[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

SOLUBILITY. XII. REGULAR SOLUTIONS[1]

BY JOEL H. HILDEBRAND

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In a systematic study of deviations from Raoult's law, or other relations which may be derived from it, the author[2] has made much use of solubility data for solids and has shown that, particularly among substances of low polarity, there exist families of solubility curves which bespeak a marked regularity even where the deviations are very large. Evidently, the equations for the curves belonging to these families for systems which we will call *regular*, are to be sought before those of divergent and often highly individualistic curves, shown by *irregular* systems. In the case of iodine, for example, the solvents which give a violet color, similar to that of iodine vapor, give regular solubility curves, while the solvents which give brown solutions give irregular curves. Fig. 1, giving solubility curves for stannic iodide in various solvents found by plotting log N_2, where N_2 is the mole fraction of the solute, against $1/T$, illustrates such a family of regular curves. It has been easy to show that the positions of the curves accord fairly well with the differences in internal pressure between the solvents and the solute, but it has not heretofore been possible to get from the solubility data as a whole any simple measure of the deviations from Raoult's law, for the spacing of the curves depends upon the distance from the melting point of the solute.

Mortimer,[3] it is true, has given an approximate treatment by assuming that the solubility curves are straight lines converging to the melting point, the slopes representing the heats of solution calculable upon an additive basis from a table of relative internal pressures. While this treatment is practically useful for systems deviating but moderately from Raoult's law, it is unsatisfactory, first, because the solubility curves are not linear, as Mortimer himself recognized; second, because where the solute melts to give a second liquid phase, its solubility curve does not converge to the melting point, but behaves as does heptane in Fig. 1; and, third, because the slope of the solubility curve does not, in general, give directly the partial molal heat of solution but requires a correcting term to be discussed later.

The course of the solubility curve for a solid depends upon the variation

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[1] A brief preliminary paper has been published in the *Proc. Nat. Acad. Sci.*, **13**, 267 (1927).

[2] (a) Hildebrand, THIS JOURNAL, a series of ten papers beginning in 1916, *cf.* "Bibliography," ref. 2b, p. 200; (b) Hildebrand, "Solubility," American Chemical Society Monograph, Chemical Catalog Company, New York, **1924**; (c) ref. 2(b), Chap. XIV, see also Dorfman and Hildebrand, THIS JOURNAL, **49**, 729 (1927).

[3] Mortimer, THIS JOURNAL, **44**, 1416 (1922); **45**, 633 (1923).

in its activity with both composition and temperature. Margules[4] long ago suggested for the variation in activity, a_2, with mole fraction, N_2, of Component 2 of a binary liquid mixture, the expression

$$\ln a_2 = \ln N_2 + {}^1/_2\beta_2 N_1^2 + {}^1/_3\gamma_2 N_1^3 + \ldots\ldots$$

and, similarly, with subscripts interchanged, for the other component. Porter[5] called attention to a fact that had also been noted by the writer, *i. e.*, that terms higher than N^2 may be omitted for many systems. In 1906, van Laar[6] gave an equation based upon the van der Waals equation of state for mixtures, which in our notation reads

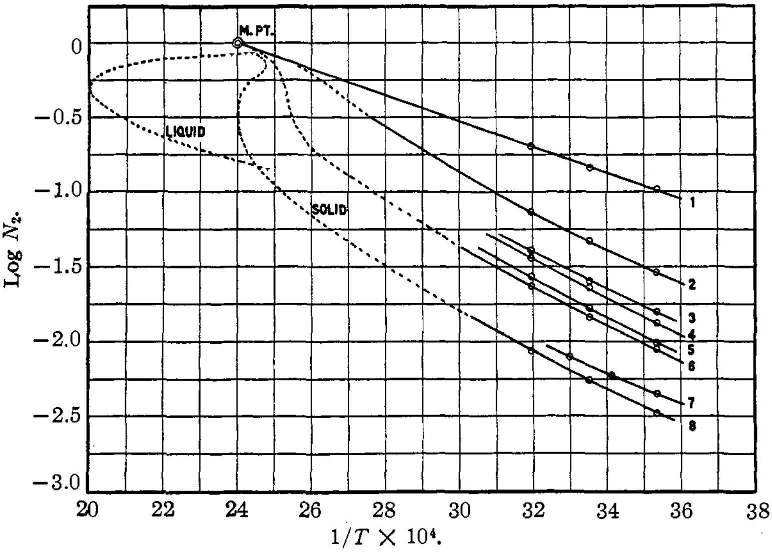

Fig. 1.—Solubilities of stannic iodide in: 1, carbon disulfide; 2, ethylene bromide; 3, *m*-xylene, 4, benzene; 5, chloroform; 6, carbon tetrachloride; 7, ether; 8, heptane.

$$RT \ln a_2 = RT \ln N_2 + \alpha N_1^2/(1 + rN_1)^2$$

where α and r are functions of the van der Waals "constants." When the van der Waals "b" is the same for the two components this reduces to

$$RT \ln a_2 = RT \ln N_2 + \alpha N_1^2$$

The term αN_1^2 is intended to represent the partial molal heat of mixing, and would be independent of temperature if the van der Waals equation were strictly applicable.

