TABLE III

	Mixtures	λ	$-\Delta\Lambda$
0.5 *N*	$CdI_2 + KI$	100.26	14.7
1 *N*	$CdI_2 + KI$	99.65	16.0
2 *N*	$CdI_2 + KI$	99.52	16.8
2 *N*	$CdBr_2 + KBr$	96.21	12.07
1 *N*	$CdBr_2 + KBr$	95.92	9.75
2 *N*	$CdCl_2 + KCl$	91.43	8.17
1 *N*	$CdCl_2 + KCl$	89.26	5.66
4 *N*	$ZnI_2 + KI$	70.92	6.84
6 *N*	$ZnI_2 + KI$	67.80	8.33
1 *N*	$CdSO_4 + K_2SO_4$	53.26	3.30
2 *N*	$ZnI_2 + KI$	50.87	2.86
1 *N*	$ZnI_2 + KI$	39.23	1.47
4 *N*	$MgCl_2 + NaCl$	17.85	0.73
5 *N*	$MgCl_2 + NaCl$	17.44	.65
2 *N*	$MgCl_2 + NaCl$	16.36	.27
1 *N*	$MgCl_2 + NaCl$	14.51	.51
9 *N*	$MgCl_2 + LiCl$	5.39	.30
5 *N*	$MgCl_2 + LiCl$	5.28	.11
2 *N*	$CdSO_4 + MgSO_4$	3.34	.03
4 *N*	$CdSO_4 + MgSO_4$	0.57	.14

for several mixtures of cadmium and zinc halides with the corresponding potassium salt, the equivalent conductivity is smaller than the contribution deduced from the mixture rule for the potassium salt alone.

Summary

1. Specific and equivalent conductivities of eight groups of binary mixtures of 2-1, 2-2 and 1-1 electrolytes with a common anion have been measured at total equivalent concentrations ranging from 0.5 to 9 *N*.

2. It is pointed out that there is a marked parallelism between the difference of the conductivities of the pure salts and the maximum departure from the mixture rule observed with the mixtures of the same total concentration.

STANFORD UNIVERSITY, CALIF.

RECEIVED NOVEMBER 3, 1936

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

Solubility. XV. The Solubility of Liquid and Solid Stannic Iodide in Silicon Tetrachloride

BY J. H. HILDEBRAND AND G. R. NEGISHI

Stannic iodide and silicon tetrachloride differ considerably in molecular size and very greatly in internal pressure or molecular field strength, so much so, indeed, that not only is the solubility of solid stannic iodide at 25° only 3% of the ideal solubility, but also in the liquid state they form two liquid phases below 140°. This system is particularly adapted to an investigation of the critical mixing phenomenon in its simplest aspects, because it is free from the complications introduced by the presence of electric dipoles or hydrogen bonds such as are present in most known cases of incomplete liquid miscibility. We have turned to it, therefore, in an effort to throw light upon the question of the extent to which the randomness of thermal mixing is affected by the tendency toward molecular clustering due to differences in the strength of intermolecular forces.[1]

The substances were prepared and purified by methods previously described.[2] The solubility of solid stannic iodide from 0 to 40° was determined by analysis of a solution saturated by shaking in a thermostat, as in earlier investigations in this Laboratory. The bulb containing a sample of saturated solution was placed, for analysis, in a thick-walled glass-stoppered 750-cc. flask containing 100 to 150 cc. of water. The air was displaced by carbon dioxide to prevent oxidation of iodide ion. The bulb was then broken and the flask shaken till the reaction was complete. The contents were transferred to a 500-cc. separatory funnel, about 25 cc. of carbon tetrachloride and a little concentrated tartaric acid solution added and the iodide ion oxidized to iodine by permanganate.[3] The iodine was extracted, separated and titrated with thiosulfate. The method proved rapid, simple and accurate. Three determinations of solubility were made at each temperature, 0.2, 25 and 40°, and the largest deviation from the mean was 0.5%.

The determinations at higher temperatures were made by the "synthetic method." The stannic iodide was introduced into each tube in a dry box, the air in the tube displaced by strongly dried and purified nitrogen and the stannic iodide melted into a single mass. The tube was then evacuated and a capillary seal broken, permitting the distillation of silicon chloride into it, after which it was sealed. The tube was weighed, both empty and after each substance had been added.

The solution temperature for each tube was determined in an oil-bath contained in a one-gallon (4-liter) unsilvered Dewar flask and heated electrically. Near the solution temperature the rate of heating was slow, 0.01° or less per

---

(1) *Cf.* (a) E. A. Guggenheim, *Proc. Roy. Soc.* (London), **148A**, 304 (1935); (b) J. H. Hildebrand, *Chem. Rev.*, **18**, 315 (1936); *Trans. Faraday Soc.*, in press, "Symposium on the Liquid State" September, 1936.

(2) G. R. Negishi, THIS JOURNAL, **58**, 2293 (1936).

(3) W. C. Bray and C. M. J. Mackay, *ibid.*, **32**, 1193 (1910).

minute. The solution temperature of solid stannic iodide could be determined only with rising temperature, since supercooling occurred with falling temperature. When the stannic iodide was liquid, however, the consolute temperature was determined going in both directions, the observations agreeing within 0.05°.

