

of calcium hydroxide explains the copious generation of hydrogen in the case of calcium chloride solutions and might also explain why it has been found impossible, for example by Smith and Bennett,¹¹ to prepare by electrolysis in aqueous solution an amalgam with over 0.09% of calcium. In the case of zinc chloride, since any zinc hydroxide that might be formed on the surface would dissolve in the excess of hydroxyl ions as sodium zincate or the zincate ion, ZnO_2 , no catalytic decomposition of the amalgam takes place. The fact that in the presence of zinc chloride the gelatin solutions gave no such trouble, is interesting because of the conclusions of Isgarischew¹² from experiments on the electrolysis of zinc sulfate in the presence of gelatin that adsorption compounds are formed between the zinc ion and the gelatin and that this adsorption is greatest at 0.025% concentration of gelatin.

Summary

1. The accuracy of the sodium amalgam electrode for determining sodium-ion concentration in aqueous solution has been investigated.

2. The effect of various concentrations of ammonium, potassium, calcium and zinc chlorides and gelatin on the potential of 0.1 *N* sodium chloride solution has also been studied.

The author desires to thank Professor E. K. Marshall for courtesies extended during this work.

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MELTING POINT, LATENT HEAT OF FUSION AND SOLUBILITY

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Received January 30, 1922

Introduction

Commercial laboratories as well as educational laboratories which are working with organic compounds are constantly confronted with questions having to do with solubility and choice of solvent for use in purifications. In the great majority of cases the desired information is not available from the published data. In such cases it is necessary either to determine the solubility experimentally or to resort to some method of calculation. The more successful of the various methods used for calculating solubility generally employ an equation involving Raoult's freezing-point law together with the second law of thermodynamics. Perhaps the simplest and most useful of these expressions is

$$\log N = \frac{-L}{4.58 T} + I \quad (1)$$

¹¹ Smith and Bennett, *THIS JOURNAL*, **32**, 622 (1910).

¹² Isgarischew, *Kolloidchem. Beihefte*, **14**, 25 (1921).

In this expression N represents the mole fraction of the solute. (By solute is meant that component which first crystallizes in the pure state upon cooling the system.) L is the molecular latent heat of fusion, T is the absolute temperature of the melting point of the system and I is an integration constant.

In general it may be said that these equations have been successful only for the so-called "ideal" mixture. By ideal mixture is meant those binary systems the components of which may be considered to have the same thermodynamic environment when both are in the liquid state and both are at the same temperature. Two of the criteria for such a system are that there shall be neither any heat effect nor any volume change when the two liquid components are mixed. The complete absence of any secondary molecular effects such as association and compound formation is implied in the definition. Therefore, if in any case the heat effect for the solution process of dissolving a solid in a liquid differs from the latent heat of fusion of the solute at the temperature in question, then this simple form of the solubility law does not express the true solubility.

Hildebrand¹ in a series of very able papers, has shown that the degree to which a given binary mixture of non-polar substances departs from the formula for ideal mixtures is closely related to the magnitude of the differences in internal pressures of the components. In the fourth paper of the series he has described a method for evaluating solubility data and has indicated how the solubility of many substances may be approximately calculated providing the solubility of the given substance has been determined in solvents having a similar internal pressure to that of the solvent in question.

In evaluating solubility data Hildebrand plots the common logarithm of the mole fraction of solute against the reciprocal of the absolute temperature of the melting point of the system. The experimental solubility points when plotted in this manner should, if there are no secondary molecular effects, lie on a straight or only slightly curved line over fairly wide ranges of temperature. When the solubility curves of a given solute in a variety of solvents are plotted in this way there is obtained a series of lines, such as those shown below in Figs. 1 to 4, which converge to a point at the melting temperature of the solute where $N = 1.0$ ($\log N = 0.0$).

According to the hypothesis put forward by Hildebrand the nearer the internal pressure of the liquefied solute is to that of the solvent in question the nearer will the experimental curve approach to the ideal solubility curve calculated from the latent heat of fusion of the solute. Therefore, if two solvents should be found to have exactly the same internal pressures, then the molecular solubility of each solute should be the same

¹ Hildebrand, *THIS JOURNAL*, **38**, 1452 (1916); **39**, 2297 (1917); **41**, 1067 (1919); **42**, 2180 (1920).

for the two solvents. Hildebrand² has prepared a table of relative internal pressures from which, having a series of solubility curves for any solute, the solubility curve of any such solute may be approximately located for any other solvent the position of which in the table of relative internal pressures is known.

