2. The oxidation takes place according to the theoretical requirement of 2 equivalents of oxygen, and the oxalate factor for the permanganate may be used. The maximum in the $\frac{\Delta E}{\Delta V} - V$ curve described usually lies a little too far to the right, but when a correction of —0.10 cc. of 0.1 *N* titrating solution is made the maximum error is less than 0.4 mg. of bromine.

3. A sub-maximum often precedes the end-point maximum in the $\frac{\Delta E}{\Delta V} - V$ curve and the intervening sub-minimum lies extremely close to the theoretical end-point. The sub-maximum does not always occur.

4. Iodide, if present, is oxidized to the corresponding iodine compound, ICN, but chloride in any quantity does not interfere. Since a selective determination of iodide is possible, the proposed method provides an excellent means for the rapid determination of bromide in the presence of any concentration of the other two halides.

5. Iodide may be accurately titrated electrometrically by oxidation to iodine cyanide with permanganate in hydrocyanic acid solution in all concentrations of chloride and in moderate concentrations of bromide.

The effect of bromide is a function of the ratio of its concentration to that of iodide and also of the absolute concentration of each.

6. A more accurate method is the oxidation of iodide to iodate by excess of alkaline hypobromite, the excess being titrated electrometrically with arsenite.

The presence of any amount of bromide or chloride is without effect.

Either the bimetallic or monometallic electrode system may be used in both methods.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ILLINOIS WESLEYAN UNIVERSITY]

THE SOLUBILITY RELATIONS IN MIXTURES CONTAINING POLAR COMPONENTS

BY F. SPENCER MORTIMER

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In a recent paper the author[1] described a graphical method for calculating the ratio of the experimental to the ideal slope of the curves obtained by plotting the logarithm of the mole fraction of solute against the reciprocal of the absolute temperature of the solubility point of the mixture and, hence, for calculating the solubility in non-ideal solutions.

In applying this method the most serious difficulties are encountered in mixtures containing polar components. It is the purpose of this article

[1] Mortimer, THIS JOURNAL, **44**, 1416 (1922).

to show to what extent the generalizations previously discussed may be applied to such systems. Incidentally, the results of some of our own solubility measurements will be given. We shall also attempt to show that relative values for the internal pressures may be calculated from solubility data.

In Table I will be found the solubilities, in terms of the mole fraction of the solute, for a number of substances having various degrees of internal pressure and polarity. There are also included the observed slopes of the curves obtained by plotting the logarithm of the mole frac-

Table I[2]

The Solubility Relations of Fluorene

M. p. of fluorene, 114.5. Molecular latent heat of fusion in small calories (calc.), 4800

Temp. °C.	Ideal	Ethylene dichloride[a]	Chloro-benzene[a]	Nitro-benzene[a]	*p*-Xylene[a]	Toluene[a]	Benzene[a]
0	0.075	0.071	0.066	0.063	0.055	0.054	0.054
20	0.137	0.129	0.124	0 118	0.112	0.106	0.105
40	0.229	0.220	0.214	0.206	0.193	0.191	0.190
60	0.365	0.356	0.349	0.341	0.327	0.324	0.324
80	0.543	0.541	0.533	0.525	0.513	0.511	0.511
100	0.785	0.784	0.782	0.771	0.766	0.765	...
$S_{\text{obs.}}$	..	1050	1060	1090	1170	1175	1180
$S_{\text{calc.}}$	1050	1150	1130	1070	1175	1180	1180

Temp. °C.	Pyridine[a]	Carbon tetra-chloride	Aniline[a]	Acetone	Acetic acid[a]	Ethyl alcohol[a]	Methyl alcohol[a]
0	0.051	0.037	0.024	0.020	...	....	....
20	0.101	0.078	0.056	0.047	0.008	0.0050	0.0035
40	0.183	0.151	0.117	0.104	0.019	0.0085	0.0058
60	0.314	0.275	0.232	0.150 at 50°	0.045	0.0176	0.0110
80	0.499	...	0.427	...	0.113	0.0460	....
100	0.755	...	0.710	...	0.400	....	....
$S_{\text{obs.}}$	1200	1320	1510	1580	2000 to 3500	3000 to 4500	3500 to 5500
$S_{\text{calc.}}$	1120	1260	1470	1370	2020	3000	3500

