TABLE I

EXPERIMENTALLY DETERMINED CONSTANTS FOR CHLOROFORM AND METHANOL USED IN MIXTURES COMPARED WITH CONSTANTS IN "INTERNATIONAL CRITICAL TABLES"

Temperature 25°

Constant	Chloroform Exptl.	Chloroform "I. C. T."	Methanol Exptl.	Methanol "I. C. T."
Density, g./ml.	1.4793	1.4795	0.7909	0.7866
Surf. tens., dynes	26.48	26.46	22.33	22.18
Fluidity, rec. poises	173	173.6	181	181
Refr. index, n_D	1.4424	1.4426	1.3290	1.3289
Vap. pressure, mm.	196	199	126	123
Compress., beta/atm.	107.1	106.4	133.3	[a]

[a] No low pressure compressibility data are given. The chloroform value is for a range of 1 to 6 megabaryes.

The compressibility–volume per cent. composition diagram and the corresponding surface tension diagram (Fig. 2) were nearly ideal, though their slight deviations were in strict antibatic relation to each other. The maximum compressibility deviation from the ideal is plus 2% and that of the surface tension is minus 4%.

Fluidity and vapor pressure (Fig. 3) showed wide deviations from the normal, and with no apparent correlation with any other property investigated. Vapor pressure is shown in its relation to mole per cent. composition, in accordance with Raoult's law. All other properties are shown in relation to volume per cent. composition as simple additive properties.

Index of refraction (Fig. 4) follows strictly a straight line function of volume per cent. composition, so that it is an accurate means of determining the composition of mixtures of chloroform and methanol from the indices of the pure components.

Density also follows a straight line function very closely (Fig. 4). The maximum deviation from the ideal was found to be 0.0009.

Summary

1. In the system, chloroform–methanol, close correlation was found between surface tension and compressibility, both being nearly ideal functions of composition.

2. Vapor pressure data deviated widely from the ideal. The system does not conform to Worley's rule of the antibatic relation between surface tension and vapor pressure.

MANHATTAN, KANSAS RECEIVED MARCH 11, 1935

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

Solubility. XIV. Experimental Tests of a General Equation for Solubility

BY JOEL H. HILDEBRAND

The writer, with the collaboration of Mr. S. E. Wood,[1] derived the equation

$$\mathrm{E}' = \frac{2\pi N^2}{\mathrm{V}} \int^{\infty} \varphi W r^2 dr \qquad (1)$$

for the potential energy of an assemblage of molecules of the same species and the equation

$$E' = \frac{2\pi N_2}{V}\left[n_1{}^2 \int \varphi_{11} W_{11} r^2 dr + n_2{}^2 \int \varphi_{22} W_{22} r^2 \mathrm{d}r + 2n_1 n_2 \int \varphi_{12} W_{12} r^2 \mathrm{d}r\right] \qquad (2)$$

for the potential energy of a mixture of n_1 moles of one species with n_2 moles of another. In these equations, N is the Avogadro number; v, the molal volume; V, the volume of the mixture; the φ's are the potential functions between pairs of molecules whose species are denoted by the subscripts; the W's are the "probability functions" expressing the structure of the assemblage, as used by Prins,[2] and by Debye and Menke.[3]

These equations are perfectly general, regardless of the type of molecule or molecular field; indeed, Equation 1 reduces to familiar forms, both in the case of a gas, when W becomes unity immediately above the collision diameter, and in the case of the solid, where W is discontinuous. For the liquid state, in the absence of more exact knowledge concerning the probability functions and the repulsive potentials, we are forced at present to make certain approximations, as set forth in the original publication. These include non-polar character and spherical symmetry for the molecular species considered, the identity of the probability functions when expressed in terms of molecular diameters, the neglect of the repul-

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(1) J. H. Hildebrand and S. E. Wood, *J. Chem. Physics*, **1**, 817 (1933); *cf.* also, G. Scatchard, *Chem. Rev.*, **8**, 321 (1931); THIS JOURNAL, **56**, 995 (1934); J. H. Hildebrand, *ibid.*, **56**, 996 (1934).

(2) J. A. Prins, *Physica*, **6**, 315 (1926); *Z. Physik*, **56**, 617 (1929); *Physik. Z.*, **30**, 525 (1929); F. Zernike and J. A. Prins, *Z. Physik*, **41**, 184 (1927).