More recently van Laar and Lorenz[7] have published a derivation of

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[4] Margules, *Sitzb. Wien. Akad.*, [2] **104**, 1243 (1895).

[5] Porter, *Trans. Faraday Soc.*, **16**, 336 (1921).

[6] Van Laar, "Sech Vorträge über das thermodynamische Potential," Vieweg und Sohn, Braunschweig, 1906; *cf.* also *Z. physik. Chem.*, **72**, 723 (1910).

[7] J. J. van Laar and R. Lorenz, *Z. anorg. allgem. Chem.*, **145**, 239 (1925).

the above equation. Experimental tests of their equations have rarely been made by the van der Waals "school" beyond the mere citing of systems which conform as to type, and the present case is no exception. It is also unfortunate that the generally accurate thermodynamic methods employed in Holland have been so inextricably bound up with an inadequate equation of state.

Shortly before the publication of the previous paper by the writer on this subject, there appeared an important paper by Heitler[8] in which the simplified equation given by van Laar was derived without reference to the van der Waals constants, by considering the solution as a lattice, examining the probability of the various arrangements of the two molecular species therein, and by the aid of certain other assumptions that cannot be repeated here. He tested the formula by showing that the isotherms for the vapor pressure of five mixtures can be calculated with fairly good agreement by getting the heat of mixing from the curve itself, although the agreement with the experimental heat of mixing was not at all good. He further applied the formula to the calculation of the liquid–liquid solubility curve, and tested it with existing data for eight systems, finding that the experimental curves are in all cases somewhat flatter.

Most of the systems cited by Heitler involve one more or less polar constituent and one involves solvation. The writer believes it to be important in this connection to distinguish the systems here designated as regular from those involving solvation or association, in order to gain a correct prediction of the temperature effect, and also that the change in volume on mixing should be taken into consideration. The following simple considerations are advanced regarding the entropy of regular solutions.

If a solution is ideal, in the sense of obeying Raoult's law, the change in free energy corresponding to the transfer of a mole of component X_2 from the pure liquid state to a large amount of solution, in which its mole fraction is N_2, is[9]

$$\overline{F}_2^{i} - F_2^{\circ} = RT \ln N_2 \tag{1}$$

The corresponding entropy change is

$$\overline{S}_2^{i} - S_2^{\circ} = \frac{d(\overline{F}_2^{i} - F_2^{\circ})}{dT} = R \ln N_2 \tag{2}$$

which thus depends upon composition only. From the standpoint of the interpretation of entropy in terms of probability, we can say that a mixture represents a more probable state for such a system than do the separate liquids. Now suppose that the component X_2 is transferred from an ideal solution to any regular solution in which it has the same

[8] Heitler, *Ann. Physik*, [4] **80**, 630 (1926).

[9] Ref. 2b, p. 29.

mole fraction. From our picture of a regular solution as one in which orienting and chemical effects are absent, and in which the distribution and orientations are random, just as in the ideal solution, we may conclude that the probability of X_2 is the same in the two solutions and, therefore, that the difference in entropy is zero. We cannot expect this conclusion to hold unless the random distribution of the molecules persists. We may expect, further, that a small correction should be applied to take care of the change in entropy accompanying changes in volume, given by

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{3}$$

or we may state our principle in the following form. *A regular solution is one involving no entropy change when a small amount of one of its components is transferred to it from an ideal solution of the same composition, the total volume remaining unchanged.* Let us examine the consequences of this simple postulate.

When one mole of X_2 is transferred from the pure liquid to a regular solution, the change in free energy is

$$\bar{\mathrm{F}}_2 - \mathrm{F}_2^{\circ} = RT \ln a_2 \tag{4}$$

where a_2 is the activity of X_2 in the solution referred to the pure liquid as the standard state. The change in free energy in transferring one mole of X_2 from the ideal solution to a regular solution is found by subtracting Equation 1 from Equation 4, giving

$$\bar{\mathrm{F}}_2 - \bar{\mathrm{F}}_2^{\mathrm{i}} = RT \ln \frac{a_2}{\mathrm{N}_2} \tag{5}$$

The corresponding entropy change is zero, according to our postulate, except for the volume correction, hence the right-hand member of Equation 5, as a first approximation, is not a function of temperature, and is equal to the partial molal heat of mixing

$$\bar{\mathrm{F}}_2 - \bar{\mathrm{F}}_2^{\mathrm{i}} = \bar{\mathrm{H}}_2 \tag{6}$$

This is, however, a function of composition, the approximate form of which has been derived by Heitler as parabolic. This follows, also, in a less rigid way, from the following simple considerations. The excess of heat content of a mole of regular solution over an ideal solution, $\Delta \mathrm{H}$, may be expected to be greatest in an equimolal mixture, falling off continuously to zero at the ends, as shown in Fig. 2. A simple equation for the course of such a curve is $\Delta F = b\mathrm{N}_1\mathrm{N}_2$, where b is a constant. Since $\mathrm{N}_1 + \mathrm{N}_2 = 1$, either mole fraction could be eliminated, but we prefer to keep the symmetrical form. From the definition of partial molal quantities, it follows that

$$\bar{\mathrm{H}}_2 = b\mathrm{N}_1^2, \text{ and } \bar{\mathrm{H}}_1 = b\mathrm{N}_2^2 \tag{7}$$

Substituting in Equation 5 by the aid of 6, we get

$$RT \ln \frac{a_2}{\mathrm{N}_2} = b\mathrm{N}_1^2 \tag{8}$$

and the same, with subscripts interchanged, for the other component. One may prefer to express a_2/N_2 as γ, the activity coefficient.