The Solubility Relations of Para-dibromo-benzene

M. p., 89.0°. Latent heat of fusion, 4850 cal. per mole.

Temp. °C.	Ideal	Benzene[a]	Toluene[a]	Carbon tetra-chloride[a]	Nitro benzene[a]	Aniline[a]	Phenol[a]	Ethyl alcohol
0	0.114	0.110	0.105	0.079	0.069	0.033	...	...
20	0.207	0.202	0.197	0.159	0.144	0.085	...	0.028
40	0.355	0.349	0.343	0.298	0.279	0.197	0.017	0.041
60	0.564	0.557	0.551	0.511	0 491	0 396	0.286	0.110
80	0.851	0.845	0.840	...	0.811	0.776	0.720	...
$S_{\text{obs.}}$	1060	1070	1090	1210	1300	1640	2000 to 2300	2300 to 4000
$S_{\text{calc.}}$	1060	1070	1080	1200	1270	1640	1910	3200

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[2] All solubilities are expressed in terms of the mole fraction of the solute.

THE SOLUBILITY RELATIONS OF BENZOIC ACID

M. p., 121.0°. Latent heat of fusion, 4120 (calc.) cal. per mole.

Temp. °C.	Ideal	Acetone[a]	Acetophenone[a]	Phenol[a]	Nitrobenzene[a]	Toluene[a]	Benzene	Acetic acid[3]	Carbon tetrachloride[a]
0	0.096	0.158	0.083	...	0.044	0.032	...	...	0.017
20	0.160	0.205	0.144	...	0.092	0.058	0.061	0.078	0.042
40	0.254	0.269	0.236	0.169	0.163	0.136	0.126	0.118	0.094
60	0.378	0.362	0.359	0.282	0.276	0.243	0.237	0.210	0.200
80	0.536	...	0.516	0.442	0.434	0.400	0.417	0.368	...
100	0.733	...	0.716	0.670	0.660	0.646	...	0.617	...
$S_{obs.}$	...	700 to 960	960	1170	1200	1320	1380	1460	1400 to 1550
$S_{calc.}$	900	945	960	1240	1190	1300	1290	1420	1400

THE SOLUBILITY RELATIONS OF RESORCINOL

M. p., 110.2°. Latent heat of fusion, 2296 (obs.) cal. per mole. The heat of fusion calculated from solubility is 2060.

Temp. °C.	Ideal	Urethan[a]	Ethyl alcohol	Water	Acetic acid[a]	Nitrobenzene[a]
0	0.332	...	0.354	0.098	...	...
20	0.431	...	0.389	0.166	0.176	0.066
40	0.546	0.468	0.438	0.268	0.272	0.160
60	0.663	0.563	0.507	0.404	0.394	0.322
80	0.795	0.682	0.640	0.588	0.563	0.553
100	0.931	0.855	...	0.833	0.810	0.833
$S_{obs.}$	...	about 550	450 to 850	950 to 1000	930 to 1300	1200 to 1600
$S_{calc.}$	450	495	630	935	1170	1560

THE SOLUBILITY RELATIONS OF ACETAMIDE

M. p., 78.5°. Latent heat of fusion, 1830 (calc.) cal. per mole.

Temp. °C.	Ideal	Water	Ethyl alcohol	Urethan[a]	*p*-Toluidine[a]
0	0.467	0.296	0.185	...	...
20	0.590	0.408	0.338	...	...
40	0.723	0.555	0.531	0.498	0.330
60	0.865	0.760	0.758	0.730	0.608
70	0.937	...	...	0.871	0.795
$S_{obs.}$	...	650 to 750	780 to 900	870	1370
$S_{calc.}$	400	760	780	550	1370

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[3] Kendall, THIS JOURNAL, **36**, 1722 (1914).