(3) P. Debye and H. Menke, "Fortschritte der Röntgen-forschung," Akademische Verlagsges., Leipzig, 1931, Chap. I; H. Menke, *Physik. Z.*, **33**, 593 (1932); *cf.* also O. Kratky, *ibid.*, **34**, 482 (1933).

sive potentials and of the small changes of volume on mixing, and the assumption that the attractive potential constant for the unlike molecules is the geometric mean between those for the like molecules. According to the London theory, all that can be said is that $k_{12} \leqq (k_{11}\, k_{22})^{1/2}$, and it is impossible to tell, theoretically, how far the relation departs from equality; hence any solubility formula derived from Equation 2 by assuming the equality will represent an upper limit of solubility, and experiment alone will suffice to reveal the seriousness of the departure. We also assume that E' and E' are sufficiently independent of temperature that we can set free energy equal to total energy.

Applying these approximations gives the formula

$$RT \ln \frac{a_2}{\mathrm{N}_2} = \mathrm{V}_2 \left(\frac{\mathrm{N}_1\mathrm{V}_1}{\mathrm{N}_1\mathrm{V}_1 + \mathrm{N}_2\mathrm{V}_2}\right)^2 \left[\left(\frac{\Delta\mathrm{E}_1}{\mathrm{V}_1}\right)^{1/2} - \left(\frac{\Delta\mathrm{E}_2}{\mathrm{V}_2}\right)^{1/2}\right]^2 \tag{3}$$

where a_2 is the activity of component 2 of the solution referred to the pure liquid as the standard state (we shall adhere to the convention of Lewis and Randall of regarding the "solvent" as component 1); N_1 and N_2 are the respective mole fractions of the two components in the pure liquid form; the V's are the molal volumes and the $\Delta\mathrm{E}$'s the molal energies of vaporization. The right-hand member of the equation contains only properties of the pure components. Where the solution is in equilibrium with pure solid 2, we can write

$$\ln a_2 = \ln \mathrm{N}_2^i = -\frac{\Delta\mathrm{H}}{R}\left(\frac{1}{T} - \frac{1}{T_\mathrm{m}}\right) \tag{4}$$

where N_2^i is the ideal solubility, $\Delta\mathrm{H}$ is the heat of fusion of the solid and T_m its melting point.

In cases where $\mathrm{V}_1 \cong \mathrm{V}_2$, also when N_2 is small, the "volume-fraction" in Equation 3 reduces to the mole fraction, N_1; again, since the other factors in the right-hand member vary but little with temperature, we find it adequate for many cases to write the equation

$$RT \ln a_2/\mathrm{N}_2 = b\mathrm{N}_1^2 \tag{5}$$

whose applicability has been extensively shown.[4] Here b is a constant, approximately equal to $\mathrm{V}_2[(\Delta\mathrm{E}_1/\mathrm{V}_1)^{1/2} - (\Delta\mathrm{E}_2/\mathrm{V}_2)^{1/2}]^2$.

The accuracy of the more fundamental Equation 3 has been thus far tested only in a few cases, and a more general and vigorous test is here undertaken.

The solubilities of iodine[5] are particularly suitable for our purpose because, first, the ease with which iodine can be titrated has enhanced the accuracy of the experimental data, second, the number of solvents used has been considerable, third, the irregular cases presenting solvation can readily be excluded by the color test, and, fourth, the high value of the "internal pressure," $\Delta\mathrm{E}_2/\mathrm{V}_2$, leads to unusually large deviations from the ideal solubility.

Equation 3 has been tested by substituting therein the experimental values of solubility, volumes of the pure liquid components and the energy of vaporization of the solvents and calculating therefrom the value of $(\Delta\mathrm{E}_2/\mathrm{V}_2)^{1/2}$ for iodine. The magnitude of this quantity serves as a sort of "energy level" in determining deviations from Raoult's law. If the equation holds, these values should be uniform for a given substance. The figures in the last column of Table I show this to be the case to an extent which is altogether astonishing, in view of the approximations that have been made; moreover, the mean of these values, excluding the one for ethylene bromide, whose curve is slightly irregular, agrees within the limit of error with the value calculated for pure iodine by the aid of its vapor pressure curve. The agreement is the more surprising in view of the extrapolation necessary in most cases to get $\Delta\mathrm{E}$ at 25°, the presence in the list of solvents of several whose molecules are not strictly spherical and three possessing dipole moment. These last we would be justified in excluding, for dipoles may be expected to deviate from the simpler behaviors postulated in deriving Equation 3. That they fall in line is so much to the good. It is evident that by substituting the value 13.6 for $(\Delta\mathrm{E}_2/\mathrm{V}_2)^{1/2}$ in Equation 3 we could calculate the solubilities of iodine in the several solvents in very close agreement with experiment.