The parabolic shape of the exponential term is illustrated by figures in Ref. 2b, pp. 43, 49 and 63.

In cases where the system proves unsymmetrical, we may add higher powers of N_1 and write Equation 8 as

$$\ln \frac{a_2}{N_2} = \frac{1}{RT}(bN_1^2 + cN_1^3 + \ldots\ldots) \tag{9}$$

where b, c, etc., are not functions of temperature, except for the correction due to volume changes, which we shall, in general, neglect. The corresponding equation for the other component then becomes, by the aid of the Duhem equation

$$\ln \frac{a_1}{N_1} = \frac{1}{RT}\left(b + \frac{3}{2}c\right)N_2^2 + cN_2^3 + \ldots\ldots \tag{10}$$

We will examine extensive experimental evidence in support of this formulation, using the simpler Equation 8, so far as possible.

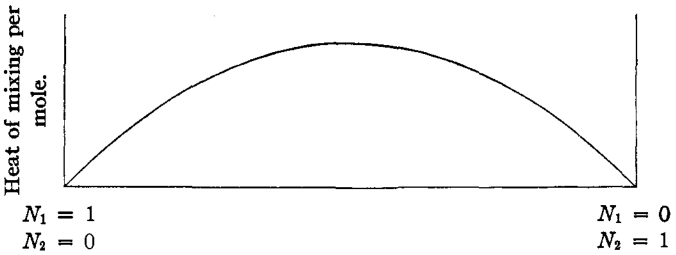

Fig. 2.—Relation between mole fraction and heat of mixing per mole.

Solubilities in Regular Solutions.—We can test Equation 8, first, by the use of solubility data, provided that they cover a considerable range in temperature. Since the activity of the solute, a_2, is the same in its saturated solutions in all solvents, including those in which it obeys Raoult's law, we may write $a_2 = N_2^i$, where N_2^i is the solubility in the ideal solution, which can be calculated by the aid of a knowledge of the melting point and heat of fusion of the solute. Equation 8 thus becomes

$$\ln \frac{N_2^i}{N_2} = \frac{bN_1^2}{RT} \tag{11}$$

which may be written

$$\log \frac{N_2^i}{N_2} = \frac{kN_1^2}{T} \tag{12}$$

where $k = 0.4343b/R$.

We will first apply this equation to data upon the solubility of sulfur in various solvents published by Hildebrand and Jenks,[10] together with

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[10] Hildebrand and Jenks, THIS JOURNAL, **43**, 2172 (1921); *cf.* also ref. 2b, p. 151.

some data by Étard reproduced in the same paper. Table I contains values for 100 N_2, the mole per cent. of sulfur in the solutions, and the corresponding value of k calculated from the solubilities. It will be seen that, in spite of the large variations in N_2 and t, the value of k is remarkably constant. It is true that N_1^2 does not vary greatly from 1, hence the constancy of k does not indicate at all certainly that the system is to be described by Equation 8 rather than Equation 9. It is even conceivable that the constancy of k is only apparent, due to a canceling of a variation with temperature and a more complex variation with N_1. That this should be the case in so many systems is, however, very improbable, or is, at any rate, an effect of a higher order, not seriously interfering with the practical value of the simpler Equation 8. Moreover, we shall see evidence later in which N_1 undergoes large variations with but little effect on k.

Table I

Values of $k = b/2.303R$ for Sulfur Solutions

Solvent	t	0	25	35	45	54	Mean k	
CCl_4	$100N_2$	0.203	0.500	0.697	0.966	1.212		
	k	529	529	528	527	528	528	
C_7H_{16}	$100N_2$	0.0484	0.1413	0.2005	0.274	3.363		
	k	696	688	689	693	694	692	
$C_6H_5CH_3$	$100N_2$	0.324	0.734	0.995	1.330	1.797		
	k	474	479	483	483	480	480	
m-$C_6H_4(CH_3)_2$	$100N_2$	...	0.825	...	1.523	...		
	k	...	466	...	475	...	471	
	t	9	22	40	50	72	95	Mean k
$C_2H_4Br_2$	$100N_2$	1.253	1.77	3.26	4.77	9.42	24.05	
	k	354	331	356	342	339	334	343
	t	8	21	39	65	72	100	
C_6H_6	$100N_2$	0.368	0.557	1.029	2.18	2.79	6.07	
	k	493	498	495	497	487	485	493
	t	24	43	54	61	74	85	
$(C_2H_4Cl)_2S$	$100N_2$	0.922	1.525	2.13	2.72	3.88	5.87	
	k	448	458	456	450	452	(439)	453

There appears to be a slight increase in k with increasing temperature for xylene, and a slight decrease for benzene. This is borne out by the fact that the critical mixing temperature with benzene is lower than that with xylene, indicating a crossing of the solubility curves at higher temperatures. It is noteworthy that this is in harmony with the correction for volume change given in Equation 3. The volume of liquid sulfur at 20° is 135 cc. (extrapolated), while the partial molal volumes of sulfur in the solvents benzene, toluene and xylene at 25° are, respectively, 138.7 cc., 133.4 cc. and 123.6 cc., indicating an expansion in forming the benzene solution and a contraction for the xylene solution.