THE SOLUBILITY RELATIONS OF ACETANILIDE

M. p., 113.0°. Latent heat of fusion, 2100 (calc.) cal. per mole.

Temp. °C.	Ideal	Phenol[a]	Ethyl alcohol	Methyl alcohol	Urethan[a]	Toluene[a]
0	0.141	...	0.128	0.048	...	0.0015
20	0.221	...	0.212	0.095	...	0.0037
40	0.332	0.427	0.319	0.181	0.148	0.011
60	0.469	0.501	0.464	0.315	0.274	0.056
80	0.652	0.605	0.633	...	0.468	0.338
100	0.851	0.795	...	...	0.757	0.708
$S_{obs.}$	...	500 to 1100	820	1220	1400	2000 to 3000
$S_{calc.}$	795	1620	870	1220	1340	2270

[a] These systems were determined in this Laboratory by Mr. Jesse W. Smith. Carefully purified solutes and solvents were used in all cases. The other data, with the exceptions noted, have been taken from the compilations in Landolt-Börnstein-Roth, "Phys.-Chem. Tabellen."

tion of the solute against the reciprocal of the absolute temperature. The corresponding calculated values are included for comparison. These calculated slopes are determined either by the graphical method described in the first article by the author or from the table of relative internal pressures as given in a later section of this paper.

In order that a more direct comparison may be made between the observed and calculated solubilities, there are given in Table II the calculated results for a typical non-polar solute, *p*-dibromo-benzene and a typical polar solute, acetanilide. These results have been calculated from the modified Raoult expression,

$$\log N = \frac{-L.f}{4.58}\left[\frac{T_m - T}{T_m \cdot T}\right] \qquad (1)$$

in which N is the mole fraction of the solute at the absolute temperature,

TABLE II

THE SOLUBILITY RELATIONS OF PARA-DIBROMO-BENZENE (CALCULATED)

Temp. °C.	Benzene	Toluene	Carbon tetrachloride	Nitrobenzene	Aniline	Phenol	Ethyl alcohol
0	0.110	0.108	0.083	0.072	0.033	...	...
20	0.202	0.200	0.163	0.148	0.085	...	0.008
40	0.349	0.347	0.302	0.283	0.197	0.151	0.042
60	0.557	0.565	0.510	0.496	0.396	0.347	0.171
80	0.845	0.845	...	0.813	0.776	0.737	...

THE SOLUBILITY RELATIONS OF ACETANILIDE (CALCULATED)

Temp. °C.	Ethyl alcohol	Methyl alcohol	Urethan	Toluene
0	0.118	0.048	...	0.0031
20	0.193	0.096	...	0.011
40	0.305	0.181	0.160	0.038
60	0.447	0.315	0.288	0.108
80	0.628	...	0.489	0.276
100	...	...	0.768	0.617

T, T_m is the absolute melting point of the solute, L is the molecular latent heat of fusion of the solute in small calories and f is the factor relating the internal pressures of solute and solvent. The term, $L.f/4.58$ is equivalent to the "calculated slope" given in Table I.

For purposes of reference the system of curves for acetanilide as solute has been plotted graphically in Fig. 1 using the common logarithm of the mole fraction of the solute and the reciprocal of the absolute temperature of the melting point of the system as the coördinates.

A comparison of the observed and calculated slopes of the log N vs. $1/T$ curves and of the observed and calculated solubilities in Table II will indicate the degree of precision to be expected in calculations of this kind.

For purposes of discussion the various types of curves may be classed under three heads. First are those which follow the generalization. These may be called the normal. This class requires no further discussion than has been given in the previous articles, except to state that in general the nearer the internal pressures and the more nearly similar the polarities of the components of the solutions, the more nearly will the system follow the regular rule. Even here, however, if the components have very similar structures, mixed crystals or solid solutions may be expected to occur. This is well illustrated by the system, acetanilide–acetamide, which forms an unbroken series of mixed crystals.

