EQUILIBRIA IN NON-ELECTROLYTE SOLUTIONS IN RELATION TO THE VAPOR PRESSURES AND DENSITIES OF THE COMPONENTS

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The method to be outlined is an outgrowth of the treatment of gaseous systems used in the laboratory of the Massachusetts Institute of Technology. It may be regarded also as a quantitative development of the treatment of Hildebrand, although it disagrees with his ideas in some important details, or as a method of freeing the van Laar treatment from the inadequacies of the van der Waals equation. In this paper is presented the simplest first approximation. Though its success is not astounding, it is hoped that the presentation will show some of the reasons for the limitations of so simple a theory, as well as indicate some of the possibilities of improvement. It will also serve as a comparative review of the different theories.

The general method is to make all variations of composition[1] and temperature at such low pressures that the perfect gas laws are applicable, and to make the pressure variations at constant temperature and composition (1). There is no obvious method of extending to liquids the treatment of free energy itself, but progress may be made through the energy. We may express the energy of a mole of liquid as $U_l = U_0 - u$. U_0 is the molal energy of the gas at zero pressure, and we need not consider it further for it is a function only of the temperature, independent of the pressure, the state of aggregation, and of the composition unless there is a chemical change which persists at zero pressure.

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[1] "Composition" is used in the stoichiometric sense of ratio of the components, disregarding any chemical reaction which may occur.

We shall call u the cohesive energy. At sufficiently low vapor pressures it is equal to $L - RT$. For those substances for which the computation can be made, that is, those for which the constants of the Beattie-Bridgeman equation of state (2) have been determined, u is about 1 per cent greater than $L - RT$ at the boiling point, the difference varying from 0.8 per cent for ammonia to 1.3 per cent for argon. So, at the boiling point or below, we may take $L - RT$ as the cohesive energy.

For most substances the heat of evaporation has not been determined, but we may make use of an extension of Hildebrand's amendment (3) of Trouton's law. We may express the vapor pressure as

$$\log \frac{p}{T} = \frac{B - A/T}{1 + 0.05(B - A/T)} \qquad L - RT = \frac{2.303\ RA}{[1 + 0.05(B - A/T)]^2}$$

By the Trouton-Hildebrand law, B has the same value for all normal liquids, and the single specific constant, A, may be determined from a single vapor pressure or boiling point measurement. Taking B as 4.7 for normal liquids, as 5.0 for esters, aldehydes and ketones, and as 5.7 for water and the alcohols, the agreement is excellent for pressures from 3 to 2000 mm. The few available measurements indicate that the agreement is not so good for lower pressures. Since the measurements of boiling points are generally more accurate than those of vapor pressure, we shall use them to measure A and u. We shall be interested in the cohesive energy per unit volume or cohesive energy density, u/V. Since the measurements of volume are generally made at 20°, we shall use u and u/V calculated for that temperature.

Our first problem is to determine the shape of the energy composition curve for liquid mixtures. We shall attack it by considering an ideal solution—one with zero change in volume and energy on mixing. The forces acting on a given molecule must be independent of the composition, but what is the relation between the forces acting on a molecule of the first species to those acting on one of the second? We might expect that two substances should form an ideal solution, not when their cohesive energies per mole are equal, but when they have the same energy density. This corresponds to the facts.

For non-ideal solutions also we shall neglect the change in volume, and we shall consider only the case in which the interaction between any pair of molecules is independent of the composition. We may then split the cohesive energy of a mole of the mixture in the following way

$$u_x = \frac{a_{11}V_1^2x_1^2 + 2\,a_{12}V_1V_2x_1x_2 + a_{22}V_2^2\,x_2^2}{V_1x_1 + V_2x_2}$$

where the a's are constants. For the pure components $u_1 = a_{11}V_1$ and $u_2 = a_{22}V_2$, so that a_{11} and a_{22} are the cohesive energy densities of the components. The energy increase of mixing is

$$\Delta\,U = u_1x_1 + u_2x_2 - u_x = (a_{11} - 2\,a_{12} + a_{22})\;V_1V_2\,\frac{x_1x_2}{V_1x_1 + V_2x_2}$$

$$= A_{12}V_1V_2\,\frac{x_1x_2}{V_1x_1 + V_2x_2}$$

From our assumption of additivity of volumes, it follows immediately that $\Delta H = \Delta U$. The next step is more daring, although it or its equivalent is made in every physical theory of liquid solutions, and some of the justifications are more entertaining than convincing. We shall satisfy ourselves with Hildebrand's statement (4) that when "orienting and chemical effects are absent and the distributions and orientations are random," the entropy of mixing is the same as for an ideal solution. Then

$$\Delta\,F = \Delta\,U + x_1RT\ln x_1 + x_2RT\ln x_2$$

and

$$\mu_1 - \mu_{10} = RT\ln a_1 = RT\ln x_1 + A_{12}V_1V_2^2\left(\frac{x_2}{V_1x_1 + V_2x_2}\right)^2$$