The obvious disadvantages of this method of calculating solubilities are, first, the internal pressures are known for only a relatively small number of substances. Second, the method has not been applied to polar substances. Third, in any case the solubility must have been determined in a series of selected solvents before the solubility in other solvents can be determined.

In the pages which follow we have described a method of calculating solubility which requires but a minimum of physical measurements. It will be shown that the proposed method applies approximately not only to systems of non-polar components but also to those systems containing polar substances, providing that the internal pressures of the components are not widely different and that there are no molecular complexes or solid solutions produced. It should be possible also to foretell which mixtures will give partially miscible liquid systems, and also something of the degree of miscibility of the two liquids.

Development of the Method

From Equation 1 it is evident that the slope of the $\log N$ vs. $1/T$ curves is related to the latent heat of fusion of the solute in the following manner

$$\text{Slope} = S = \frac{\Delta \log N}{\Delta(1/T)} = \frac{-L}{4.58} \quad (2)$$

Equation 2 applies only to those binary mixtures in which the heat effect of the solution process is equal to the latent heat of fusion of the solute. Now it is a general rule, providing no secondary molecular effects are produced, that the negative heat effect accompanying the solution process is greater than the latent heat of fusion. In all such cases the slope of the logarithmic curves must be greater than that of the ideal curve. This is well shown in each of the Figs. 1 to 4 below.

The ideal slope for any solute is that slope which would be obtained with a solvent which gives a thermodynamically ideal mixture. It is evident from Equation 2 that the value of the ideal slope may be calculated by dividing the latent heat of fusion of the solute (in small calories per mole) by the constant 4.58.

If now the experimental values of the slopes of the $\log N$ vs. $1/T$ curves for a given solute in a variety of solvents, be divided by the value of the ideal slope for that solute there is obtained a series of factors the magnitude of which is a measure of the non-ideality of the mixture.

² Hildebrand, *THIS JOURNAL*, **38**, 1452 (1916); **41**, 1067 (1919).

TABLE I

SLOPES OF THE LOG N vs. $1/T$ CURVES FOR THE SOLUTES NAPHTHALENE, FLUORENE, BENZOIC ACID AND URETHANE AND THE VALUES OF THE FACTORS OBTAINED BY DIVIDING THE EXPERIMENTAL SLOPE BY THE IDEAL SLOPE

Solvent	Slope of the log. N vs. $1/T$ curves	Experimental slope	Ideal Slope	Factor taken from Fig. 5	Solvent	Slope of the log. N vs. $1/T$ curves	Experimental slope	Ideal slope	Factor taken from Fig. 5
Naphthalene as solute					Fluorene as solute				
Ideal solvent.....	970	1.00	1.00	1.00	Ideal solvent.....	1050	1.00	1.00	1.00
Diphenylamine.....	960	1.00	1.00	1.00	Chlorobenzene.....	1060	1.01	1.01	1.01
Fluorene.....	970	1.00	1.00	1.00	Nitrobenzene.....	1090	1.04	1.04	1.04
Phenanthrene.....	970	1.00	1.00	1.00	Benzene.....	1180	1.12	1.10	1.10
Chlorobenzene.....	970	1.00	1.00	1.00	Pyridine.....	1200	1.14	1.10	1.10
Ethylene dichloride..	980	1.01	1.01	1.01	Carbon disulfide.....	1210	1.15	1.12	1.12
Ethylene dibromide..	990	1.02	1.02	1.02	Carbon tetrachloride..	1320	1.25	1.22	1.22
Nitrobenzene.....	1010	1.04	1.05	1.05	Aniline.....	1510	1.44	1.35	1.35
Benzene.....	1020	1.05	1.06	1.06	Acetone.....	1580	1.50	1.37	1.37
Toluene.....	1030	1.06	1.07	1.07	Benzoic acid as solute				
Phthalic anhydride..	1040	1.07	1.09	1.09	Ideal solvent.....	900	1.00	1.00	1.00
Carbon disulfide.....	1050	1.08	1.11	1.11	Acetone.....	940	1.04	1.04	1.04
Pyridine.....	1060	1.09	1.10	1.10	Benzil.....	940	1.04	1.04	1.04
Ethyl acetate.....	1160	1.20	1.19	1.19	Acetophenone.....	940	1.04	1.04	1.04
Ether.....	1180	1.22	1.22	1.22	Nitrobenzene.....	1200	1.33	1.34	1.34
Thymol.....	1200	1.24	1.30	1.30	Benzene.....	1350	1.50	1.45	1.45
Acetone.....	1260	1.30	1.33	1.33	Toluene.....	1360	1.51	1.47	1.47
<i>p</i> -Toluidine.....	1270	1.31	1.35	1.35	Acetic acid.....	1460	1.62	1.58	1.58
α -Naphthylamine...	1270	1.31	1.32	1.32	Carbon tetrachloride..	1530	1.70	1.67	1.67
α -Naphthol.....	1310	1.35	1.40	1.40	Urethane as solute				
Aniline.....	1430	1.47	1.45	1.45	Ideal solvent.....	795	1.00	1.00	1.00
Phenol.....	1700	1.75	1.75	1.75	Methyl alcohol.....	995	1.25	1.25	1.25
Hexane.....	1740	1.80	1.80	1.80	Ethyl alcohol.....	1150	1.45	1.45	1.45
					Propyl alcohol.....	1290	1.62	1.62	1.62
					Water.....	1900	2.39	2.40	2.40
					Toluene.....	2900	3.65	3.65	3.65