The $\Delta\mathrm{E}$ values have been calculated in most cases from the direct calorimetric values of $\Delta\mathrm{H}$ obtained by J. H. Mathews.[6] The value for bromoform has been estimated from its boiling point by the aid of the "Hildebrand Rule."[7] Other values in the table are principally from the "International Critical Tables."

Solutions of stannic iodide[8] are represented in

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(4) J. H. Hildebrand, THIS JOURNAL, **51**, 66 (1929).

(5) G. R. Negishi, L. H. Donnally and J. H. Hildebrand, *ibid.*, **55**, 4793 (1933). The value for hexane is from J. H. Hildebrand, E. T. Ellefson and C. W. Beebe, *ibid.*, **39**, 2301 (1917).

(6) J. H. Mathews, *ibid.*, **48**, 562 (1926).

(7) J. H. Hildebrand, *ibid.*, **37**, 970 (1915); **40**, 45 (1918).

(8) M. E. Dorfman and J. H. Hildebrand, *ibid.*, **49**, 729 (1927). Its solubility in silicon tetrachloride has just been determined in this Laboratory by Mr. G. R. Negishi.

TABLE I

IODINE SOLUTIONS AT 25°. v_2 = 59.0 cc. 100 N_2 = 21.2

Solvent	Dipole moment × 10^{18} e. s. u.	Mole % iodine	ΔE_1, cal./mole	v_1, cc.	$(\Delta E_1/v_1)^{1/2}$	$(\Delta E_2/v_2)^{1/2}$
n-Hexane	0	0.456	7270	131.3	7.44	13.67
Silicon tetrachloride	0	.499	6610	115.3	7.57	13.71
i-Octane[a]	0	.592	9340	166.0	7.50	13.51
n-Heptane	0	.679	8200	147.6	7.45	13.35
Carbon tetrachloride	0	1.147	7080	97.1	8.54	13.99
Titanium tetrachloride	0	2.15	8360	110.5	8.70	13.52
Chloroform	1.1	2.28	6430	80.7	8.93	13.71
Carbon disulfide	0	5.76	6040	60.7	9.98	13.82
Bromoform	1.0	6.16	8980	87.8	10.1	13.78
Ethylene bromide	1.0	7.82	8100	86.5	9.86	(13.03)
					Mean	13.67
					Calculated from vapor pressure	13.6

[a] 2,2,4-Trimethylpentane.

Table II. The fluctuations of the calculated values of $(\Delta E_2/v_2)^{1/2}$ for stannic iodide, given in the last column, are again small, in spite of the presence in the list of five solvents with dipole moment. Mr. G. R. Negishi, at the author's request, has just determined the vapor pressure curve of stannic iodide, the complete results to be published later, from which we have calculated the heat of vaporization to be 13,670 cal. per mol. From this we get ΔE = 13,100 cal. per mole at 25° (the Hildebrand rule gives 13,600) and $(\Delta E/v)^{1/2}$ = 9.32. This is considerably smaller than the mean value of 11.44 from the solubility data and suggests that here $k_{12} < (k_{11}K_{22})^{1/2}$; however, the absence of a direct value for the heat of fusion lends some uncertainty to the value for the ideal solubility used in the calculations. If the discrepancy should be substantiated, it may prove more satisfactory to construct tables of $(\Delta E/v)^{1/2}$ for various substances on the basis of solubility data rather than direct energies of vaporization.

TABLE II

STANNIC IODIDE SOLUTIONS AT 25°. v_2 = 151 cc.

