid of the heat of fusion of iodine and difference between the specific heats of the solid and liquid.

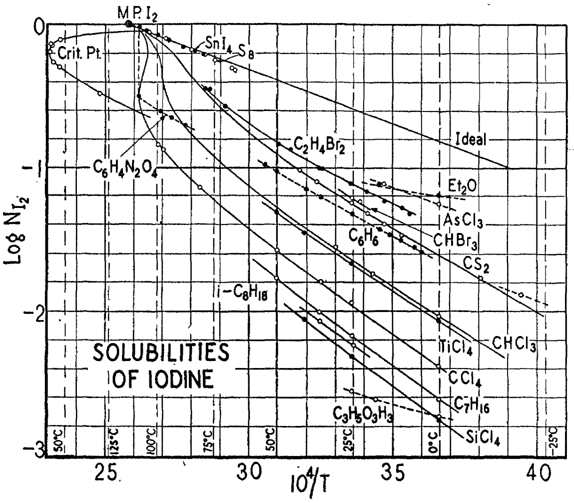

FIG. 5. Solubilities of iodine.

Iodine has a high attractive field. Sulfur and stannic iodide do not differ from it much in this respect and are therefore able to mix with iodine in obedience to Raoult's law. As we descend the plot we encounter solvents of steadily diminishing internal pressures which are, therefore, progressively poorer solvents. The spacing of these curves corresponds rather closely to the difference between the internal pressure of iodine and that of the solvent in question. All we need to know in order to calculate the solubility of iodine in a solvent which gives a violet solution, where effects that we may call chemical are absent, is its energy of vaporization per cc. Of course, if we have one point on the solubility curve it is still better, for the general parallelism of the whole family of curves is quite evident.

An interesting extension of the curve for carbon tetrachloride was invited by the S-shape near the melting point, resulting from plotting the equation which fitted the observed points at lower temperatures. This S-shape indicates that there are two solutions of different composition in equilibrium with each other at the same temperature and that on raising the temperature iodine should melt to give a liquid incompletely miscible with carbon tetrachloride. It was estimated that these two liquid phases should have a critical solution temperature somewhat under 180° at a composition of about 71 mole per cent. of iodine. It was impossible to detect the presence of two phases by visual observation because of the opacity of iodine, consequently, a method was devised depending on the difference in density between the two liquid phases. The result was the determination of the liquid liquid-solubility curve shown in the upper left-hand portion of the figure, with a consolute temperature of 161° and a composition of 67 mole per cent. of iodine. This experiment constitutes a striking example of the value of the concept of regular solution. It is the more remarkable because in the region near the critical temperature there is undoubtedly an opposition between the mixing effect of thermal agitation and the segregating effect of different molecular attractions, which gives rise to clustering and departure from the randomness assumed in deriving the equation. Experiment shows, however, that this clustering is fortunately not sufficiently serious to introduce any serious error. This experimental conclusion has been recently brilliantly confirmed by Kirkwood by statistical mechanical analysis.

To recapitulate, there are but very few perfect liquids. There are many normal or approximately perfect liquids; still more which are abnormal due to pronounced lack of symmetry either of shape or of electrostatic field, and there are a number which are highly abnormal due to the presence of hydrogen bonds or other chemical bonds.

Similarly, there are but very few solutions which are ideal or perfect with any high degree of accuracy, at least through any considerable range of composition. A much larger number are approximately regular, *i.e.,* they show ideal entropy of mixing, although their free energy of mixing is not ideal. They may be regarded therefore as approaching a considerably lower, more easily attainable ideal.

Let us now turn our attention to solutions which show marked departure from regularity. Solutions of iodine in ethylene bromide, whose solubility curve is shown in Fig. 5, present an interesting example. The slope of the curve does not correspond to the family of curves for violet solutions, in spite of the fact that these solutions alone among all the divergent solutions are violet in color, indicating absence of any type of solvation. The polar character of ethylene bromide does not suffice to explain this anomaly, for chloroform, which has almost as large a dipole moment, gives regular solutions. The explanation seems rather to lie in a change in the structure and hence in the entropy of the ethylene bromide caused by changing temperature and iodine content. The dipole moments of ethylene chloride, and doubtless also of ethylene bromide, are highly dependent upon the particular inert solvent used in measuring them. It is evident that the rotation possible about the carbon to carbon bond introduces possibilities of structural change in the liquid which we may, at least at present, regard as responsible for the regular entropy of the solutions of iodine in this solvent.

