THEORY OF SOLUBILITY.

By Joel H. Hildebrand.

Abstract.

Theory of solubility.—(1) *Statement.* The theory of solubility advocated by the writer in a series of papers is restated. Raoult's law will be obeyed by any liquid mixture in which the internal forces of attraction and repulsion do not change with changing composition of the mixture. When this condition holds, the solubility of a gas may be calculated approximately from its saturation pressure, and the solubility of a solid from its melting point and heat of fusion. The above condition can exist only (*a*) when the components in the pure liquid state have the same internal pressures; (*b*) when the different molecules are relatively symmetrical or non-polar; (*c*) when the tendency to form chemical compounds is absent. Differences in either internal pressure or polarity alone produce approximately proportional positive deviations from Raoult's law and decreased solubilities. Tendencies towards chemical combination produce negative deviations and increased solubilities. Internal pressure is defined as $T(\partial P/\partial T)_v$; relative values can be deduced from other data, especially the solubility relations themselves. Polarity is indicated by dielectric constant, etc., and depends on the symmetry and the chemical constitution of the molecule. Chemical combinations are difficult to predict, but, in general, occur most frequently between polar molecules, especially those which can be regarded as positive and negative, or basic and acidic, respectively. (2) *Discussion of criticism by Kunerth.* Kunerth has severely criticized this theory, concluding that Raoult's law and internal pressures are practically useless as a basis for predicting the solubilities of gases. This paper points out that most of the solvents Kunerth uses are highly polar. A table of gas solubilities in non-polar solvents is given. The solvents are arranged according to increasing internal pressure, and the table includes the solubility as calculated approximately by the aid of Raoult's law. Though the solubilities cover a wide range the agreement with the theory is good.

In a series of papers by the author and his collaborators during the past six years[1] a theory of solubility has been advocated which may be briefly summarized as follows.

1. The tendency of a given molecule to escape from a solution into some other phase will be independent of the composition of the solution whenever that molecule is subject to the same attractive and repulsive forces in the solution as it is in its own pure liquid. If the number of molecules of the species X_1 in the solution is the fraction N_1 of the total number of molecules of all species present, then their tendency to escape from the

[1] Hildebrand, J. Am. Chem. Soc., *38*, 1452 (1916); *39*, 2297(1917); *41*, 1067 (1919); Hildebrand and Jenks, ibid., *42*, 2180 (1920); Hildebrand and Buehrer, ibid., *42*, 2213 (1920); Hildebrand, ibid., *43*, 500 (1921); Hildebrand and Jenks, ibid., *43*, 2172 (1921).

solution into some other phase, f_1, is the same fraction of their tendency to escape from their own pure liquid, f_1^0, viz., $f_1 = f_1^0 N_1$. For the species X_2, X_3, etc., we would have the similar expressions, $f_2 = f_2^0 N_2$, $f_3 = f_3^0 N_3$, etc. When the escaping tendency or fugacity[1] is measured by the vapor pressure and the vapor is assumed to obey the gas laws, this becomes $p_1 = p_1^0 N_1$, which is the well-known law of Raoult.

2. When the above condition holds N_1 may be regarded as the solubility of X_1 in the solution for a given value of f_1/f_1^0. The solubility of a vapor at any arbitrary pressure, p_1, can, therefore, be calculated from its saturation pressures, p_1^0. Where the substance is a gas above its critical temperature an approximate estimate of the solubility may still be made by extrapolating above the critical temperature to get a fictitious value for p_1^0. When the solubility of a solid is being considered, f_1/f_1^0 can be calculated from the melting point and the heat of fusion.

3. The above relations can be expected to hold only under the following conditions: (*a*) the components when in the state of pure liquids must have equal internal pressures or cohesions; (*b*) the fields of force around the molecules of the components must be sufficiently symmetrical or non-polar; (*c*) the molecules of different species must not exert abnormally large attractions upon each other such as appear in the tendency to form chemical compounds.

4. Where conditions (*b*) and (*c*) hold, differences in internal pressure lead to approximately proportional increases in escaping tendency and decreases in solubility.