The expressions are simpler using volumes as units rather than moles, when the energy increase per unit volume of the mixture is A_{12} multiplied by the product of the volume fractions of the components, and the chemical potential per unit volume of one component is equal to that in an ideal solution plus A_{12} multiplied by the square of the volume fraction of the other component. The application to vapor pressures, solubility of solids, and miscibility of liquids follows by the standard thermodynamic methods.

To determine the behavior of a mixture from the properties of its components, it is necessary to make one more assumption, regarding the value of a_{12}. We will assume that the cohesive energy behaves as the gravitational energy between point masses, or the electrostatic energy between point charges, and that

$$a_{12} = \sqrt{a_{11}a_{22}}.$$

Then

$$A_{12} = (\sqrt{a_{11}} - \sqrt{a_{22}})^2,$$

which is twice the difference between the arithmetic and the geometric mean of a_{11} and a_{22}. The cohesive energy densities must differ by 20 per cent of their mean, about the difference for benzene and carbon bisulfide, if A_{12} is to be 1 per cent of the mean. The accuracy of our assumption must then be very great if we are to predict the behavior of mixtures to a good approximation.

This assumption implies homogeneous molecules. Given a pair like naphthalene and acetone, which have nearly the same energy densities while one is homogeneous and the other has a much stronger field in one part than another, we should not expect them to give ideal solutions. They should be described more accurately by a method analogous to that of Langmuir.

Hildebrand (5) uses the "internal pressure," $\left(\frac{\partial U}{\partial V}\right)_T$ as a criterion instead of $\frac{u}{V}$, although he suggests the latter as an approximate measure of the former. For a van der Waals fluid, the two are identical. Our derivation indicates that, when they differ, it is the latter which is important rather than the former.

Hildebrand (6) and Mortimer (7) also state that the deviations should be at least approximately proportional to the difference between the internal pressures, which is always larger than the square of the difference between their square roots, and is very much larger when the difference is small, so that nearly ideal solutions should be much rarer by the Hildebrand-Mortimer hypothesis.

Heitler (8), by assuming that the liquid mixture corresponds to a cubic crystal lattice, obtains an expression similar to ours, except that mole fractions replace volume fractions. His basic assumption is equivalent to assuming equal molal volumes of the components, and his results should be limited to this case, for which his equation is the same as ours.

Langmuir's equation (9) may be put in the same form as ours by replacing energy density by energy per unit surface, and volume fraction by surface fraction. It involves the assumption that the surface of contact between two surfaces is proportional to the product of the surfaces, which seems to me very doubtful; Langmuir makes the further assumption that the surface of any molecule is proportional to the two-thirds power of its volume, which seems to me certainly wrong.

van Laar's equation (10) is the same as ours except that van der Waals' b_1 replaces V_1, and van der Waals' a_1/b_1 replaces a_{11}.

Dolezalek's theory (11) may be expressed as the assumption that $a_{12} = (a_1 + a_2)/2$ unless there is chemical action. In this case it makes no difference whether the composition be expressed as mole, surface, or volume fraction. The long polemic between van Laar and Dolezalek and their adherents is then based on the small difference between the arithmetic and geometric means. Dolezalek is in the peculiar position of denying that a force is physical unless it behaves as no known physical force behaves. Of course there are more pragmatic grounds for not accepting Dolezalek's theory as general (12).

We have to test, then, four consequences of the theory: the shape of the curve for the change of heat content or free energy on mixing; the equality of these two functions; the equality of each to the value calculated from the cohesive energy densities; and the use of the extended Trouton-Hildebrand law to compute these energy densities. In general the last two cannot be tested independently.