The dotted curves in Fig. 5 all correspond to solutions which are brown in color and whose absorption bands shift with temperature, indicating changes in structure attending changes in degrees of solvation and, in certain cases also, of degree of association of the solvent.

An interesting departure from regularity has been recently reported by Scatchard and Wood for a solution that might have been expected to behave quite regularly, namely, benzene and cyclohexane. It was shown, however, that the heat and free energy of mixing are different, indicating an increase of entropy upon forming the solution. If we turn back to the evidence presented in Table I that both benzene and cyclohexane possess some structure, we can see that a decrease in the amount of structure when the two components are mixed would account for the increase in entropy. Since benzene rings are flat while cyclohexane rings are puckered, it is easy to see how the two slightly different kinds of structure would tend to interfere with each other and give rise to an increase in the general disorder.

This point of view has suggested itself so recently that not many cases have been examined to test its general validity. However, the cases so far examined give great promise that the theory will prove useful.

The large deviations, not only from ideal but also from regular behavior that accompany chemical combination are highly specific, and often strain our skill in predicting the strength of chemical union. We are assisted, however, by a large body of knowledge regarding the relative strengths of acids and bases and can safely predict that the stronger the union between a basic and acidic substance the more strongly will their solution deviate from regular behavior in the direction of increased solubility.

Again, there are only a few types of strong hydrogen bonds, since strong union through hydrogen occurs only with nitrogen, oxygen and fluorine. There is considerable hope that we may be able to set up approximate values of the strength of the bond between the like and unlike combinations of these three elements, which values will be subject to modification depending upon the rest of the molecule. We may hope that in many cases this modification may prove to be small, *e.g.*, the strength of the bond in alcohol can not be changed very much by the size of the alkyl group. The amino acids and proteins, despite their almost infinite variety, contain but a few types of hydrogen bonds, and we may hope to arrive at a good deal of understanding of their solubility relations by the aid of this simplification.

I should like to conclude by emphasizing a particular liquid structure which has a greater practical importance for us than any other, namely, the structure of water. We are still under the spell of an over-simplified theory of solution, which regarded the solvent mainly as affording space in which the solute could masquerade as a gas. It is true that we have now ascribed to this space a dielectric constant, but most papers dealing with aqueous solutions, particularly those of electrolytes, ascribe no further physical properties to the water than this. Any deviation from the laws of perfect solution, which for such substances can at best be true only at high dilution, are often "explained" by subtracting some of the water from its role as solvent and calling it water of hydration. What this can mean, physically, is often obscure, for all the water molecules are linked together by hydrogen bonds except in so far as they are momentarily disturbed by thermal agitation and, if the solute is chemically bound to some of the water and this is in turn chemically bound to water molecules farther removed, I do not see how one can draw a definite boundary between the water which is acting as solvent and that which is acting as water of hydration.

It seems to me that if we were not so influenced by the accident of the particular historical approach to the theory of solution upon which most of us have been brought up, we would not find it so difficult to approach an aqueous solution from the opposite point of view, which is to think of water as a chemical substance whose role in the solution is just as dignified as that of the solute and which is, moreover, a substance having a high degree of structure. We may then inquire what might be expected to happen if we would introduce into this structure solutes of different types, including, first, ions, small and large, with single or multiple charges; second, molecules with dipoles or, third, molecules which themselves can participate in the formation of hydrogen bonds. Latimer, in a series of important studies, has already shown that the entropy of solution of ions can be explained on the basis of alterations in the structure of the water. I venture to assert that the fruitfulness of such an approach is far from being exhausted.