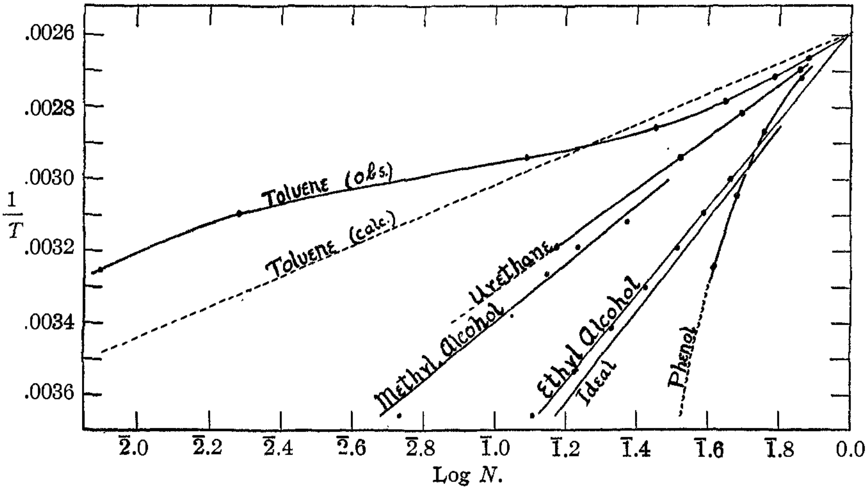

Fig. 1.—Solubility relations of acetanilide.

The second class consists of those systems showing positive deviations from the normal, and is well illustrated by the system, acetanilide–phenol shown in Fig. 1. In these systems the solubility is greater than would be expected and is commonly higher, even, than in the ideal solvents. It is probable that this is caused by the formation of molecular complexes in solution. This type is most commonly found in those systems containing components of dissimilar polarities and is quite common in systems in which both components contain carbonyl or hydroxyl oxygen. It is probable that in systems containing inorganic components this is the most common phenomenon.[4] Other illustrations among the organic substances are resorcinol or the naphthols in alcohols, benzoic acid in acetone, phenol in aniline, etc.

The third type consists of those systems showing negative deviations from the normal. This type commonly occurs in systems in which one of the components is non-polar while the other is polar in nature or where there is a rather great difference in the internal pressures of the solute and solvent. The solubilities of hydrocarbons and their halogen derivatives in the alcohols or organic acids and of polar substances in hydrocarbons or their halogen or nitro derivatives are generally of this type. A peculiarity of this type is the reversed *S*-form of the log N against $1/T$ curve, as shown for acetanilide in toluene in Fig. 1. The observed log N against $1/T$ curves for this type become roughly parallel to the calculated curve at the lower temperatures but it may be displaced so far that the calculated solubilities do not even approximate the observed results. Unsatisfactory as this is, still the calculation is much better than that obtained by the unmodified Raoult equation and will at least serve to give maximum values for the solubilities in these systems.

The Calculation of Relative Internal Pressures from Solubility

Hildebrand has been able to show that there is a close relation between the magnitude of the deviations from Raoult's ideal solubility law and the relative internal pressures of the solute and solvent constituting the solution. It would seem, then, that by reversing the procedure it should be possible to calculate relative values for the internal pressures from a knowledge of the solubilities. Table III shows data from which the relative internal pressures calculated from solubility may be compared with the values obtained by other methods.

In this table the values in Cols. 3 and 6 have been calculated from the data given by Hildebrand.[5] The results of the three methods of calculating internal pressures used by Hildebrand were first calculated to strictly relative values using the value for naphthalene in each case as unity. The mean of the 3 values so obtained is given in Table III.

The data given in the second and fifth columns in Table III have been calculated from solubility measurements. These values are the "factors" described in the first paper; or, they are the ratios of the experimental to the ideal slopes of the log N against $1/T$ curves referred to naphtha-

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[4] Kendall, *Proc. Nat. Acad. Sci.*, **7**, 56 (1921).