Further evidence is furnished by the solubility data for violet solutions of iodine, which are taken from a paper by Hildebrand and Jenks.[11] Table II gives, as in Table I, the values of *k* for a series of temperatures. As in the previous table, *k* shows a very satisfactory constancy. In the case of carbon disulfide, the variation in N_1 is sufficient to make a considerable difference between N_1^2 and N_1^3, which are 0.83 and 0.75, respectively, at the highest concentration, showing that the equation with N_1^2 only suffices. It is interesting to state two further facts. The first is that the value of *k* for carbon disulfide falls to 181 at −20° and to 106 at −63°, but in this region the solution becomes brown and is no longer regular. Arsenic trichloride, which likewise gives brown solutions, behaves similarly, giving for *k*, 337 at 96°, 112 at 15° and 93 at 0°. The second fact is that while *k* remains constant for carbon disulfide solutions between 0 and 40°, there is a slight falling off for both heptane and carbon tetrachloride. It is possible, however, to correlate this behavior with the effect of volume changes mentioned earlier. From measurements of the density of these solutions made by Dawson,[12] we have calculated the partial molal volumes of liquid iodine in heptane, carbon tetrachloride and carbon disulfide to be, respectively, 63.9, 65.8 and 61.1 cc., which may be compared with the volume of 58.5 cc. for the extrapolated molal volume of liquid iodine.

TABLE II

SOLUTIONS OF IODINE—VALUES OF *k*

t	−63	−20	0	18	25	30	35	40	50
In C_7H_{16}	...	...	457	...	452	...	448	...	443
In CCl_4	...	...	395	...	386	...	389	...	384
In $CHCl_3$	...	...	302	298	...	299	...	...	...
In CS_2	(106)	(181)	188	...	190	192	...	191	...

Solubilities of naphthalene have been determined by Ward[13] over a wide temperature range. Table III gives random selections from his data for two non-polar solvents, hexane and carbon tetrachloride. Here

TABLE III

SOLUTIONS OF NAPHTHALENE

In Hexane

t	8.7	27.7	45.8	58.4	64.6	Mean *k*
$100N_2$	6.20	13.18	28.7	50.8	66.0	
k	158	155	149	152	146	152

In Carbon Tetrachloride

t	0.4	13.0	19.5	28.2	39.5	64.8	
$100N_2$	11.95	17.8	21.7	28.2	38.9	73.1	
k	35	37	37	38	35	37	37

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[11] Hildebrand and Jenks, THIS JOURNAL, **42**, 2180 (1920); *cf.*, also, ref. 2b, p. 148

[12] Dawson, *J. Chem. Soc.*, **97**, 1046 (1910).

[13] Ward, *J. Phys. Chem.*, **30**, 1316 (1926).

the concentrations of naphthalene become very high, so that the use of a cN_1^3 term would lead to very different results.

The data for stannic iodide obtained by Dorfman and Hildebrand[14] offer further opportunity for testing the equation. Unfortunately, we have no direct value for the heat of fusion of stannic iodide wherewith to calculate the ideal solubility; however, we have two ways of making reasonably good estimates. The first is to assume that all tetrahalides of this type will have about the same entropy of fusion. Table IV gives values of the melting points, T_m, and heats of fusion, ΔH_m, for several such halides, together with their quotient, the entropy of fusion. The values for ΔH_m are from Latimer,[15] except the last, which is from Tolloczko.[16]

TABLE IV

CONSTANTS OF HALIDES

	T_m	ΔH_m	$\Delta H_m/T_m$
Silicon tetrachloride	203.3	1845	9.08
Titanium tetrachloride	248	2233	9.00
Stannic chloride	240	2188	9.11
Stannic bromide	303	2750	9.08
		Mean	9.07

If we assume that $\Delta H_m/T_m$ for stannic iodide is also about 9.07, then, since T_m is 416.5, $\Delta H_m = 3775$. Another estimate may be made by assuming that stannic iodide forms a nearly ideal solution with carbon disulfide, the evidence for which is given in the paper by Dorfman and Hildebrand. The slope of this solubility curve gives $\Delta H_m = 3940$. We shall select in round numbers 3850. Calculating the ideal solubilities from this value, Equation 12 gives the values of k shown in Table V, omitting the figures for mole per cent.