In Table I are given the values of the slopes and of the factors which have been calculated for the four solutes naphthalene, fluorene, benzoic acid and urethane. The corresponding solubility curves are shown in Figs. 1 to 4. A glance at the solubility relations of these four substances shows that with naphthalene as solute, the substances which come most nearly to forming ideal solutions are the aromatic hydrocarbons with their halogen and nitro derivatives. These are followed by the substances having lower internal pressures such as ether, carbon tetrachloride, the esters and the acid anhydrides and also by the substances having higher internal pressures, namely, the amines, acids, alcohols and water.

Comparing the solubility relations of naphthalene and fluorene it is found that the relative positions of the log N vs. $1/T$ curves are the same

for both substances. Hence it may be concluded that the internal pressures of these two solutes are nearly the same.

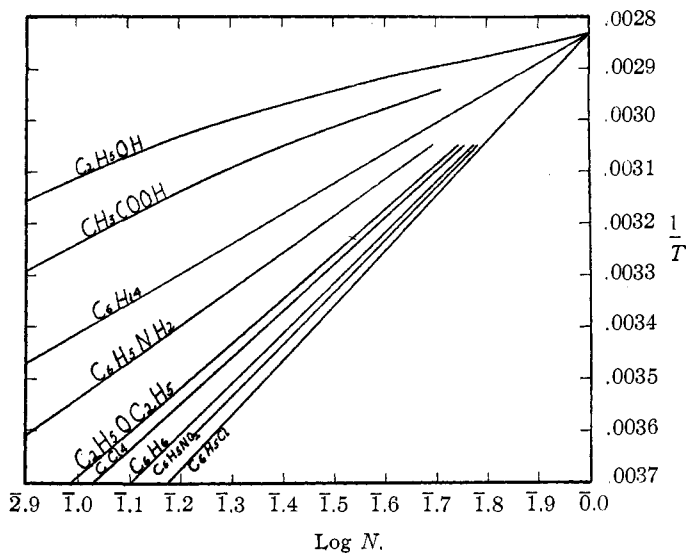


Fig. 1.—Solubility relations of naphthalene.

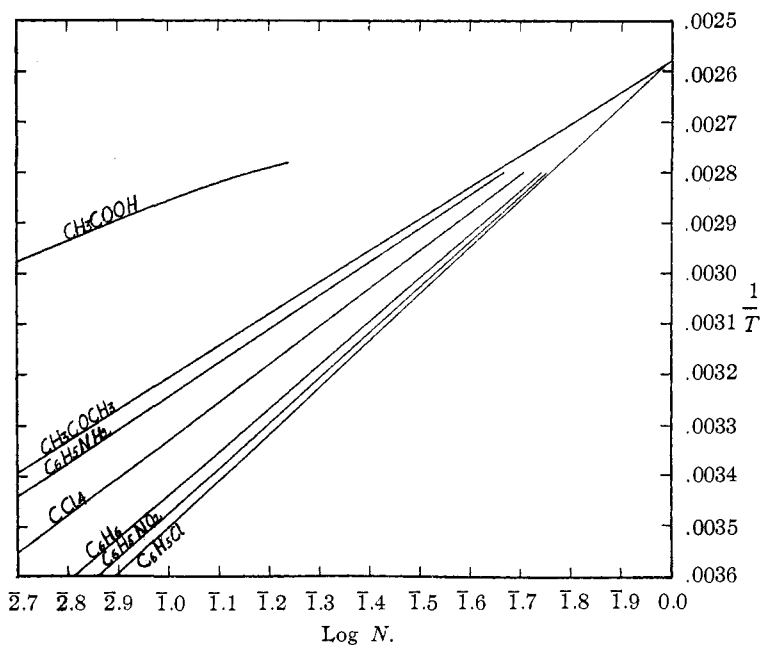


Fig. 2.—The solubility relations of fluorene.