Solvent	Dipole moment × 10^{18} e. s. u.	Mole % of SnI_4	$(\Delta E/v)^{1/2}$ Solvent	$(\Delta E/v)^{1/2}$ SnI_4
$SiCl_4$	0	0.382	7.57	11.42
n-C_7H_{16}	0	.553	7.45	11.11
$(C_2H_5)_2O$	1.1	.690	7.45	11.00
CCl_4	0	1.459	8.54	11.69
$CHCl_3$	1.1	1.692	8.93	11.97
C_6H_6	0	2.181	9.00	11.92
$C_6H_5CH_3$	.4	2.507	8.64	11.43
m-$C_6H_4(CH_3)_2$	.3	2.558	8.10	10.88
CH_2Br-CH_2Br	1.0	4.714	9.68	12.07
CS_2	0	14.64	9.98	10.89
Ideal	0	16.2	..	...
			Mean	11.44

Sulfur solutions[9] are represented in Table III.

TABLE III

SULFUR SOLUTIONS AT 25°. v_2 = 135 cc.

Solvent	Dipole moment × 10^{18} e. s. u.	Mole % of sulfur	$(\Delta E/v)^{1/2}$ Solvent	$(\Delta E/v)^{1/2}$ Sulfur
n-C_7H_{16}	0	0.141	7.45	12.3
$(C_2H_5)_2O$	1.1	.295	7.45	12.0
CH_2Cl-CH_2Cl	1.2	.321	9.08	13.5
CCl_4	0	.500	8.54	13.2
$CHCl_3$	1.1	.570	8.93	12.9
C_6H_6	0	.641	9.00	12.9
$C_6H_5CH_3$	0.4	.735	8.64	13.6
m-$C_6H_4(CH_3)_2$	0.3	.825	8.10	11.8
C_6H_5I	1.3	1.66	9.41	12.9
CH_2BrCH_2Br	1.0	1.95	9.68	13.5
CS_2	0	13.8	..	..
Ideal	0	28.2		
			Mean	12.8
			Calcd. from vapor pressure	11.7

Here the fluctuations from the mean value of 12.8 for $(\Delta E/v_2)^{1/2}$ are greater than in the previous cases, but they show no systematic drift over the large range of solubility represented, and the inclusion of a large proportion of polar solvents seems to produce no very serious effect. Here again, the value of $(\Delta E_2/v_2)^{1/2}$ from the vapor pressure is somewhat less, although the presence of S_μ in the liquid may disturb the calculation of ΔE for pure S_λ.

Solutions of phosphorus present a particularly interesting case. We have data for only three solvents and these give evidence of inferior accuracy in their fluctuation from smooth curves as shown in the plot of log N_2 *vs.* $1/T$ in Fig. 1; however they present an enormous range in solubility and include the supercooled liquid–liquid curve for carbon disulfide.

The ideal solubility of phosphorus falls off but slowly as the temperature is lowered, due to its small heat of fusion. The latter changes rapidly with the temperature, but the effect of this varia-

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[9] Hildebrand and Jenks, THIS JOURNAL, 43, 2172 (1921).

tion upon our calculations is so small in comparison with the effect of the fluctuations in the data and the other uncertainties involved that we have considered the heat of fusion constant at 625 cal./mole from a consideration of the old and not very concordant data of Pettersson[10] and Person.[11] We find it necessary in this case to compare solubility data at different temperatures; this we do by utilizing the relation,[12] $\Delta E/V = a/V^2$, where a is a constant. Table IV gives the results of these calculations for representative solubility data. The formula is very sensitive in the region represented by solid phosphorus in carbon disulfide, and $[N_1V_1/(N_1V_1 + N_2V_2)]^2$ varies rapidly at the large values of N_2 represented at 0° and above, nevertheless the constancy of $a^{1/2}$ under such wide variations in solubility is all or, indeed, more than could be expected.

TABLE IV

PHOSPHORUS SOLUTIONS

t	V_2[e]	V_1	100 N_2	$a_1^{1/2}/V_1$	$a_2^{1/2}/V_2$	$a_2^{1/2}$
		Carbon disulfide, solid[a] P_4				
−10	69.2	58.2	21.9	10.18	14.38	990
− 7.5	69.3	58.4	25.5	10.16	14.36	990
− 5.0	69.4	58.5	30.7	10.15	14.37	995
− 3.5	69.4	58.6	34.5	10.14	14.59	1010
− 3.2	69.4	58.6	60.7	10.14	14.61	1010
− 2.5	69.5	58.7	64.7	10.14	14.69	1015
0	69.6	58.8	72.7	10.13	14.69	1020
5	69.7	59.2	79.4	10.11	14.67	1020
10	69.9	59.6	84.4	10.08	14.60	1020
		Carbon disulfide, liquid[b] P_4				
− 6		Obsd.	40	10.11	14.19	985
		Calcd.	44.5			
			Benzene[c]			
10	69.9	87.7	1.487	9.16	14.96	1050
25	70.4	89.3	2.28	9.00	14.67	1040
			Ether[d]			
10	69.9	102.0	0.505	7.64	14.12	990
25	70.4	104.5	.823	7.45	13.81	975
					Mean	1010
			Calcd. from vapor pressure			980