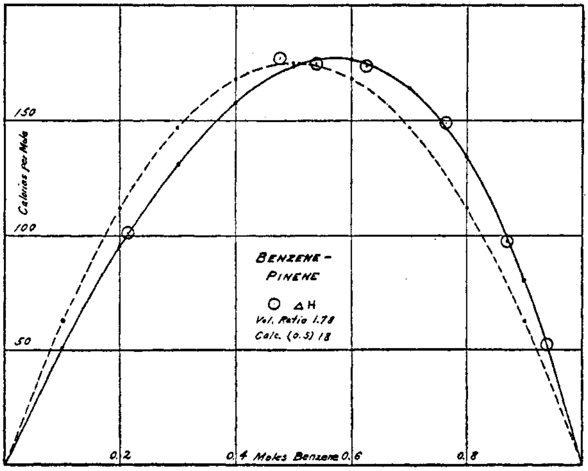

Fig. 1. Heat of Mixing and Volume
Benzene-Pinene

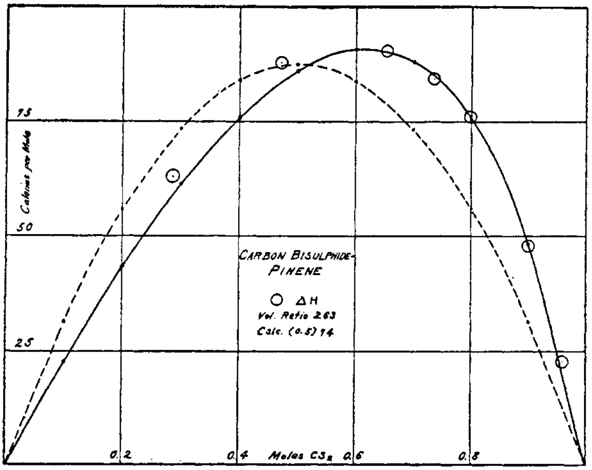

Fig. 2. Heat of Mixing and Volume
Carbon Bisulfide-Pinene

The shape of the curve is shown better by the measurements of heat content (14), because they appear to be more reliable than those of free energy, and because there happen to be some for