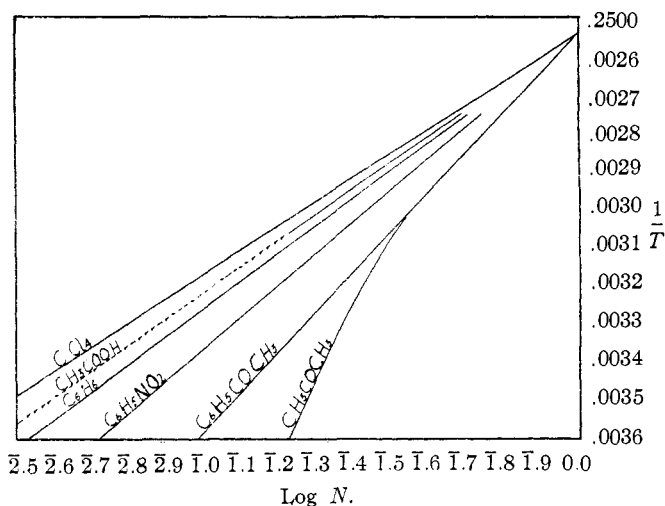


Fig. 3.—Solubility relation of benzoic acid.

When we come to consider the solubility relations of benzoic acid it must be remembered that this substance is moderately polar, hence the moderately polar solvents, or those having moderately high internal pressures, come most nearly to giving ideal mixtures. Finally, it is evident from Table IV that urethane has an internal pressure corresponding to that of the lower alcohols. The very high slope obtained for this substance in toluene should be noted. It will be observed that water is a better solvent for this substance than is toluene.

In order to coördinate these solubility relations and many others which have been studied we have made use of the chart³ shown in Fig. 5. It will be observed that the right and left sides of this chart are alike except that one side is the inverse of the other. On the left side of the chart the internal pressures increase downward while on the right side they necessarily increase upward. The figures in the middle of the chart, increasing both upward and downward from unity, are the factors obtained by dividing the experi-

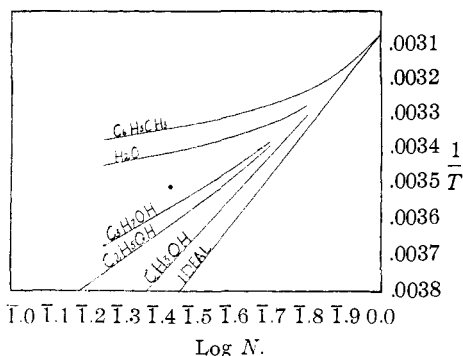


Fig. 4.—Solubility relations of urethane.

³ Owing to the difficulty of reproducing a more extensive chart it is impossible to represent substances having high internal pressures in Fig. 5. The following table will indicate the positions of some of these substances.

Under Col. 1 of this table are given the substances, under Col. 2 the positions of

mental slopes of the $\log N$ vs. $1/T$ curves by the ideal slope calculated from the latent heat of fusion.

In this chart naphthalene has been taken as the starting point. The

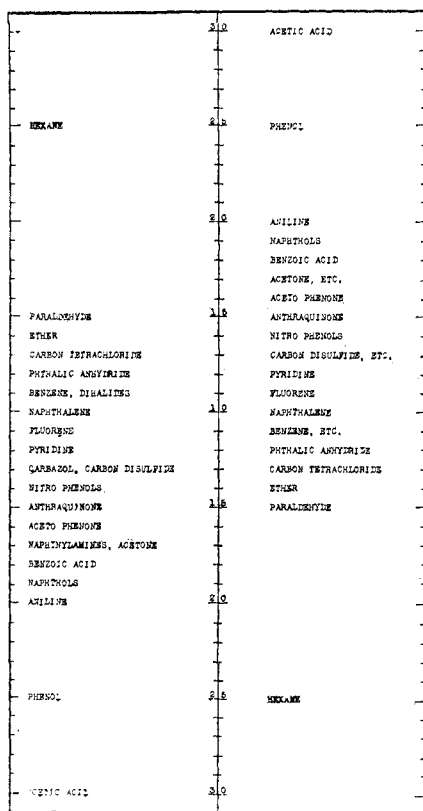


Fig. 5.—Chart of relative internal pressure.