For a long while we were satisfied with the classification of liquids into normal liquids, polar liquids and fused salt solutions. It became evident, however, that the mere fact of dipole moment was inadequate to account for solubility relations. We find, on the one hand, that iodine dissolves in chloroform, which is polar, and in carbon tetrachloride, which is non-polar, to give approximately regular solutions in both cases. Again, naphthalene, with zero dipole moment, dissolves in nitrobenzene, with a very large moment, to give an almost perfect solution. The polar character of the nitrobenzene causes little or no tendency for it to associate with itself rather than with the non-polar solute. We find, moreover, that although solubility in water has usually been regarded as proportional merely to the polar character of the substance in question, dipole moment alone is actually a very misleading guide. A striking illustration of this is given in Table II.

TABLE II

SOLUBILITY OF LIQUIDS IN WATER, 20°

	Per cent.	$\mu \times 10^{18}$
Benzene	0.06	0.
Nitrobenzene	0.19	4.19
Aniline	3.49	1.51
Phenol	8.2	1.70
Ethyl iodide	0.40	1.66
Ethyl alcohol	∞	1.70
Propyl chloride	0.27	2.0
Propyl iodide	0.11	1.6
Propyl alcohol	∞	1.7
Water	...	1.85

We see that the solubilities of benzene and its three substitution products in water do not at all follow their dipole moments. These solubilities do, however, accord with the amount of hydrogen bond formation that may be expected in solutions of water with aniline and phenol, respectively. A similar difference exists between ethyl and propyl halides and alcohols. It is the ability of the hydroxyl of the alcohol or the phenol or the amino group in aniline to enter more or less into the structure of the water which accounts for their solubility. The structure of ice is an open, continuous structure, like that of trydimite, and contains no permanent individual molecules. The structure of water at lower temperature is the same, more or less broken down by thermal agitation. Hydroxyl containing substances such as the alcohols are similar except for the fact that the substituted groups diminish the number of hydrogen bonds. The profound difference between liquids containing ordinary dipoles, such as acetone and chlorobenzene and liquids containing hydroxyl, such as the alcohols, is illustrated in Fig. 6 showing the alteration in molar polarization when mixed with varying amounts of an inert solvent. The carboxyl group of organic acids, however, allows two molecules of the acid to form a closed ring so that the polymerization is limited to a double molecule. This molecule may, except in extreme dilutions, behave as a constituent of regular solutions.

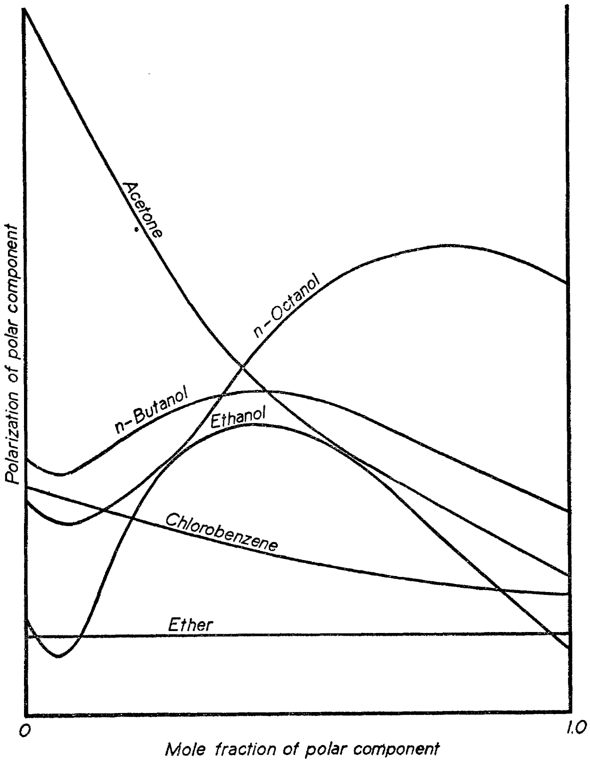

FIG. 6. Variation of molar polarization with concentration.

OBITUARY

DAVID TODD

WITH the passing of David Todd, on June 1 in Lynchburg, Virginia, at the age of 84, Amherst College lost another of the distinguished group of professors who added much to its prestige around the beginning of the century. The names of Tyler, Emerson, Olds, Loomis, Todd and the others were well known and respected both within and without the walls; and the last named of these was likely to receive the vote of the graduating class as the best known of all.

David Todd was born on March 19, 1855, in Lake Ridge, New York, the son of Sereno Edwards and