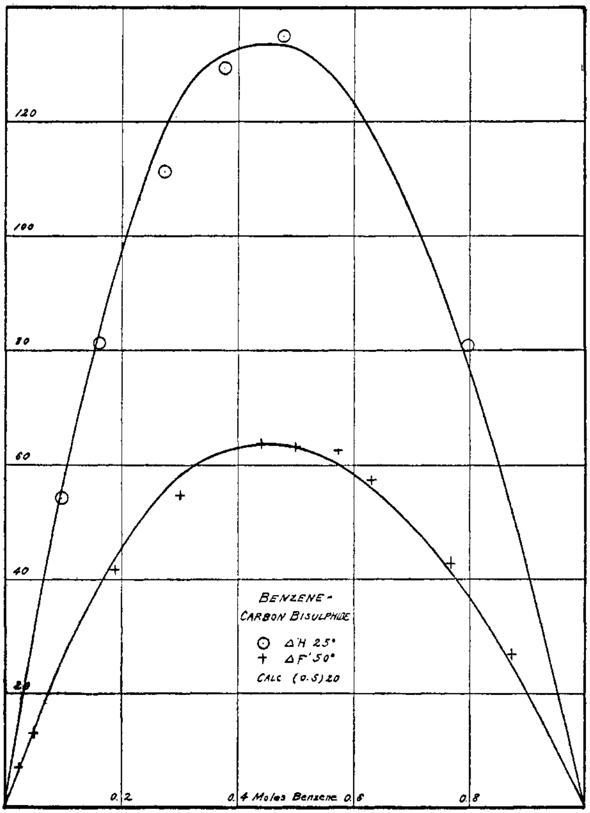

FIG. 3. HEAT AND FREE ENERGY OF MIXING BENZENE-CARBON BISULFIDE

$$\Delta F' = \Delta F - x_1 RT \ln x_1 - x_2 RT \ln x_2$$

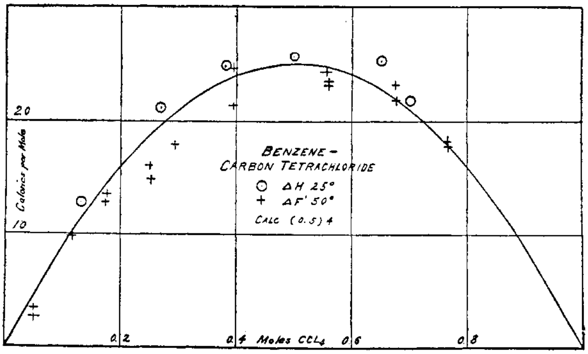

FIG. 4. HEAT AND FREE ENERGY OF MIXING BENZENE-CARBON TETRACHLORIDE

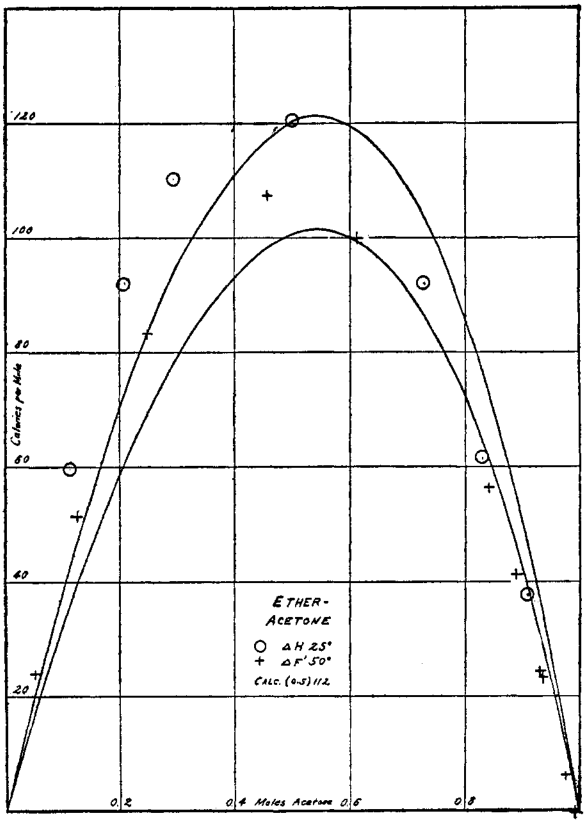

FIG. 5. HEAT AND FREE ENERGY OF MIXING ETHER-ACETONE

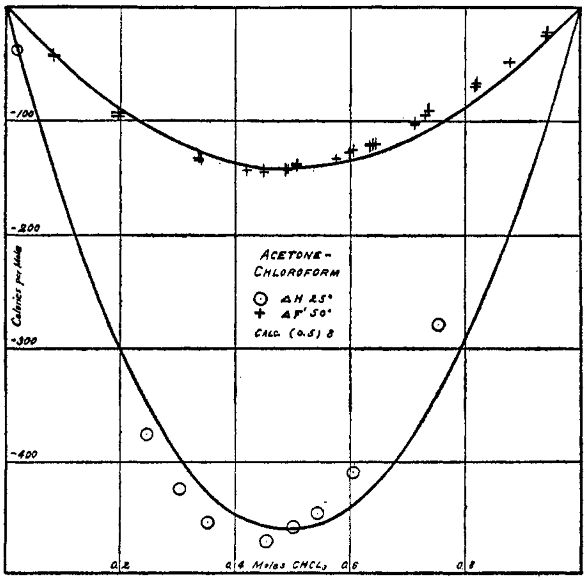

FIG. 6. HEAT AND FREE ENERGY OF MIXING ACETONE-CHLOROFORM

substances which would be expected to behave normally and which have widely different volumes. The evidence in figures 1 and 2 is clearly in favor of the volume fraction rather than the mole fraction. The calculated value is good in one case, and poor in the other.

Figures 3 to 6 show ΔH and $\Delta F' = \Delta F - x_1 RT \ln x_1 - x_2 RT \ln x_2$ for all the systems for which Hirobe (14) found large heats of mixing and for which the change in free energy can be computed (from vapor pressure measurements) (15). For benzene-carbon tetrachloride and ether-acetone ΔH and $\Delta F'$ are nearly equal. The calculated value agrees well in the first case, but less well in the second. For benzene-carbon bisulfide and chloroform-acetone, the discrepancy is large. In each case $\Delta F'$ is nearer to the calculated value than it is to ΔH.