value of the ideal slope is taken to be 970. This corresponds to a latent heat of fusion of 4450 calories per mole, a value which is somewhat less than that commonly accepted for naphthalene, namely, 4550 calories. In order to fix the positions of the other substances relative to naphthalene it was found convenient to locate first those substances which had been used as solvents for naphthalene. Now, a large number of freezing-point and solubility curves of binary systems involving naphthalene as solute are given in the literature. Of this number about 20 appear to have been determined with the required degree of accuracy. The experimental slopes of each of these curves are given in Table I together with the value of the factors obtained by dividing the experimental slope by the ideal slope, 970. Each factor was then located on the middle line and a straight edge was so placed across the chart that it passed through this factor and the point

the substances relative to the line of factors and under 3 the relative internal pressures as determined from the line of factors.

Substance	Position relative to line of factors	Relative internal pressure
Phenol.....	2.5	1.75
Acetic acid.....	3.0	2.00
Butyl alcohol.....	4.6	2.80
Propyl alcohol.....	4.9	2.95
Ethyl alcohol.....	5.3	3.15
Methyl alcohol.....	5.7	3.35
Urethane.....	6.1	3.55
Acetamide.....	6.6	3.80
Resorcinol.....	7.5	4.25
Water.....	9.0 ?	5.00 ?

chosen for naphthalene. The point at which this line cuts the opposite side of the chart is the location of the substance in question. Having located these substances they were then used in finding the locations of other substances of which the binary systems with naphthalene had not been determined.

In making the calculations involved in finding the locations of these other substances in the chart it was often found that the positions of the substances already fixed in the table could be repeatedly checked. In all cases shown the positions finally adopted are the mean values of several closely agreeing experiments using different solutes or solvents.

It will be observed that there may be some question, especially where the factor has a value near to unity, as to whether the factor should be slightly above or slightly below the ideal position. In deciding this question one may be guided somewhat by Hildebrand's² table of relative internal pressures and also by the solubility relations in other systems.

In making the complete table we have calculated to mole fractions the solubility and freezing-point measurements of over 400 binary mixtures. Not all of the substances studied appear in the chart. A large number of isolated systems have been investigated which need only a few measurements in order to coördinate the complete solubility relations of these substances. We hope soon to make these measurements and to publish the results in a later communication.

Uses and Limitations of the Chart

The uses of this chart are quite evident from the foregoing discussion. In the first place it may be used to calculate the freezing-point curve, or the solubility, of any substance in the table with any other substance in the table providing the latent heat of fusion (ideal slope of the $\log N$ vs. $1/T$ curves) is known and the assumption is warranted that there are no complicating molecular effects. In making the calculation all that is necessary is to find the factor by which the ideal slope must be increased in order to make it equal to the slope which would be determined experimentally. This factor is found by placing a straight edge across the chart in such a position that it joins the components of the desired system. The point at which this cuts the line of factors will then be the ratio sought. Evidently, the nearer two substances are to one another in the table, the more nearly will their reciprocal solution approach to that of the ideal mixture.

In determining molecular weights by the melting-point or boiling-point method one should choose a solvent which has approximately the same position in the chart as the solute to be used. If this rule is not observed it will be found that the "molecular association" of the solute will appear

to increase in direct proportion to the magnitude of the factor relating the solute and solvent in the above chart.

This chart should also aid in the choice of solvent to be used in recrystallizations as well as for calculating the amounts dissolved by various solvents. In general it may be said that when the melting point of the substance is relatively low (below 100°) the solvent chosen should have a position in the table corresponding to a factor of about 3 or 4. As the melting point of the substance to be recrystallized increases above this temperature the solvent chosen should have more nearly the same position in the table. Such a choice of solvents permits obtaining more nearly saturated solutions upon heating, and upon cooling the solute does not crystallize in such a large amount as to make it unmanageable.

It is also possible to predict very nearly what substances will form partially miscible liquids and also something of the degree of miscibility. It has been observed that when the difference in internal pressures of two substances is so great that the factor connecting them in the chart has a greater value than about 4 to 4.5, partially miscible liquids may be expected to occur. The higher the melting points of the components the greater must be the difference in internal pressure to cause a separation into two liquid phases. It is evident also that in a system forming partially miscible liquids, the critical solution temperature of the two liquid phases will be higher the greater the difference in internal pressure, *i. e.*, the farther apart the components are in the chart (Fig. 5). When the factor joining the two components increases to a value of about 5.0-5.5 the substances may be considered as practically immiscible. Mixtures of two components containing enolic or ketonic oxygen may not follow these very general rules, due to the formation of oxonium compounds.