TABLE V

VALUES OF k FOR SOLUTIONS OF STANNIC IODIDE

t, °C.	C_7H_{16}	CCl_4	$CHCl_3$	C_6H_6	$C_6H_4(CH_3)_2$	$C_2H_4Br_2$
10	434	315	305	268	249	177
25	436	317	298	267	249	174
40	440	313	296	261	246	171

It is interesting to note the form of the curve given by Equation 12 in Fig. 1, for several systems, using the mean values of k given in Table V. It can be seen that while the curves are nearly linear for small values of k, illustrated by ethylene bromide, as k becomes larger the curves take on the reversed S-shape noted particularly by Mortimer.[3] Furthermore, as the value of k becomes still larger, as in the case of heptane, there appear three values of log N_2 for a single temperature, two of which are stable

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[14] Dorfman and Hildebrand, THIS JOURNAL, **49**, 729 (1927).

[15] Latimer, THIS JOURNAL, **44**, 90 (1922).

[16] Tolloczko, *Chem. Zentr.*, 1901, I, 989.

corresponding to the appearance of a second liquid phase, all three phases, containing stannic iodide at the same activity. Above this triple point the solid disappears and we are in the region of two liquid phases. The equation thus accounts for the type of system previously encountered with sulfur.[10] This portion of the system will be discussed in the following section. Illustrations similar to the above might be multiplied almost indefinitely, but that is hardly necessary.

Two-Phase Liquid Systems.—Equations 8, 9 and 10 invite application to systems of incompletely miscible liquids, as has been done by Heitler. Part of this section parallels his work, but this is done for the sake of completeness. We have as the condition of equilibrium that the activity of each component is the same in both phases, that is, $a_1' = a_1''$ and $a_2' = a_2''$, where the primes distinguish the two phases. Equation 9 then gives

$$\ln a_2' = \ln N_2' + \frac{b}{RT} N_{1'}^2 = \ln a_2'' + \ln N_2'' + \frac{b}{RT} N_{1''}^2$$

from which, since $N_{1'} + N_{2'} = 1$, and $N_{1''} + N_{2''} = 1$, we get

$$\ln \frac{1 - N_{1'}}{1 - N_{1''}} = \frac{b}{RT} (N_{1''}^2 - N_{1'}^2)$$

Equation 9 for component 2 is identical except for the exchange of subscripts. The two equations are simultaneous when $\frac{1 - N_1'}{1 - N_1''} = \frac{1 - N_2'}{1 - N_2''} = \frac{N_1'}{N_1''}$, when $N_1'' = N_2' = 1 - N_1'$. Substituting this in the above gives

$$\ln \frac{1 - N_{1'}}{N_{1'}} = \frac{b}{RT} (1 - 2N_{1'}) \tag{13}$$

which can be used for calculating the composition of the liquid phases when b is known, or *vice versa*. The former calculation, unfortunately, requires the method of successive approximations, so it is best to calculate T from given values of b and N. This equation becomes indeterminate at the critical mixing temperature, T_c, so that it is best to relate T_c to N in the following way.

At the critical mixing point, we have the conditions that[17] $\left(\frac{\partial a}{\partial N}\right)_T = 0$ and $\left(\frac{\partial^2 a}{\partial N^2}\right)_T = 0$. Applying these to Equation 8 gives $RT_c = 2bN_1N_2$, and $N_1 = N_2 = 0.5$, whence

$$2RT_c = b \text{ or } T_c = 1.15\,k \tag{14}$$

The same methods can be applied to the unsymmetrical Equation 9, giving, in place of Equation 13, two simultaneous equations requiring a graphic solution, and in place of Equation 14 two equations giving b and c in terms of T_c and the critical composition, from which calculation can be made in either direction. The discussion will be confined, however, to the simpler symmetrical case given by Equations 13 and 14.

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[17] Ref. 2b, p. 55.

The solubility of stannic iodide in heptane between 10 and 40° gives $k = 437$. If we assume that there is no entropy of expansion and that k remains constant to the region of two liquid phases, above about 125°, we would have from Equation 13 the liquid solubility curve shown in Fig. 1, with a critical mixing temperature of 230°, instead of the experimentally determined value of 137°.[18] This discrepancy would be reduced somewhat, 10°, by the use of the unsymmetrical equation, and the uncertainty regarding the heat of fusion of stannic iodide permits of some variation between the two figures. We have noted, however, some tendency of k to diminish with rising temperature, and have seen in Equation 3 a reason why it should. It is evident, therefore, that an extrapolation of over 100° from solid solubility to critical mixing temperature would be extraordinarily sensitive to slight changes in k. If we calculate k from the critical mixing temperature by Equation 14, we get 356, while around 25° we found 437. The drift may be expressed by using $k = 643 - 0.7T$. If we use 356 as constant to calculate the liquid solubility curve, it is especially significant that, although this gives the correct critical temperature, the descending branches are too near together, while if we use the slightly variable k, the spread of the curve is nearly satisfactory, bringing the liquid and solid curves into approximate agreement. The values of k in Table V indicate that instead of the variation being linear with T, a more rapid variation exists; this would satisfy also the experimental points for the liquid-liquid system.

Mr. A. Wachter, at the author's request, has made a determination of the solubility of stannic iodide in *iso*-octane (2,2,4-trimethylpentane) at 25°, getting for the mole per cent. of stannic iodide 0.3399 and 0.3441, mean 0.342. This gives a value of k of 503. The critical solution temperature for the two liquid phase system is 195°, from which we can calculate k from Equation 14 to be 407. If the change of k with T is assumed to be linear, we can write $k = 671 - 0.565T$, which very nearly accounts for the experimental points, although here again a slightly more rapid variation with T would be required to give perfect agreement.