[5] Hildebrand, This Journal, **38**, 1452 (1916); **39**, 2297 (1917); **41**, 1067 (1919); **42**, 2180 (1920).

lene as solute. It should be noted that in case the solvent has a lower internal pressure than that of naphthalene, the relative internal pressure is then the reciprocal of the factor which relates the solvent to naphthalene.

TABLE III

A COMPARISON OF VALUES FOR RELATIVE INTERNAL PRESSURES CALCULATED FROM SOLUBILITY WITH THE RESULTS OBTAINED FROM OTHER SOURCES

Substance	Relative internal pressure from solubility	Relative internal pressure from other sources	Substance	Relative internal pressure from solubility	Relative internal pressure from other sources
Hexane	0.56	0.56	Chloroform	0.95	0.90
Ethyl ether	0.66	0.62	Chlorobenzene	0.98	0.96
Carbon tetrachloride	0.84	0.81	Naphthalene	1.000	1.000
Bromobenzene	0.94	0.96	Pyridine	1.10	1.17
Benzene	0 94	0.96	Carbon disulfide	1.13	1.18
Toluene	0.93	0.84	Iodine	1.85	1.82
Ethylene dibromide	0.95	1.13	Water	4.60	4.55
p-Dibromo-benzene	0.95	1.09			

The fair agreement between the values in Cols. 2 and 3 in Table III seems to warrant the conclusion that the solubility method is at least as accurate as the methods previously used. Accordingly, there have been collected in Table IV the values of the relative internal pressures thus calculated for a great number of substances.

Between 400 and 500 binary systems have been employed in making the calculations for Table IV. Hence, the values finally adopted for most of the substances are the means of several closely agreeing results.

It has been shown that a more or less definite relation exists between solubility and the difference in relative internal pressures of solute and solvent. It remains now to show how solubility may be calculated directly from the results given in Table IV.

Returning then to the log N against $1/T$ curves, in general it may be said that the experimental slopes of these curves will be greater than the ideal slope calculated from the latent heat of fusion of the solute. The numerical value of the factor relating the slopes of the experimental to the ideal curves may be calculated from the table of relative internal pressures, Table IV. This calculation will obviously be as follows. When both the solute and the solvent in the desired system have relative internal pressures greater than naphthalene, the ratio of the experimental to the ideal slope of the log N against $1/T$ curves is given by the expression,

$$f = \pi_1 - \pi_2 + 1 \qquad (2)$$

in which π_1 and π_2 represent the relative internal pressures of the components of the system under investigation, taken from Table IV. When both the solute and the solvent have internal pressures less than that of naphthalene the ratio of the slopes is

$$f = 1/\pi_1 - 1/\pi_2. + 1. \qquad (3)$$

Table IV

Relative Internal Pressures, Referred to Naphthalene, as Calculated from Solubility Data

Substance	Relative Int. Pres.	Substance	Relative Int. Pres.
Hexane	0.56	Carbazole	1.12
Ethyl ether	0.66	Carbon disulfide	1.13
Acetic anhydride	0.76	Trinitrophenol	1.14
Paraldehyde	0.77	Dinitrophenol	1.15
Menthol	0.78	*p*-Nitrophenol	1.17
Ethyl acetate	0.83	Benzanthrone	1.20
Carbon tetrachloride	0.84	Anthraquinone	1.22
Phthalic anhydride	0.91	Antimony trichloride	1.23
Bromotoluene	0.93	Antimony tribromide	1.25
Bromobenzene	0 94	Thymol	1.26
Benzene	0.94	Benzophenone	1.27
Toluene	0.93	Acetophenone	1.30
Ethylene dibromide	0.95	Benzil	1 30
p-Dichloro-benzene	0.95	Aluminum bromide	1.30
p-Dibromo-benzene	0.95	Acetone	1.32
Chloroform	0.95	Naphthylamines	1.33
Chlorotoluene	0.97	Toluidines	1.35
Chlorobenzene	0.98	Benzoic acid	1.38
Acenaphthene	0.98	Naphthols	1.40
NAPHTHALENE	1.000	Trichloro-acetic acid	1.42
Diphenylamine	1.00	Aniline	1.46
Phenanthrene	1.02	Nitro-anilines	1.65
Fluorene	1.04	Sulfur	1.70
Anthracene	1.05	Iodine	1.85
Diphenyl methane	1.06	*p*-Azoxy-anisole	1.87
Triphenyl methane	1.07	Acetic acid	1.95
Nitrobenzene	1.07	Acetanilide	2.78
Nitronaphthalene	1.08	Ethyl alcohol	2.90
m-Dinitro-benzene	1.08	Hydroquinone	3.27
Other nitro compounds	1.08	Methyl alcohol	3.35
p-Chloronitro benzene	1.08	Urethan	3.50
Other nitro halides	1.08	Resorcinol	3.55
Pyridine	1.10	Acetamide	3.80
Pyrrole	1.10	Water	4 60