In making the calculations involved in constructing this table some generalizations have been observed which, although probably well known, will be repeated because of their use in helping to place other substances in the table. They will also show some other uses as well as the limitations of this method of calculating solubilities.

It is commonly assumed that the heat of solution of a given substance is equal to its heat of fusion. This, indeed, is always the case for ideal mixtures. Moreover, it has been observed that in dilute solutions of even non-ideal mixtures (saturated solutions far removed from the melting point of the solute) the $\log N$ vs. $1/T$ curves tend to become parallel to the curve having the ideal slope. Hence, the heats of solution of non-ideal mixtures very often closely approximate the heats of fusion of the solutes.

It has been found that structural isomers very seldom form mixed crystals or chemical compounds. Phenanthrene and anthracene, however, do form an unbroken series of mixed crystals.

Structural isomers generally have very nearly the same internal pressures. Hence the freezing-point curves between isomers are useful in determining the "ideal slope" of the solute.

It has been observed that when substances containing hydroxyl groups enter into systems containing enolic or ketonic oxygen, positive deviations from Raoult's law may be expected to occur, *i. e.*, the solubility will be greater than that calculated from the principles outlined above.

A typical exception to this rule is found in the system resorcin:water, the $\log N$ vs. $1/T$ curve for which is almost a straight line.

Binary systems of similarly constituted molecules may be expected to form mixed crystals. Examples are *p*-chloronitrobenzol, and *p*-bromonitrobenzol, and *p*-bromotoluene and *p*-iodotoluene.

It is interesting to note that substances having similar structures occupy approximately the same place in the table; thus,

Acetone, benzophenone, acetophenone, benzil.	Simple amines.
Pyridine, pyrrole, carbazole.	Simple nitro derivatives.
Ethers, anhydrides, esters.	Simple halogen derivatives.

In describing the above method of calculating solubility we have made the assumption that the $\log N$ vs. $1/T$ curves having the ideal slope is known or may be determined. We shall now consider some of the methods of obtaining this ideal slope in cases where it is not known.

Methods of Finding Latent Heat of Fusion and Ideal Slope

The method which has been found to give the most consistent results is the following. There is first obtained a complete freezing-point curve of the substance in question, for convenience called A, with some other substance, B, the ideal slope for which is known and the position of which in the chart of relative internal pressures has been determined. In choosing the exact binary system to be used it is necessary that there shall be no molecular complexes formed in the solution and it is convenient to choose as the second component a substance having about the same melting point as that of the substance to be investigated. The factor to be used between solute B and solvent A is first determined by dividing the value of the ideal slope for B into the value experimentally obtained when the substance A, of unknown internal pressure, is used as solvent for B. Having determined this factor the position of the substance A in the chart may be found. If now the substance A be used as solute, and B, or any other substance whose position in the chart is known, be used as solvent and the slope of the $\log N$ vs. $1/T$ curve of the system is determined, then the ideal slope for A is obtained by dividing this experimental slope by the appropriate factor obtained from this chart.

From the ideal slope so obtained the latent heat of fusion of the solute may now be calculated. This is done by multiplying this ideal slope by

the constant 4.58 which gives the latent heat in calories per gram mole. In Table II are given some values of latent heats calculated in this way. It will be observed that these values compare favorably with those determined calorimetrically.

A second method for determining the ideal slope and the position in the table may be called the "cut and try" method. This method may be used in those cases in which the solubility of a solute has been determined in a series of solvents whose positions in the chart have been determined. It is evident that there is only one position in the chart which will satisfy the demands of the factors of more than one solvent when the solute has been given any value for the ideal slope. The object is to find that set of values for the ideal slope and for the position in the chart which comes the most nearly to fitting all of the solvents involved. Evidently only 2 such solvents are needed but if more have been investigated greater confidence may be placed in the results obtained.

A third method for determining the ideal slope of the $\log N$ vs. $1/T$ curves may be used in those cases in which L , the latent heat of fusion, is accurately known. This is seldom the case, however. It is regrettable that such an important physical property has been so long neglected. In cases where it has been determined the results are often so discordant that doubt is thrown upon many of the published data. This variation is due, partially at least, to the fact that many of the values have been calculated from Van't Hoff's equation and hence the values obtained will depend upon the nature of the solvent used.