[a] Cohen and Inouye, *Z. physik. Chem.*, **72**, 411 (1910). [b] J. H. Hildebrand and T. F. Buehrer, THIS JOURNAL, **42**, 2213 (1920). [c] Giran, *J. phys. radium*, **2**, 208, 809 (1903). [d] Christomanos, *Z. anorg. Chem.*, **45**, 132 (1905). [e] Pisati and de Franchis, *Gazz. chim. ital.*, **4**, 497 (1874).

To obtain the energy of vaporization of phosphorus for comparison the vapor pressure measurements of Smits and Bokhorst[13] have been used. These authors have calculated that $\Delta H = 16{,}380 - 7.106\ T$, which gives, at $T = 298.1$, $\Delta H = 14{,}250$ cal., $\Delta E = 13{,}660$, $(\Delta E/V)^{1/2} = 13.95$ and $a^{1/2} = 980$, which is in excellent agreement with the values from solubility shown in Table IV.

The inclusion of the data for liquid phosphorus is particularly significant. At the critical mixing temperature of two liquids we have the conditions[14] that $da_2/dN_2 = 0$ and $d^2a_2/dN_2^2 = 0$. Performing these operations upon Equation 3 yields the equations

$$RT_c = \frac{2N_1N_2V_1^2V_2^2}{(N_1V_1 + N_2V_2)^3}\left[\frac{a_1^{1/2}}{V_1} - \frac{a_2^{1/2}}{V_2}\right]^2 \qquad (6)$$

and

$$N_1 = ((V_1^2 + V_2^2 - V_1V_2)^{1/2} - V_2)/(V_2 - V_1) \qquad (7)$$

at the critical point. Substituting $V_2 = 69.4$ cc. and $V_1 = 58.5$ cc. in Equation 7 gives $N_1 = 0.555$ and $N_2 = 0.445$. This agrees with the maximum of the experimental curve as closely as can be determined. Substituting these values and also $T_c = 257$ in Equation 6 gives the value of $a^{1/2}$

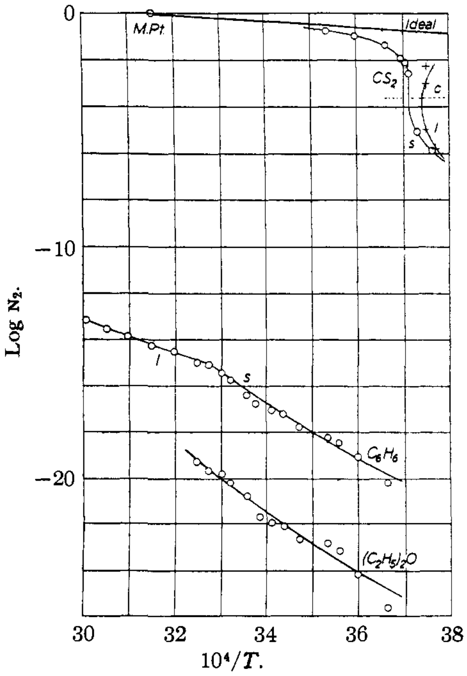

Fig. 1.—Solubility of phosphorus.

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(10) Pettersson, *J. prakt. Chem.*, **24**, 129 (1881).

(11) Person, *Compt. rend.*, **23**, 163, 336 (1846); *Ann. chim. phys.*, **21**, 295 (1847).

(12) J. H. Hildebrand, *Phys. Rev.*, **34**, 984 (1929).

(13) Smits and Bokhorst, *Z. physik. Chem.*, **91**, 249 (1916).

(14) J. H. Hildebrand, THIS JOURNAL, **51**, 66 (1929).

entered in Table IV, which agrees sufficiently well with the values from the other solutions.