Finally, when the components of the desired system have internal pressures, one greater and one less than naphthalene, the factor relating the experimental to the ideal slope is,

$$f = \pi_{\text{greater}} - 1/\pi_{\text{less}} + 1. \qquad (4)$$

If it is desired to calculate only a few values of the solubility instead of the complete solubility curve it is generally more convenient to use the modified Raoult expression, Equation 1.

Summary

1. The deviations from Raoult's ideal solubility law are proportional to the magnitude of the differences of the internal pressures of the com-

ponents of the system.

2. The ratio of the experimental slope of the curve of log N against $1/T$ to the ideal slope, calculated from the latent heat of fusion, for any solute, is a measure of the relative internal pressures of the solute and solvent.

3. Not only may the latent heat of fusion of solids be determined but relative values for the internal pressures of many solids and liquids may be calculated from solubility data by the application of the principles developed.

4. The results of the calculations of relative internal pressures have been given and compared with those obtained by direct measurement or from other methods of calculation.

5. The principles entering into the procedure for calculating solubilities of organic compounds in various solvents have been discussed both for polar and non-polar substances. The limitations of the method have been pointed out.

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[Contribution from the Department of Chemistry of Washington and Lee University]

A STUDY OF THE COBALTINITRITES OF BISMUTH AND CADMIUM

By S. C. Ogburn, Jr.

Received November 13, 1922

Inorganic cobaltinitrites of the following elements have been previously prepared and described: potassium, sodium, lead, silver, lithium, thallium, barium, mercury (ous), strontium, zinc, magnesium, cobalt, ammonium, cesium and rubidium. This work has been done mainly by Aide and Wood,[1] Rosenheim and Koppel,[2] Cunningham and Perkin,[3] Burgess and Kamm,[4] and Drushel.[5] A survey of the literature, however, failed to disclose to the author any attempt at the preparation of the cadmium and bismuth compounds. This is, perhaps, due to their instability at formation, thus making their isolation by ordinary precipitation methods rather difficult.

Preparation of the Cobaltinitrite of Bismuth. Bismuthyl Cobaltinitrites

To a saturated solution of sodium cobaltinitrite, $Na_3Co(NO_2)_6$, an equal quantity of a saturated solution of bismuth nitrate was added drop by drop, without shaking. A yellow-to-orange precipitate slowly appeared. At the end of 1 minute, it was filtered off by suction with as little agitation as possible. The precipitate was not washed,

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[1] Aide and Wood, *J. Chem. Soc.*, **77**, 1076 (1900).

[2] Rosenheim and Koppel, *Z. anorg. Chem.*, **17**, 42 (1898).

[3] Cunningham and Perkin, *J. Chem. Soc.*, **95**, 1562 (1909).

[4] Burgess and Kamm, *Am. J. Sci.*, **24**, 433 (1907); **26**, 329, 555 (1908).

[5] Drushel, This Journal, **34**, 652 (1912).