The results are given in Table I.

TABLE I

SOLUBILITY OF STANNIC IODIDE IN SILICON TETRACHLORIDE

t, °C.	Mole % of SnI_4		t, °C.	Mole % of SnI_4	
0.2	0.155	Solid	139.4	32.53	Liquid
25.0	.381		139.8	37.62	
40.0	.639		139.7	43.16	
81.3	2.36		139.5	43.54	
112.1	6.43		139.1	45.06	
115.6	7.40		138.8	46.95	
131.0	65.36		135.7	51.21	
130.9	21.56	Liquid	135.8	51.62	
133.4	24.21		132.4	55.12	
138.2	29.58				

The figures for the liquid–liquid portion are plotted in Fig. 1. We read the critical solution temperature and composition from this curve as 139.9° and 39 mole per cent. of stannic iodide. The results for both solid and liquid are plotted in Fig. 2 in the form of the logarithm of the mole fraction of stannic iodide against the reciprocal of the absolute temperature, as has been customary in reporting the data obtained in this Laboratory on the solubility of solids.

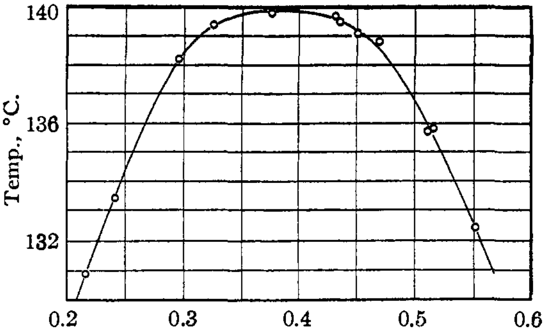

Fig. 1.—Solubility in the liquid–liquid system.

We will now examine the correlation between the curves for solid and liquid stannic iodide by applying the approximate equation[4]

$$RT \ln \frac{a_2}{\text{N}_2} = \text{v}_2 \vartheta_1^2 D_1^2 \qquad (1)$$

where a denotes activity in terms of the pure liquid; N, mole fraction; v, molal volume of the pure liquid; ϑ, the volume fraction of one component; and D the difference between square roots of the energy of vaporization per cc. of the pure components. The subscript 2 we shall take as referring to stannic iodide and the subscript 1 to silicon chloride. When the solution is in equilibrium with solid stannic iodide we can write $a_2 = \text{N}_2^i$, the ideal solubility, calculated from its melting point and heat of fusion by the equation

$$\log \frac{1}{\text{N}_2^i} = \frac{\Delta \text{H}}{2.303R} \frac{T_\text{m} - T}{T_\text{m} T} - \frac{\Delta \text{C}_p}{2.303R} \frac{T_\text{m} - T}{T} + \frac{\Delta \text{C}_p}{R} \log \frac{T_\text{m}}{T} \qquad (2)$$

where ΔH is the heat of fusion at the melting point, T_m, and ΔC_p is the excess of the molal heat capacity of the liquid over that of the solid. We shall use the recent values obtained in this Laboratory by the junior author,[2] *i. e.*, ΔH = 4600 cal. and ΔC_p = 5.7 cal. per degree. The melting point is 144.5°. The curve in Fig. 2 marked "ideal" has been obtained in this way.

To apply equation 1 we must know also the molal volumes of both components in the liquid form; the equation neglects any change of volume that may occur on mixing. The values for stannic iodide are extrapolated from the observations of Dorfman[5] obtained in the range, 144.5 to 275°.

For silicon chloride we use the equation of Pierre,[6] $v/v_0 = 1 + 0.001294t + 0.0_5 2184t^2 + 0.0_7 4086t^3$, obtained over the range −32 to +59°. This gives values differing appreciably from those of Thorpe, but agrees excellently with a single value reported by Mendelejeff[7] at 99.9°. Our

TABLE II

VALUES OF THE PARAMETER D^2 IN EQUATION 1

t	$-\log \text{N}_2$	$-\log \text{N}_2^i$	v_1, cc.	v_2, cc.	ϑ_1		D^2
0	2.810	1.142	111.5	148.3	0.998		14.20
25.0	2.414	0.886	115.4	151.1	.995		13.98
40.0	2.208	.747	117.2	153.0	.992		13.78
81.3	1.628	.413	127.4	157.6	.970		13.27
88.0	1.536	.362	129.4	158.8	.964		13.13
12.1	1.191	.203	137.2	161.6	.925		12.60
115.6	1.131	.175	138.6	162.0	.917		12.50
131.0	0.185	.079	145.0	163.7	.313		12.16
		$-\log \text{N}_2'$				ϑ_1'	
132.0	0.642	0.256	145.4	163.8	.750	0.416	11.20 11.95
136.0	.577	.292	147.2	164.2	.713	.463	11.05 10.80
139.9	.409	.409	149.0	164.7	.586	.586	10.55

---

[4] J. H. Hildebrand, "Solubility," Chem. Catalog Co., New York, 1936, p. 66 ff.