TABLE 1

Solubility of naphthalene at 20°

SOLVENT	u/V	V	SOLUBILITY		log a/x	
			Measured	Calculated	Measured	Calculated minus measured
	calories per cc.					
Naphthalene (ideal)	101.5	123	0.261	0.261	0.000	
Chlorobenzene	93.4	101.63	0.256	0.256	0.008	0.000
Benzene	83.9	88.89	0.241	0.240	0.034	0.002
Toluene	81.0	106.31	0.224	0.228	0.064	−0.006
Carbon tetrachloride	76.1	96.45	0.205	0.210	0.104	−0.010
Hexane	54.2	130.47	0.090	0.067	0.462	0.128
Aniline	154.5	91.06	0.130	0.110	0.302	0.073
Nitrobenzene	143.1	101.95	0.243	0.158	0.030	0.187
Acetone	97.0	73.34	0.183	0.260	0.153	−0.152
n-Butyl alcohol	123.7	91.45	0.0495	0.232	0.721	−0.671
Methyl alcohol	213.7	40.44	0.0180	0.00075	1.161	1.380
Acetic acid	172.6	57.23	0.0456	0.0540	0.767	−0.083

Lest these results give the impression that the usefulness of the theory is extremely limited, let us look in table 1 at the measured and computed solubilities of naphthalene at 20°. The measured values are interpolated from the measurements of Ward (16).

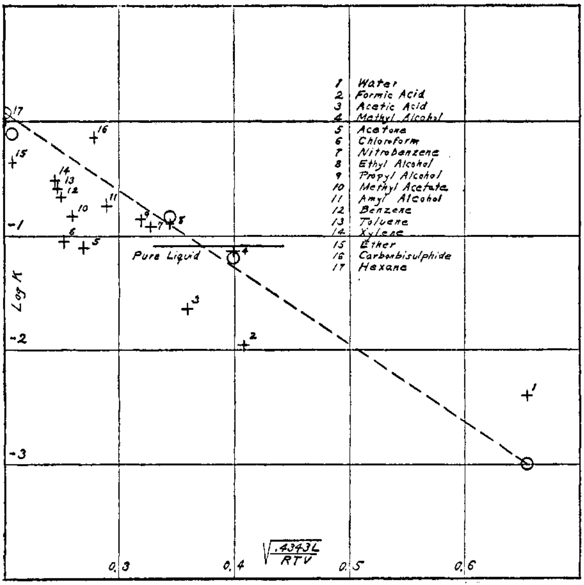

FIG. 7. KETO-ENOL ISOMERISM IN ACETOACETIC ESTER
VERY DILUTE SOLUTIONS

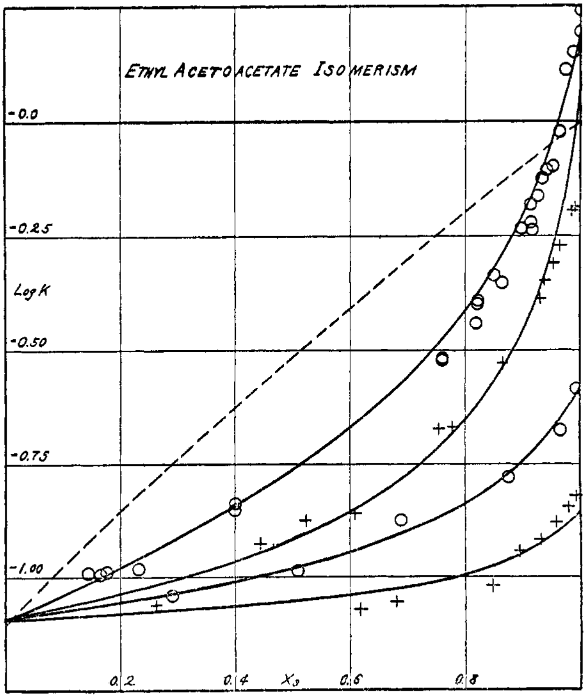

FIG. 8. KETO-ENOL ISOMERISM IN ACETOACETIC ESTER
EFFECT OF CONCENTRATION

Solvents (in order of decreasing intercepts): hexane, carbon bisulfide, benzene, ethyl alcohol.

The cohesive energy density of naphthalene itself is computed from the heats of fusion and sublimation; those of the solvents are computed by the equations given. For the non-polar solvents the agreement is as good as could be expected, and for aniline it is not much worse. For the more polar solvents the discrepancies are large, except for acetic acid, where the agreement is probably a coincidence.

In our treatment of solutions we are inclined to forget that for a chemist the most important equilibria are chemical. In the simplest case, isomerism, only two molecular species are involved and the volumes may be taken as equal. The equations for three component mixtures will not be presented. At infinite dilution, log K should be a linear function of the square root of the energy density of the solvent. The intercept on the zero axis is log K for the perfect gas system, and the slope is proportional to the volume of the reactants and to the difference in the square roots of their energy densities. From these quantities and the reaction constant for the solvent-free system, it is possible to calculate the constant for a solution of any composition. If the energy densities of the reactants are known, one measurement of the equilibrium constant is sufficient to determine all.