Sulfur solubility curves suggest an application of these same equations and a number of calculations have been made with results agreeing about as well as with stannic iodide. They are not here reproduced, however, since the presence of S_μ in the liquid adds a considerable complication.

The E.m.f. of Concentration Cells.—The measurements made in this Laboratory by Taylor[19] on the e.m.f. of molten alloy concentration cells and their temperature coefficients offer a peculiarly direct check on the existence of regular solutions of the sort conforming to our definition. A cell consisting of a pure metal and its alloy with a nobler metal, as

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[18] Dice and Hildebrand, THIS JOURNAL, **50**, 3023 (1928).

[19] N. W. Taylor, THIS JOURNAL, **45**, 2865 (1923); *cf.* also ref. 2b, Chap. XVI.

electrodes, separated by an electrolyte containing the ion of the baser metal, has an e.m.f. given by the equation

$$\mathrm{E} = \frac{RT}{\mathrm{NF}} \ln a_2 \tag{15}$$

Combining this with Equation 9 gives

$$\mathrm{E} = \frac{RT}{\mathrm{NF}} \ln \mathrm{N}_2 + b\mathrm{N}_1^2 + c\mathrm{N}_1^3 + \ldots\ldots \tag{16}$$

The temperature coefficient of the cell is then

$$\frac{\mathrm{dE}}{\mathrm{d}T} = \frac{R}{\mathrm{NF}} \ln \mathrm{N}_2 \tag{17}$$

that is, the temperature coefficient is the same as for an ideal solution of the same composition. That various alloys obey this relation remarkably well is shown in Table VI. This is all the more striking because only the first alloy conforms to Equation 8, the other two requiring the more complicated Equation 9. What difference there is is in the direction expected, that is, the observed values are greater.

TABLE VI

TEMPERATURE COEFFICIENTS OF E.M.F. OF ALLOY CONCENTRATION CELLS, IN MILLIVOLTS PER DEGREE

Alloy, Cd-Sn

Mole per cent. of Cd		8.35	25.8	56.9	63.0
$\frac{\mathrm{dE}}{\mathrm{d}T}$	(obs.)	0.0113	0.067	0.030	0.026
	(calcd.)	.0107	.058	.025	.020

Alloy, Cd-Pb

Mole per cent. of Cd		12.3	26.9	50.9
$\frac{\mathrm{dE}}{\mathrm{d}T}$	(obs.)	0.095	0.063	0.036
	(calcd.)	.090	.057	.026

Alloy, Zn-Cd

Mole per cent. of Zn		15.0	25.1	34.4	69.1
$\frac{\mathrm{dE}}{\mathrm{d}T}$	(obs.)	0.079	0.061	0.047	0.016
	(calcd.)	.082	.060	.046	.016

Not all such solutions are regular. The alloys of zinc and tin, and also of cadmium and bismuth, investigated by the same author, are irregular. This is not surprising in view of the departure of each, especially the latter, from the usual type of relation between log (a/N) and N.

Other Relations. 1. The Heat of Solution.—When the temperature of a saturated solution of X_2 is changed, saturation is maintained by having the change in fugacity of the solid phase, with the temperature only, equal to the change in fugacity of the same substance in solution, due to changes in both temperature and composition. Formally expressed this gives

$$\mathrm{d} \ln f_2^s = \mathrm{d} \ln f_2 = \left(\frac{\partial \ln f_2}{\partial T}\right)_{\mathrm{N}} \mathrm{d}T + \left(\frac{\partial \ln f_2}{\partial \ln \mathrm{N}_2}\right)_T \mathrm{d} \ln \mathrm{N}_2$$

But

$$\frac{\mathrm{d}\ln f_2^{\mathrm{s}}}{\mathrm{d}T} = \frac{\mathrm{H}_2^* - \mathrm{H}_2^{\mathrm{s}}}{RT^2} \text{ and } \frac{\ln f_2}{T} = \frac{\mathrm{H}_2^* - \overline{\mathrm{H}}_2}{RT^2}$$

where H_2^* and $\mathrm{H}_2^{\mathrm{s}}$ are the heat contents of the vapor and solid, respectively, and $\overline{\mathrm{H}}_2$ is the partial molal heat of solution; we can write, therefore

$$\frac{\overline{\mathrm{H}}_2 - \mathrm{H}_2^{\mathrm{s}}}{RT^2} = \left(\frac{\partial \ln f_2}{\partial \ln \mathrm{N}_2}\right)_T \frac{\mathrm{d}\ln \mathrm{N}_2}{\mathrm{d}T} \tag{18}$$