5. Differences in polarity in the absence of chemical combination have a corresponding effect.

6. The tendency to chemical combination between the components leads to decreased escaping tendency and hence increased solubility.

7. Internal pressure has been defined as $T(\partial P/\partial T)_v$, one of the terms in the thermodynamic equation of state. Its value may be calculated from the coefficients of expansion and compressibility. Approximate relative values may also be obtained by the aid of other data, such as surface tensions and heats of vaporization.

8. Relative internal pressures can also be deduced from solubility data themselves since it is possible thereby to arrange non-polar substances in a series in which the more widely separated are any pair of substances, the more strongly does their solution deviate in a positive direction from Raoult's law.

9. Polarity of a molecule or a group within a molecule can be related to dielectric constant and other physical properties, also to symmetry and chemical nature.

[1] G. N. Lewis, Proc. Am. Acad., *37*, 49 (1901); Z. physik. Chem., *38*, 205 (1901).

10. The prediction of chemical combination in connection with solubility offers the same difficulties that it does elsewhere, and is a very complicated problem. In general, however, it occurs most frequently between polar substances, and between substances which may be regarded as respectively positive and negative, or basic and acidic.

The writer claims but a small portion of credit for this comprehensive theory. So important a problem as solubility has not escaped attention from a host of investigators, and nearly all parts of the theory above outlined have been separately stated more or less clearly by others, and I have tried to indicate them as adequately as possible in my series of papers. The chief cause of failure hitherto has been the neglect of some of these factors while studying the others.

In a paper in THE PHYSICAL REVIEW entitled "Solubility of CO_2 and N_2O in certain solvents" Professor Wm. Kunerth[1] has recently made such sweeping objection to the theory here outlined as to call for some words of explanation and reply.

This investigator, upon comparing the solubilities of CO_2 and N_2O in a number of solvents with the solubility calculated from Raoult's law, concludes that "the procedure of Dolezalek" who first used Raoult's law for this purpose, attempting to correct for deviations from the gas laws by using $p^0 + a/v^2$ from the van der Waals equation in place of p^0, "is utterly worthless for predicting solubility of gases in liquids."

Now it would seem to the writer that a procedure is not utterly worthless which can yield even an approximate prediction of so important a property as solubility, especially if we are able to say which substances will approximate most closely to our prediction. According to the theory above outlined this will be the case with non-polar substances whose pure liquid phases have equal internal pressures. We will therefore expect better agreement with non-polar gases like nitrogen and methane than with somewhat polar gases like carbon dioxide, ammonia and hydrogen chloride, and better agreement with the less polar solvents such as hexane, carbon tetrachloride and ethylene bromide, than with water, the alcohols, acids and amines. Furthermore, we will expect that the value for solubility got by the aid of Raoult's law will be most closely approached as the internal pressure of the solvent corresponds to that of the condensed gas.

A fair test of the theory should, of course, have due regard to the conditions stated. In my first paper on the subject I stated "(1) Raoult's law should be obeyed by mixtures of non-polar liquids having the same internal pressures; (2) non-polar liquids of different internal pressures

[1] Kunerth, PHYS. REV., *19*, 512 (1922).

will show greater vapor pressures in the mixture than would be expected from Raoult's law; (3) the same holds true for mixtures of polar with non-polar liquids; (4) mixtures of polar liquids may show either positive or negative deviations from Raoult's law, but in most cases the latter will predominate; (5) these deviations will modify the predictions of solubility for gases, liquids, and solids based upon Raoult's law alone, the solubilities being greater where negative deviations occur and *vice-versa*." In the same paper a section of four pages is devoted to the discussion of polarity, and dielectric constants are given in the table of internal pressures. I have also been careful in later papers, when examining relatively non-polar systems because of their greater regularity of behavior, to limit my conclusions to this class. In spite of this Kunerth states the internal pressure theory without reference to this limitation. He proceeds to test the internal pressure theory on the basis of solubilities in a series of twenty-one solvents, of which only eight have dielectric constants as low as 5, and amyl acetate, though having a dielectric constant of only 4.8, contains the highly polar—COO—group. In my own tests of the effect of internal pressure I have seldom used substances with dielectric constants above 5, or containing groups commonly recognized by chemists as highly polar, such as hydroxyl, carboxyl, amino and aldehyde. I can agree with Kunerth when he says that so far as his own table goes "its indications are that the solubility of gases in liquids is connected with polarity rather than with . . . internal pressures," because he has chosen mainly polar solvents, but for this very reason his data do not furnish an adequate basis for a general denial of the connection between internal pressure and solubility in cases of low polarity.