The only system which has been measured in a large variety of solvents is acetoacetic ester. Both forms should be highly polar, as are many of the solvents. The theory is doubtless insufficiently developed to fit this case. In figure 7 the circles represent the measurements of Hantsch (17) on very dilute solutions, and fall on a straight line better than would be expected. The crosses represent the measurements of Kurt Meyer, generally on 3 per cent solutions, and the discrepancies are large. It might be noted that the Hildebrand-Mortimer law would lead to log K at infinite dilution independent of the solvent.

Figure 8 shows the change of constant with composition for four solvents. The broken line is that calculated for hexane, and the agreement is very poor. The full lines are calculated on the more general theory which permits a_{12} to be independent of a_{11} and a_{22}. To compute these curves we need the value of the constant for no solvent, one point on each curve, and one other constant, which is the same for all the curves. The reason why they appear not to belong to the same family is that they are plotted against the mole fraction rather than the volume fraction. Here the agreement is excellent. The only difficulty is that the values of the constants require that the vapor pressure of the enol form be more than a hundred thousand times that of the keto form. The experimental evidence indicates that the ratio is of the order of a hundred, and the larger value seems out of the question. Even the ratio of a hundred is quite surprising, for we might expect the enol form to have the smaller pressure. So this system, which appears simple on paper, may be much too severe a test of the theory. It is possible that the a factors vary with the composition, though more experimental information is necessary to establish such a variation, or it may be, as suggested by Knorr (18), that there is equilibrium between three forms instead of two.

SUMMARY

The properties of liquid mixtures are calculated from the following assumptions (of which only the first is general).

- The energy of a liquid may be split into two parts: the energy under perfect gas conditions, which is additive and may be ignored; and a second part which is nearly equal to the energy of liquefaction, and which may be calculated approximately from the boiling point.
- The energy of mixing of two liquids depends upon their difference in cohesive energy density.
- The interaction between two molecules is independent of the composition.
- The interaction between unit volumes of two different species is the geometric mean of those for the two species taken separately.
- The entropy of mixing is the same as for perfect gas conditions.

The theory is compared with other theories of liquid solutions, and with some measurements of the heat of mixing, of equilibria with the gaseous phase and with one solid component, and of the chemical equilibrium between isomers.

BIBLIOGRAPHY

(1) Gillespie: J. Am. Chem. Soc. **47,** 305 (1925); **48,** 28 (1926).
Beattie: Phys. Rev. **31,** 680 (1928).
(2) Beattie and Bridgeman: Proc. Am. Acad. Arts Sci. **63,** 229 (1928); Z. Physik **62,** 95 (1930).
(3) Hildebrand: J. Am. Chem. Soc. **37,** 970 (1915).
(4) Hildebrand: ibid. **51,** 69 (1929).
(5) Hildebrand: Solubility, pp. 69, 99. Chemical Catalog Co., New York (1924).
(6) Hildebrand: J. Am. Chem. Soc. **51,** 79 (1929).
(7) Mortimer: ibid. **44,** 1416 (1922); **45,** 633 (1923).
(8) Heitler: Ann. Physik [4] **80,** 630 (1926).
(9) Langmuir: Third Colloid Symposium Monograph, p. 3. Chemical Catalog Co., New York (1925).
(10) van Laar: Z. physik. Chem. **72,** 723 (1910); **83,** 599 (1913).
(11) Dolezalek: ibid. **64,** 727 (1908).
(12) Hildebrand: Solubility, p. 83. Chemical Catalog Co., New York (1924).
(13) Hirobe: J. Faculty Sci. Imp. Univ. Tokyo **1,** 155 (1925).
(14) Sameshima: ibid. **1,** 63 (1925) for benzene-carbon bisulfide and ether-acetone.
Zawidski: Z. physik. Chem. **35,** 129 (1900) for benzene-carbon tetrachloride and acetone-chloroform.
(15) Ward: J. Phys. Chem. **30,** 1316 (1926).
(16) Hantsch: Ber. **43,** 3049 (1910); **44,** 1771 (1911).
(17) Meyer: Ann. **380,** 226 (1911); Ber. **47,** 826 (1914).
(18) Knorr, Rothe and Averbeck: Ber. **44,** 1138 (1911).