[5] M. E. Dorfman and J. H. Hildebrand, THIS JOURNAL, **49**, 729 (1927).

[6] Pierre, *Ann. chim. phys.*, **15**, 325 (1845).

[7] D. I. Mendelejeff, *Compt. rend.*, **51**, 97 (1860).

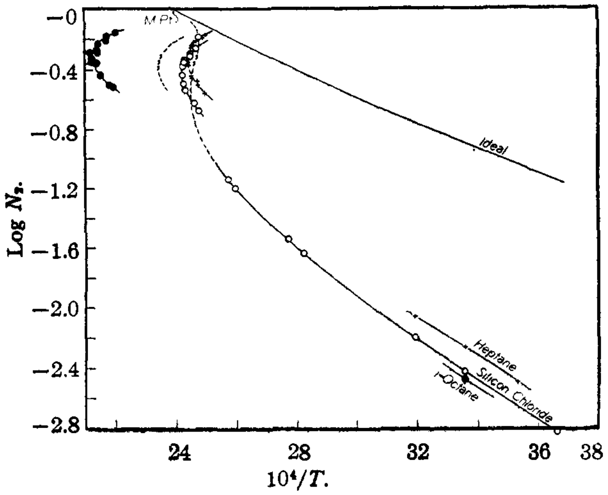

Fig. 2.—Solubility of stannic iodide.

higher temperatures involve, unfortunately, an extrapolation of this formula, but since other errors involved in the use of equation 1 cannot be avoided until a great deal more is known about the system we must be content with the following approximate analysis which, nevertheless, permits significant conclusions to be drawn.

Table II contains the values of N_2, N_2^i, v_1, v_2 and ϑ_1 used in calculating D^2, given in the last column, from equation 1.

The values for the liquid–liquid system are calculated by putting $a_2 = a_2'$ and $a_1 = a_1'$, where the unprimed letters denote the activity in one saturated liquid phase and the primed letters in the other. Writing equation 1 for both liquid phases and for both components (interchanging subscripts) yields the equation

$$RT \ln (N_2'/N_2) = v_2(\vartheta_1^2 - \vartheta_1'^2)D^2 \qquad (3)$$

and its symmetrical counterpart. This equation becomes indeterminate at the critical solution temperature, where we must use the equation[4] (p. 144)

$$RT_c(N_1v_1 + N_2v_2) = 2v_1v_2\vartheta_1\vartheta_2D^2$$

The values of D^2 so calculated are plotted against temperature in Fig. 3. It is evident that the gradual drop in D^2 becomes suddenly accentuated in the immediate neighborhood of the critical point, so that this accentuation may be regarded as a measure of the failure of equation 1 to take into account the clustering which, according to all theoretical and experimental criteria that we possess,[8] appears rather sharply in the neighborhood of the critical point, and falls off rapidly on departing therefrom either in temperature or composition. If the rate of drop of D^2 found for the solid curve were continued right up to the critical point, we would get about 11.9 instead of 10.6, and if we reversed the calculation, using 11.9 to calculate the critical temperature, we would miss it by the amount shown by the dotted curve in Fig. 2.

Although it will be desirable to make a study of the effect of volume changes and structure in the critical region before attempting a more rigid analysis, the above figures serve to show fairly well the inaccuracy caused by neglect of clustering in this region. We hope to carry out an X-ray determination of the structure of these solutions; meanwhile the attention of students of the problem by the methods of statistical mechanics is invited to this system.

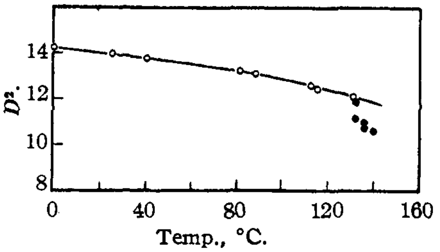

Fig. 3.—Effect of temperature on deviations for stannic iodide solutions in silicon chloride: ○, solid, ●, liquid.

Summary

Solubilities in the system silicon chloride–stannic iodide have been determined from 0 to 140°, including the range of both solid and liquid stannic iodide up to the critical solution temperatures.

This system is "regular" and free from effects of unsymmetrical molecular fields, hence is exceptionally well suited to estimate the effect of clustering in the critical region in causing deviations from the equations for regular solutions which have been derived with neglect of this effect. The error involved is about 10% in the absolute critical temperature.

BERKELEY, CALIF. RECEIVED DECEMBER 9, 1936

---

[8] (a) M. v. Schmoluchowski, *Ann. Physik*, [4] **25**, 205 (1908); (b) A. Einstein, *ibid.*, **33**, 1275 (1910); (c) Wo. Ostwald, *ibid.*, **36**, 848 (1911); (d) Krishnan, *Proc. Indian Acad. Sci.*, **1**, 211, 915 (1934); **2**, 221 (1935); (e) R. Gans, *Physik. Z.*, **37**, 12 (1936); V. S. Vrklijan, *ibid.*, **37**, 482 (1936); (f) G. Scatchard and W. J. Hamer, THIS JOURNAL, **57**, 1805 (1935); (g) J. H. Hildebrand, ref. 4, p. 65.