In Table II, Col. 5, are given the latent heats of fusion of a representative number of organic compounds. These values have been taken largely from the Landolt and Börnstein "Tabellen" and only those results which have been calorimetrically determined are included. In the fourth column of this table are given the latent heats of fusion as calculated from the ideal slopes of the $\log N$ vs. $1/T$ curves. Finally, in Col. 6 are given the quotients obtained by dividing the calculated molecular latent heats of fusion by the absolute melting point of the substance. This, according to Walden,⁴ should equal about 13.5. It will be observed that the constant, 13.5, applies very well to most halides and nitro compounds and to many other isolated compounds especially to those substances which have relatively high molecular weights and moderately high melting points. In general it may be said that the Walden constant for the more highly polar substances such as the hydroxides, ketones, amines, etc., has a value somewhat smaller than the normal. Hence it is manifestly impossible, with our present knowledge, to describe an exact method for calculating solubility when only the melting point of the solute is known. On the other hand, it should be possible, by reference to Table II, to calculate the

⁴ Walden. *Z. Elektrochem.*, **14**, 713 (1908).

approximate value of the latent heat of fusion and hence the ideal slope for any substance whose structure and melting point are known. Presuming the structure to be known, it is then possible to locate the approximate position of the substance in the chart, Fig. 5. With this information it is then possible to make a fair estimate of the solubility of the substance in question in all of the substances shown in the chart which do not form compounds or solid solutions.

TABLE II
THE LATENT HEATS OF FUSION OF ORGANIC COMPOUNDS

Substance	M. p. (T_m) °Abs.	Ideal slope (S_f)	$S_f \times 4.57$ ($L_{calc.}$)	$L_{obs.}$	$L_{calc.}$ (T_m)
Hydrocarbons					
Benzene.....	278.5	510	2330	2350	8.36
<i>p</i> -Xylene.....	287.4	840	3840	4170	13.4
Diphenylmethane.....	299.3	810	3700		12.4
Diphenyl.....	343.2	960	4390	4390	12.8
Naphthalene.....	353.1	970	4440	4550	12.6
Triphenylmethane.....	366.0	970	4440		12.6
Acenaphthene.....	366.5	1090	5000		13.6
Phenanthrene.....	371.0	980	4470		12.1
Fluorene.....	386.5	1050	4800		12.4
Pyrene.....	421.0	1150	5260		12.5
Anthracene.....	489.6	1500	6870	6890	14.0
Halides					
Ethylene dibromide.....	282.8	550	2540	2540	9.0
<i>p</i> -Bromotoluene.....	299.8	800	3680	3650	12.2
<i>p</i> -Dichlorobenzene.....	325.5	960	4400	4390	13.5
<i>p</i> -Dibromobenzene.....	360.0	1060	4850	4860	13.5
<i>p</i> -Di-iodobenzene.....	401.0	1200	5500		13.7
Nitro Compounds					
<i>p</i> -Nitrotoluene.....	324.3	800	3660		11.3
α -Nitronaphthalene.....	328.0	950	4340	4380	13.2
1,3,4-Dinitrotoluene.....	332.0	990	4520		13.6
1,2,6-Dinitrotoluene.....	338.0	1000	4570		13.5
1,2,4-Dinitrotoluene.....	344.0	1020	4650		13.5
<i>m</i> -Dinitrobenzene.....	363.0	1070	4900	4870	13.5
<i>o</i> -Dinitrobenzene.....	389.5	1160	5300		13.6
Nitro Halides					
<i>p</i> -Fluoronitrobenzene.....	299.5	710	3240		10.7
<i>o</i> -Chloronitrobenzene.....	305.3	850	3900		12.8
<i>o</i> -Bromonitrobenzene.....	311.2	900	4110		13.2
<i>m</i> -Chloronitrobenzene.....	315.8	930	4250	4630	13.5
<i>p</i> -Chloronitrobenzene.....	357.0	1060	4850		13.6
<i>p</i> -Bromonitrobenzene.....	396.5	1200	5490		13.8
<i>p</i> -Iodonitrobenzene.....	446.0	1500	6850		15.3
1,2,4-Dichloro-nitrobenzene.....	313.6	810	3700		11.8
Amino Compounds					
Aniline.....	267.5	425	1940	1940	7.26
<i>p</i> -Toluidine.....	316.5	870	3980		12.6

TABLE II (continued)