For regular solutions, the partial differential can be obtained from Equations 8 or 9. Using the latter, and remembering that $f_2/\overset{\circ}{f_2} = a_2$, where $\overset{\circ}{f_2}$ is the fugacity of the pure liquid, we get

$$\left(\frac{\partial \ln f_2}{\partial \ln \mathrm{N}_2}\right)_T = 1 - \frac{2b\,\mathrm{N}_1\mathrm{N}_2}{RT} \tag{19}$$

where $\mathrm{N}_1 + \mathrm{N}_2 = 1$. This equation expresses the deviation of a system from either Henry's law, $f_2 = l\mathrm{N}_2$, where l is a constant, or from Raoult's law, where the constant becomes $\overset{\circ}{f_2}$. It occurs frequently in the derivations of thermodynamic equations. It should be noted that $(\partial \ln f_2/\partial \ln \mathrm{N}_2)_T$ approaches unity, first, when b approaches zero, that is, when Raoult's law is obeyed throughout the entire range of composition; second, when either N_1 or N_2 approaches zero, that is, when the solution is very dilute in either component. Only under these conditions, therefore, does the slope of the solubility curve, log N_2 *vs.* $1/T$, give directly the heat of solution. The equation for the heat of solution results from the substitution of Equation 19 in 18, giving

$$\frac{\overline{\mathrm{H}}_2 - \mathrm{H}_2^{\mathrm{s}}}{RT} = \left(1 - \frac{2b\mathrm{N}_1\mathrm{N}_2}{RT}\right) \frac{\mathrm{d}\ln \mathrm{N}_2}{\mathrm{d}T} \tag{20}$$

In view of the form of the curve for large deviations from ideal shown in Fig. 1, it is evident, as stated earlier, that a straight line drawn through the melting point gives a very erroneous value for the heat of solution. On the other hand, the tangent to the curve when log N is small gives the heat of solution rather accurately.

2. **The Heat of Mixing.**—In deriving Equation 8, the assumption was made that the heat of mixing is given by an equation such as 7. It may, of course, prove necessary in dealing accurately with some regular systems to add higher powers of N. Data upon heats of mixing are very meager, but the evidence is favorable for the approximate equality of free energy and heat of mixing. Taylor[19] pointed this out in connection with his measurements, and more recently Butler[20] has given a more quantitative calculation based upon these same measurements.

It is noteworthy that Equation 16 becomes equivalent to the well known Cady[21] equation, in view of the identification of the terms $b\mathrm{N}_1^2 + c\mathrm{N}_1^3 + .$

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[20] Butler, THIS JOURNAL, **47**, 117 (1925).

[21] Cady, *J. phys. Chem.*, **2**, 551 (1898).

with the heat effect. The failure of this equation to give a more complete agreement with the experimental data we attribute to its application to irregular systems, and to the use of concentration instead of mole fraction to express composition.

3. Volume Change on Mixing.—Differentiating Equation 8 with respect to the pressure, P, upon the liquid phase at constant N and T gives

$$\left(\frac{\partial \ln a_2}{\partial P}\right)_{\mathrm{N},T} = \frac{\mathrm{N}_1^2}{RT}\frac{\mathrm{d}b}{\mathrm{d}P}$$

(the second differential is not written as a partial since b is practically independent of N and T) but this is equal[22] also to $(\bar{\mathrm{v}}_2 - \mathrm{v}_2)/RT$, where v_2 is the molal volume and $\bar{\mathrm{v}}_2$ the partial molal volume. We therefore write

$$\bar{\mathrm{v}}_2 - \mathrm{v}_2 = \mathrm{N}_1^2\frac{\mathrm{d}b}{\mathrm{d}P} \tag{21}$$

This harmonizes with a relation discovered by Biron[23] that the expansion of two liquids upon mixing to form a mole of mixture is

$$\Delta V = (\bar{\mathrm{v}}_1 - \mathrm{v}_1)\mathrm{N}_1 + (\bar{\mathrm{v}}_2 - \mathrm{v}_2)\mathrm{N}_2 = K\mathrm{N}_1\mathrm{N}_2$$

where K is $\mathrm{d}b/\mathrm{d}P$. It also gives justification for the relation discovered some years ago by the writer[24]

$$\ln\frac{a_2}{\mathrm{N}_2} = K'(\bar{\mathrm{v}}_2 - \mathrm{v}_2)$$

where K' is an empirical constant. Comparing this with Equation 8 gives $K'(\bar{\mathrm{v}}_2 - \mathrm{v}_2) = b\mathrm{N}_1^2$. Combining with Equation 21 gives $K'\mathrm{N}_1^2(\mathrm{d}b/\mathrm{d}P) = b\mathrm{N}_1^2$ or $(d \ln b/\mathrm{d}P) = (1/K)$, that is, K' is a constant for a given system calculable from b and its change with pressure.

4. The Gibbs adsorption equation is

$$\left(\frac{\partial\gamma}{\partial \ln f_2}\right) = -u_2RT \tag{22}$$

where γ is the surface tension of a solution, and u_2 the amount of adsorbed solute per cm.^{2} of surface. The partial differential signifies constant surface. We may write the mathematical identity

$$\left(\frac{\partial\gamma}{\partial \ln \mathrm{N}_2}\right) = \left(\frac{\partial\gamma}{\partial \ln f_2}\right)\left(\frac{\partial \ln f_2}{\partial \ln \mathrm{N}_2}\right)$$

The first differential on the right is given by Equation 22, and the second by Equation 19, giving

$$\frac{\partial\gamma}{\partial \ln \mathrm{N}_2} = -u_2RT\left(1 - \frac{b\mathrm{N}_1\mathrm{N}_2}{RT}\right) \tag{23}$$

This equation is usually written with the concentration in place of the mole fraction and without the term in parenthesis. The omission of this correcting term may be serious, for it is those solutions which deviate

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[22] Ref. 2b, p. 61.