In reference to my original table for the solubilities of H_2, CO, N_2, CH_4, C_2H_6, C_2H_4, CO_2 and NH_3 in various solvents, some of them polar, I said "the greatest uncertainty is where the polar solvents are concerned. This is not surprising, as the uncertainties are necessarily greater in such cases on account of our inability to determine how much of the internal pressure is due to the polarity. Carbon dioxide is obviously, from its chemical reactivity, much more polar than the gases previously mentioned, and additional uncertainties are thus introduced, though a distinct increase in solubility in the more polar solvents is evident." In spite of this, Kunerth implies that I based by discussion entirely upon internal pressure, and states that "the conclusion which Hildebrand draws is very obviously not warranted."

Now let us see whether this is true. Considering only the substances of low polarity, having dielectric constants not over 5, we can make a

table of gas solubilities, using data quoted in my original paper for carbon monoxide, nitrogen and methane, those given by Kunerth for carbon dioxide and nitrous oxide, some data for chlorine by Taylor, of this laboratory, and not heretofore published, and for phosgene by Atkinson, Heycock and Pope.[1]

The solvents are arranged in order of increasing internal pressure, using the values of $T(\partial P/\partial T)_v$ given in a previous paper, which order is confirmed by solubility data given in other papers for various solids. The position of carbon bisulfide is chosen in accordance with the latter basis. At the top of the table are given values of $1/p^0$, where p^0, is the saturation pressure, extrapolated in the case of CO, N_2 and CH_4 by the aid of the straight line plot of log p against $1/T$. According to Raoult's

Solubility in Mol—Per Cent.

	CO.	N_2.	CO_2.	N_2O.	CH_4.	Cl_2.	$COCl_2$.	Internal Pressure.
Temp.	20°	20°	20°	20°	25°	0°	24°	20°
Raoult's law, $1/p^0$	0.11	0.10	1.78	1.81	0.32	27.3	55.0	
Heptane						27.0		2,970
Hexane					0.31			2,970
Xylene	0.089	0.061	1.02		0.26		53.0	3,690
Carbon tetrachloride			1.00			29.6		3,690
Toluene	0.077	0.053	1.08		0.21		53.0	3,830
Chloroform	0.063	0.043	1.23	1.82				3,880
Benzene	0.061	0.041	0.94					4,100
Ethylene bromide			0.82	1.00				4,760
Carbon bisulfide	0.020	0.013	0.23					

law $1/p^0$ should give the solubility of the gas at 1 atmosphere pressure. According to our theory this should be approached most nearly in the solvents of internal pressure equal to that of the condensed gas. According to the third paper of our series the internal pressures of CO and N_2 are lower than those of any of the liquids given in the table, so that the best solvent, xylene, has a solvent power distinctly lower than $1/p^0$, while the solvent powers of the other liquids decrease regularly with their increasing internal pressures. Methane, as we might expect, dissolves in hexane as given by $1/p^0$, within the limit of error, becoming less soluble as we descend to xylene and toluene. We might safely predict its solubility in ethylene bromide to lie in the neighborhood of 0.15 mol per cent., in spite of the gloomy view of such a possibility implied by Kunerth.

The internal pressures of CO_2 and N_2O are undoubtedly higher, and N_2O, the less polar and hence more regular in behavior, dissolves in chloroform to the extent given by Raoult's law, but less in ethylene bromide, which has a higher internal pressure; CO_2 being chemically more reactive and hence itself somewhat polar is less regular, but in all

[1] J. Chem. Soc., *117*, 1410 (1920).

the solvents listed dissolves to an extent whose order of magnitude at least is correctly indicated by Raoult's law, and falling off as expected with ethylene bromide and carbon bisulfide. The internal pressures of chlorine and phosgene can be shown to be about the same as that of carbon tetrachloride, so that solvents in this region of the table should be the best, dissolving these gases to the extent calculated by Raoult's law, as is indeed the case. The reader may judge for himself whether or not the data show that "the conclusion Hildebrand draws is very obviously not warranted."