Substance	M. p. (T_m) °Abs.	Ideal slope (S_i)	$S_i \times 4.57$ ($L_{calc.}$)	$L_{obs.}$	$L_{calc.}$ (T_m)
α -Naphthylamine.....	317.7	880	3110		9.8
Diphenylamine.....	325.7	880	4020	4050	12.3
<i>o</i> -Nitro-aniline.....	343.0	840	3840		11.2
<i>m</i> -Nitro-aniline.....	387.0	1000	4570		11.8
<i>p</i> -Nitro-aniline.....	421.0	1100	5030		11.9
Oxygen-containing substances					
<i>m</i> -Cresol.....	277.3	380	1740		6.3
<i>o</i> -Cresol.....	303.7	475	2170		7.15
Phenol.....	313.6	495	2260	2340	7.2
α -Naphthol.....	367.5	1120	5120		13.9
β -Naphthol.....	395.0	1150	5250		13.3
Resorcinol.....	383.4	565	2580		6.73
Hydroquinone.....	443.0	705	3220		7.3
Thymol.....	322.2	650	2970	2980	9.2
Menthol.....	315.0	650	2970	2950	9.4
Paraldehyde.....	285.0	615	2820		9.9
Phthalic anhydride.....	403.8	1070	4900		12.1
Acetophenone.....	293.5	3980	...
Benzophenone.....	322.0	830	3800	4310	11.8
Benzil.....	388.0	1020	4650	4650	12.0
Anthraquinone.....	558.0	3560	7780	7780	13.9
Acetic acid.....	289.4	320	1460	2630	5.05
Trichloro-acetic acid.....	330.0	775	3540		10.7
β -Oxynaphthoic acid.....	489.0	1440	6580		13.5
Miscellaneous substances					
Urethane.....	318.2	795	3630	3630	8.03
Carbazole.....	518.0	1400	6400	7050	12.3
Acetamide.....	350.0	480	2200		6.3
<i>o</i> -Nitrophenol.....	319.0	810	3700	3720	11.6
<i>m</i> -Nitrophenol.....	367.5	1080	4950		13.5
<i>p</i> -Nitrophenol.....	386.0	1150	5260		13.6
1,2,4-Dinitrophenol.....	384.0	1140	5210		13.6
Picric acid.....	395.5	910	4160		10.5

Solubility measurements are being continued. It is hoped that a comprehensive method for calculating the solubilities of organic substances may be developed from these studies.

Summary

A method for calculating the solubility of non-ideal solutions has been described.

It is shown that for those systems which do not form molecular complexes or solid solutions, the ratio of the experimental to the ideal slope of the $\log N$ vs. $1/T$ curves is a factor which may be determined by a graphical method.

Several methods of finding the ideal slope of the $\log N$ vs. $1/T$ curves for any solute have been described.

It has been pointed out that the solubility or melting-point method of determining latent heat of fusion of organic compounds gives very accurate results when interpreted in the light of the principles outlined above.

Some generalizations regarding the nature of the binary systems obtained with various types of mixtures have been given.

The uses of these principles in determining the choice of solvent for crystallizations and molecular-weight determinations are suggested.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ILLINOIS WESLEYAN UNIVERSITY]

THE VAPOR PRESSURES AND HEATS OF VAPORIZATION OF NON-ASSOCIATED LIQUIDS

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Received January 30, 1922

In the application of physico-chemical principles to industrial and manufacturing processes, few questions are of more frequent occurrence than those dealing with distillation problems. The questions take a variety of forms but most of them may be answered when the vapor pressures of the substances involved are known. Occasionally the desired information may be found in, or calculated directly from, data given in the literature. More commonly this is not the case and it is then necessary either to make the measurements or to resort to some method of calculation of the desired values.

Many expressions have been developed for calculating vapor pressures and heats of vaporization of liquids. Probably the most useful of them is that obtained from the integration of the Clausius-Clapeyron equation. This integration, assuming that the heat of vaporization is constant, gives the well known expression,

$$\log P = -L/4.58 T + C \quad (1)$$

in which P is the vapor pressure measured at the absolute temperature T , L is the molecular latent heat of vaporization and C is a constant of integration.

Equation 1 indicates that if the common logarithm of the vapor pressure be plotted against the reciprocal of the absolute temperature a straight line should result, the slope,

$S \left(S = \frac{\Delta \log P}{\Delta (1/T)} \right)$ of which is given by the expression $-L/4.58$, or,

$$\log P = C - S/T. \quad (2)$$

Hildebrand¹ has shown that these $\log P$ vs. $1/T$ curves for normal liquids may be superimposed upon that of some closely related substance by the use of a factor which he calls a . This factor is simply the ratio of the molecular latent heats of vaporization of the substances involved, or it is the ratio of the absolute temperatures at which the vapors of the

¹ Hildebrand, THIS JOURNAL, 37, 975 (1915).