[23] Biron, *J. Russ. Phys.-Chem. Soc.*, **44**, 1264 (1912).

[24] *Cf.* ref. 2b, pp. 61–65.

most strongly from Raoult's law (that is, which show a large value for b) that show large adsorption. Of course this is compensated by the fact that when the solution is very dilute, $N_2 = 0$, and the correcting factor approaches unity. The usual neglect of the deviation from the ideal solution is undoubtedly partly responsible for the lack of agreement often found when testing the Gibbs equation in the simplified form. Equation 23 offers a simple means for making the correction for regular solutions.

Evaluation of the Constant.—The application of the various equations given in this paper requires, of course, the evaluation of the constant b, or, when necessary, additional constants in Equation 9. The numerous solubility data already discussed by the author show clearly that the deviations from ideality, now expressed by the magnitude of b or k, are rather closely determined by the difference in internal pressure of the two components. There is evidence, however, that this is not the only factor and efforts are being made to formulate the exact relation between b and internal pressure. This study demands certain experimental data that we are now endeavoring to secure, after which it is hoped that a report upon the subject may be made.

Meanwhile, it would be possible to give an improved substitute for Mortimer's table of solubility "factors" by constructing a table of internal pressure functions that would give values of k by difference. This is too long a task for inclusion with this paper, but anyone confronted with problems involving regular solutions may make rather good estimates of the constant upon an additive basis by the aid of existing data involving other systems. Again, where a single experimental point involving the activity of a system is at hand, its general behavior can be calculated.

In plotting activity data, it has been pointed out[25] that log (a_2/N_2) (or log γ_2, where γ_2 is the activity coefficient), when plotted against mole fraction, gives a simple expression for deviations from ideality. It is becoming rather general practice, even with aqueous solutions, which are far from regular, to plot log γ. The present treatment suggests that where temperature changes are involved the most advantageous function to plot would be T log γ_2 against N_1^2.

Summary

1. Certain solutions of a common solute in various solvents which give families of solubility curves, and from which chemical effects and association changes are absent, are designated as regular solutions. They are defined as solutions in which no change in entropy, except for the small entropy of expansion, is involved in the transfer of a constituent from it to an ideal solution of the same concentration.

2. An equation given by van Laar upon the basis of the van der Waals

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[25] Ref. 2b, Chap. V.

equation of state, and recently derived by Heitler upon different assumptions, is applied to a large number of solutions with very satisfactory results.

3. The equation is applied to the calculation of other properties dependent upon activity, including the e.m.f. of concentration cells, the heat of solution of solids, the expansion on mixing and the Gibbs adsorption equation.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

PHOTOCHEMICAL STUDIES. VIII. THE PHOTOCHEMICAL DECOMPOSITION OF MALONIC ACID BOTH IN THE PRESENCE AND ABSENCE OF URANYL SULFATE

BY WILLIS CONWAY PIERCE, A. LEVITON AND W. ALBERT NOYES, JR.

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The photochemical decompositions of many organic acids have been studied in some detail. Of these none has received more attention than the decomposition of oxalic acid. It is not necessary, at the present time, to summarize all of the work that has been done.[1] Earlier work on the nature of the products formed has been shown by Allmand and Reeve[2] not to agree with the composition of the products formed during the early stages of the reaction. These authors show that the principal reaction consists in the formation of formic acid and carbon dioxide. Since the former may be decomposed photochemically, other products would result with long exposures. They found, further, that the quantum efficiency varied with wave length, the highest value obtained being 1/100 at 265 mμ. Anderson and Robinson[3] report an average yield of 1/1392 molecule per quantum for radiation from a quartz mercury arc lamp.

The photochemical decomposition of oxalic acid sensitized by uranyl salts has also received considerable attention. Measurements of quantum efficiency of the sensitized reaction are somewhat at variance, but the best evidence indicates that the value is approximately one.[4,5] Büchi,[4] from a consideration of his determinations of the rate of photochemical decomposition of oxalic acid in solutions of varying concentration and with various amounts of uranyl sulfate, has come to the conclusion that a complex molecule, or a molecule of uranyl oxalate, is the photosensitive mole-

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[1] Kistiakowsky, "Photochemical Processes," The Chemical Catalog Co., Inc., New York, 1928, pp. 146, 229, has given a partial summary of recent work on this reaction.

[2] Allmand and Reeve, *J. Chem. Soc.*, 129, 2834 (1926).

[3] Anderson and Robinson, THIS JOURNAL, 47, 718 (1925).

[4] Büchi, *Z. physik. Chem.*, 111, 269 (1924).

[5] Bowen and Watts, *J. Chem. Soc.*, 127, 1607 (1925).