In a paper by Mr. N. W. Taylor and myself, which is being submitted to the Journal of the American Chemical Society, the data of Kunerth are discussed from the standpoint of the polarity and chemical nature of the substances involved.

It may be objected that in ruling out polar substances the scope of the internal pressure theory is so restricted as to make it of little use. No one regrets more than I the very limited progress that has been made in the theory of solubility, and I am under no illusion of having solved the problem, but I insist that it is possible to make approximate predictions of solubility in a large number of cases, which is somewhat encouraging. I have deliberately sought to simplify the problem as much as possible by studying first the substances of low polarity, for I consider that the abnormal amount of attention that has been devoted to the most complicated of all solution, aqueous solution of electrolytes, results not from sound scientific method but from the abundant presence of water upon the earth. Having gained, as I believe, some insight into simple solutions, we should be able to make more progress in the study of the more complex, but not by the denial of the progress already made. The existence of discrepancies of a nature clearly recognized is no more serious in this case than it is with gaseous mixtures, where we use quite freely Dalton's law of additive pressures, although large numbers of gaseous mixtures do not obey it on account of chemical reactions between the components.

There are several further statements of Kunerth which call for comment. He says of the theory advanced by myself and others "it should follow from the point of view of this theory that . . . all substances which are completely miscible should have the same internal pressures." Now I have endeavored to make it clear that both experiment and theory indicate that very considerable differences in internal pressure and large deviations from Raoult's law are necessary before two liquid phases appear. In the paper by myself and Buehrer, which deals with such systems, we say that "but few of the substances in the table of internal pressures given in the third paper of this series are far enough apart in

internal pressure to form two liquid layers . . . . " The subject was also discussed in the first paper, pp. 1465–1468. Fig. 1 may serve to make this clear. The straight line a on which p is proportional to N corresponds to Raoult's law. Increasing positive deviations of the usual type are illustrated by the curves b, c, d, and e. On e there are three values of N for a single value of p, the mixture separating into two liquid phases just as in the plot of the van der Waals equation we get three values of V corresponding to the two phases, liquid and gas. In d these have coalesced into a single point where the curve has a horizontal tangent and the mixture has a critical point. Curves c and b represent systems having but one liquid phase but deviating from Raoult's law, and having different internal pressures, like hexane and carbon tetrachloride, or different degrees of polarity, like ethyl alcohol and carbon bisulfide. The dictum of Kunerth quoted above is, therefore, untrue, and the difficulty which he says I recognize, p. 523, is his own, not mine.

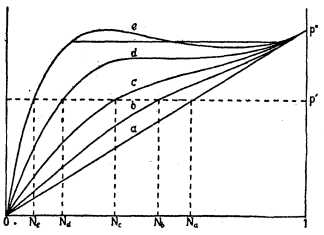

Fig. 1.

We can often produce the increasing deviations illustrated by c, d, e, by lowering the temperature, as with methyl alcohol and carbon bisulfide, or by replacing one component by another differing more from the fixed one in internal pressure or polarity. If the fixed component is under the vapor pressure p' in a series of mixtures corresponding to the curves a to e, its solubilities in these solutions will be N_a, N_b, N_c, etc. The possibility of two liquid phases appearing at higher pressures with e does not set this system at all apart from the others when the lower pressure p' is considered. Kunerth's distinction between completely miscible and incompletely miscible liquids, p. 520, seems therefore to be misleading.

The reader may be reminded, in conclusion, that a large amount of evidence is available as a test for theories of solubility in addition to the solubilities of gases discussed by Kunerth. The solubilities of solids can be calculated without the uncertainties present with gases due to violations of the gas laws, and various papers of our series present a large volume of such evidence. Evidence can be got further from critical mixing temperatures, and from the changes in boiling or freezing points produced by dissolved substances. This evidence must be considered as a whole, and that part derived only from one class of data cannot be singled out for refutation apart from the rest.

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