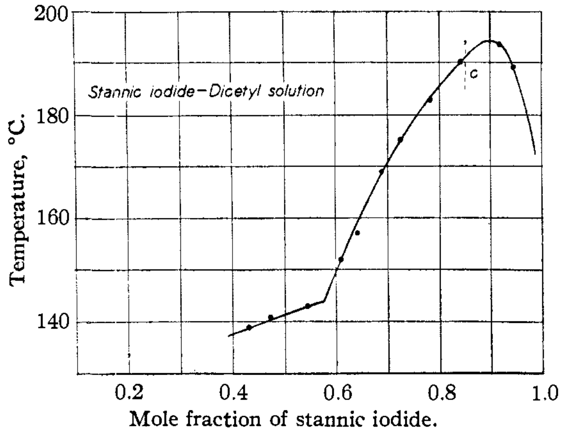

Fig. 2.—Stannic iodide–dicetyl solution.

A far more searching test of Equation 7 is furnished by the liquid–liquid system, stannic iodide with dicetyl, $n\text{-}C_{32}H_{66}$, determined by my former assistant, Mr. A. Wachter, and hitherto unpublished. The experimental points are given in Table V and plotted in Fig. 2. We have here a pair of non-polar liquids with molal volumes so different that the critical mixing temperature is at about 90 mole per cent. of stannic iodide, instead of near 50 per cent., as with most systems. We may doubt whether dicetyl is sufficiently spherical to fit our postulates, but we may try Equation 7 nevertheless. The molal volumes of stannic iodide and dicetyl at the critical solution temperature are, respectively, 151 and 563 cc. These, substituted in the equation, give 85 mole per cent. of stannic iodide instead of the experimental 90 per cent., a very gratifying degree of agreement.

TABLE V

SOLUBILITY OF STANNIC IODIDE IN DICETYL

	G. SnI_4/g. $C_{32}H_{66}$	Mole fraction	t, °C.
Solid	0.847	0.429	139
Solid	1.007	.472	141
Solid	1.353	.546	143
Liquid	1.753	.609	152
Liquid	2.009	.641	157
Liquid	2.510	.690	169
Liquid	3.005	.727	175
Liquid	4.072	.783	183
Liquid	6.026	.842	190
Liquid	12.33	.916	193.5
Liquid	18.105	.942	189

It may be of interest to trace the connection between varying deviations from ideality and the relative shapes and positions of the solubility curves for the solute in its solid and liquid forms. For this purpose we may use the simpler Equation 5 with values of $a_2 = \mathrm{N}_2^i$ identical with those for phosphorus. The equation then becomes

$$T(0.430 + \log 1/\mathrm{N}_2) = k\mathrm{N}_1^2 + 136 \qquad (8)$$

Figure 3 gives plots of this equation for three values of k, 207, 233 and 270. The positions of the liquid–liquid curves for the same values of k are also indicated on the plot. It will be seen that the liquid–liquid system could be realized only by great supercooling when $k = 207$. For $k = 233$ the liquid curve touches the solid curve, which is vertical at this point. For $k = 270$, the liquid system is stable through a large range of composition intersecting the s-shaped, and in part unrealizable, solid curve. The curve for benzene in Fig. 1 shows the break where the solid and liquid branches intersect, corresponding in type to this curve in Fig. 3.

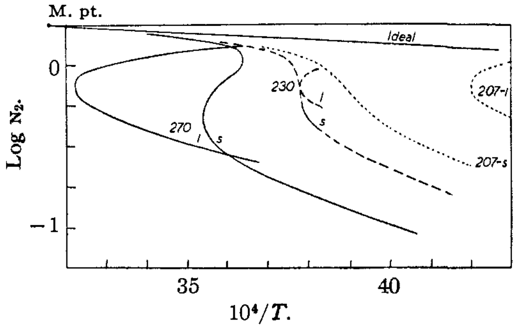

Fig. 3.—Relation between liquid–liquid and solid–liquid solubility curves.

The data presented in this paper seem to the author to constitute impressive evidence of the usefulness of Equation 3 as a first approximation for the quantitative calculation of solubilities, and invite experimental studies of the factors contained in Equations 1 and 2 in order that a higher degree of accuracy may be obtained.

To apply Equation 3 practically for calculating the solubility of a solid, one must, of course, know its melting point and heat of fusion, so as to calculate N_2^i from Equation 4. Its molal volume in the liquid state can be extrapolated to the desired temperature from densities obtained above the melting point. The heats of vaporization and the molal volumes of both substances in the liquid state permit the calculation of $(\Delta E/V)^{1/2}$ for each. The calculation of N_2 by Equation 3 can then proceed, but is best accomplished by the method of successive approximations, since the equation cannot be solved directly for N_2. By plotting both the left- and right-hand members against arbitrary values of N_2, their intersection can usually be determined from three or four substitutions.

Summary

1. An equation for the calculation of the solubility from the properties of the pure components has been tested for a large number of solutions of iodine, stannic iodide, sulfur and phosphorus and found to hold even better than could be expected in view of the approximations involved. Departure from spherical symmetry and presence of dipole moment do not necessarily vitiate the calculations.

2. The uncertainty on the basis of the London theory regarding the relation between the attraction constants of like and unlike molecules, $k_{12} \leqq (k_{11} k_{22})^{1/2}$, seems to be greatly diminished by experimental indications that the inequality is small.

BERKELEY, CALIF.

RECEIVED MARCH 12, 1935

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 47]

The Equilibrium of the Reaction between Ferric Ion and Silver

BY WALTER C. SCHUMB AND SUMNER B. SWEETSER

The equilibrium of the reaction $Fe^{+++} + Ag \rightleftarrows Fe^{++} + Ag^{+}$ is one of the comparatively few reactions in which at equilibrium the concentration of reactants and products can be determined by ordinary methods of chemical analysis. It is of interest also because the determination of the equilibrium constant affords an accurate method for obtaining the molal ferric–ferrous electrode potential and may also be of use in obtaining the activity of ferric ion when the activities of the ferrous and silver ions are known more accurately. The commonly accepted value of the equilibrium constant is 0.128, which was obtained by Noyes and Brann.[1] Later determinations of the ferric–ferrous electrode potential by Popoff and Kunz,[2] and Popoff, Fleharty and Hanson[3] also afford a means of calculating the equilibrium constant of the above reaction.

Noyes and Brann used nitrate as the acid constituent and plotted the calculated values of K against total nitrate concentration. However, their points were widely scattered so that the result of the extrapolation to zero concentration was somewhat uncertain. The present investigation was undertaken with the purpose of obtaining a more accurate value of the equilibrium constant by selecting conditions which would give points on a smooth curve and by carrying on the reaction over a wider range of concentration in order to lessen the amount of extrapolation necessary.

Reagents.—Perchlorates were used in this work in preference to the nitrates because a higher concentration of perchloric than of nitric acid could be used without attacking the powdered silver. Ferric perchlorate was prepared by dissolving hydrated ferric sulfate in water, precipitating with a slight excess of ammonium hydroxide, washing the precipitate repeatedly by decantation, and then digesting the ferric hydroxide with reagent quality 60% perchloric acid. The solution was decanted from the undissolved hydroxide, concentrated, and violet crystals of $Fe(ClO_4)_3 \cdot 6H_2O$ obtained, which were repeatedly recrystallized. The hexahydrate rather than the nonahydrate was employed, as the latter tended to be soft and pasty and retained a large amount of solution.

Finely divided silver was prepared by slowly adding a hot solution of ammonium formate to a hot 35% solution of silver nitrate. The ammonium formate was obtained by the addition of 50% formic acid to concentrated ammonium hydroxide until the solution reacted acid to litmus.

Reagent grade chemicals were used for all analytical work.

Methods of Analysis.—Tenth normal permanganate solution was standardized against Bureau of Standards ingot iron (99.85% Fe).[4] The equivalence point of the titration was obtained potentiometrically using a bright platinum gauze electrode and a saturated calomel electrode. Popoff and Kunz[2] found that failure to remove the precipitated mercurous chloride formed in the oxidation of the excess stannous chloride caused an error in the titration. However, this error was only about one part per thousand so was neglected in this work.

The iron content of ferric perchlorate solutions was determined by the same method as that used to standardize the permanganate, employing perchloric acid in place of hydrochloric acid.

Popoff, Fleharty and Hanson[3] determined the quantity of free acid in ferric perchlorate solution by adding an ex-

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[1] Noyes and Brann, THIS JOURNAL, **34**, 1016 (1912).

[2] Popoff and Kunz, *ibid.*, **51**, 382 (1929).

[3] Popoff, Fleharty and Hanson, *ibid.*, **53**, 1643 (1931).

[4] W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., 1929, p. 305.