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The Incomplete Solubility of Liquid Iodine in Carbon Tetrachloride

BY JOEL H. HILDEBRAND

I recently called attention to a method for correlating the solubilities of the liquid and solid phases of a substance[1,2] and applied it to certain solutions of phosphorus and stannic iodide.[3] The form of the solubility curve for solid iodine[4] in carbon tetrachloride indicated that this pair also should have a critical solution temperature lying well above the melting point of iodine. This system invited further investigation because, first, it would add another of the comparatively rare instances of incompletely miscible non-polar, non-metallic liquids important from a theoretical standpoint; second, we possess a wealth of good physico-chemical data concerning both pure components; third, because it would be particularly interesting to verify the prediction of incomplete miscibility in this case since the opacity of concentrated iodine solutions would make it unlikely that the incomplete miscibility would ever be discovered by accident.

It was desirable to make a preliminary estimate of the region in which the phenomenon should be sought. This was done as follows. We have experimental figures for the solubility of solid iodine in carbon tetrachloride at 0, 25, 35 and 50° from a paper by Hildebrand and Jenks.[5] The deviation from ideal solubility was expressed by calculating D^2 in the formula

$$RT \ln (N_2^i/N_2) = v_2\mathfrak{B}_1^2D \qquad (1)$$

where N_2 is the mole fraction of iodine in solution, N_2^i its solubility in an ideal solution, v_2 its molal volume in the liquid state, $\mathfrak{B}_1$ the volume fraction of carbon tetrachloride in the solution. D is defined by the relation $(\Delta E_1/v_1)^{1/2} - (\Delta E_2/v_2)^{1/2}$, where ΔE is the energy of vaporization per mole. To calculate N_2^i we need the heat of fusion. Unfortunately we have no direct figure for this quantity and its indirect calculation from the vapor pressure curves for the solid and liquid forms suffers from the fact that although the former is known with great accuracy from the work of Giauque[6] and of Gillespie and Fraser[7] the latter is known only from the much less accurate measurements of Ramsay and Young[8] and of Wiedemann, Stelzner and Niederschulte.[9] The heat of sublimation at the melting point is 14,525 cal. per mole; the heat of vaporization of the liquid is calculated to be 10,800 cal. per mole. The heat of fusion is the difference, 3725 cal. per mole, but this may be in error (probably too small) by several per cent. In view of this uncertainty there is no point in correcting for its variation with temperature, which we could do by means of the specific heat measurements of Carpenter and Harle.[10] The ideal solubilities calculated from 3725 cal. are given in Table I, expressed as $-\log N_2^i$, together with the same function of the

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[1] Hildebrand, THIS JOURNAL, **57**, 866 (1935).

[2] Hildebrand, "Solubility of Non-electrolytes," Reinhold Publishing Corp., New York, 1936, p. 161 ff.

[3] Hildebrand, *Trans. Faraday Soc.*, **33**, 144 (1937); also, J. H. Hildebrand and G. R. Negishi, THIS JOURNAL, **59**, 339 (1937).

[4] G. R. Negishi, L. H. Donnally and J. H. Hildebrand, *ibid.*, **55**, 4793 (1933).

[5] J. H. Hildebrand and C. A. Jenks, *ibid.*, **42**, 2180 (1920).

[6] W. F. Giauque, *ibid.*, **53**, 507 (1931).

[7] L. J. Gillespie and L. H. D. Fraser, *ibid.*, **58**, 2260 (1936).

[8] Ramsay and Young, *J. Chem. Soc.*, **49**, 453 (1886).

[9] F. Wiedemann, K. Stelzner and G. Niederschulte, *Ber. deut. physik. Ges.*, **7**, 159 (1905).

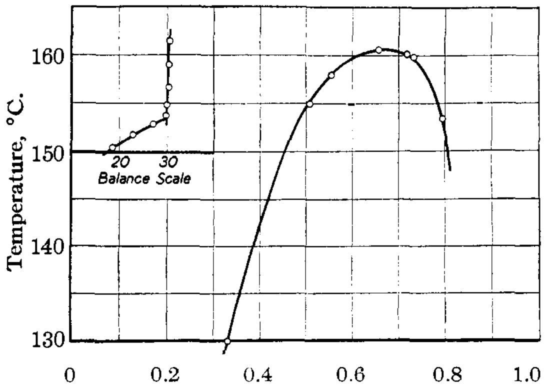
[10] L. G. Carpenter and T. F. Harle, *Phil. Mag.*, **23**, 193 (1937).

measured solubilities. The molal volumes of carbon tetrachloride are calculated from the density formula given in the "International Critical Tables;" those for liquid iodine from the density function, $d = 3.94916 + 0.003267(120 - t)$, given by Nayder.[11]

TABLE I

$t°$	$-\log N_2$	$-\log N_2$	v_2	v_1	$\mathfrak{B}_1$	D^2
0	0.877	2.379	58.5	94.4	0.998	32.3
25	.627	1.940	59.6	97.5	.993	30.5
35	.538	1.798	60.1	98.8	.990	30.1
50	.416	1.556	60.8	100.7	.984	28.7

From these data are obtained the values of D^2 given in the last column. The correspondence between this and its value derived from the internal pressures of the pure components has been discussed previously but does not concern us here, since this connection as expressed through Equation 1 is not accurate enough to take care of the temperature trend. We must be content with a long extrapolation of D^2, from 50° to a temperature well above the melting point. A linear extrapolation gives, for example, $D^2 = 20.0$ at 160°.



Mole fraction of iodine in carbon tetrachloride solution.

Fig. 1.

This is probably an upper limit, in view of the slight downward curvature shown in the cases of stannic iodide in silicon chloride and heptane. The critical composition and the critical temperature were calculated by the formulas given in the earlier paper, *i. e.*

$$N_2 = [(v_1^2 + v_2^2)^{1/2} - v_1]/(v_1 - v_2) \tag{2}$$

and

$$1.985\ T_c(N_1v_1 + N_2v_2)^3 = 2v_1^2v_2^2N_1N_2D^2 \tag{3}$$

Successive approximations, adjusting the value of D^2 to accord with T_c, gave $N_2 = 0.71$ and $T_c < 450$, or $t_c < 180°$. Allowing for the curvature of D^2, it was expected to find t_c somewhere between 150 and 170°.

The separation of two liquid phases on cooling the homogeneous solution was detected by aid of their difference in density. Pure dry iodine and carbon tetrachloride from good commercial sources were weighed into glass tubes about 12 cm. long and 0.5 cm. in internal diameter. The tubes were cooled thoroughly and evacuated before sealing. The total filling was adjusted so as to leave only a small vapor space at the higher temperatures. A tube was balanced in a sort of "cradle," provided with a long, weak steel spring in such a way that when heated to about 180° in an air-bath it could be balanced at an angle of about 15° from the horizontal. A tiny mirror attached to the cradle permitted changes in the tilt of the tube to be measured by a beam of light reflected onto a scale. The bath was heated to at least 170°, the tube balanced and rocked so as to mix its contents. The furnace was then cooled very slowly while making corresponding readings of the temperature and the position of the streak of light on the scale. This changed but little as long as the solution remained homogeneous, as shown in the insert in Fig. 1 for one of the points, but as soon as two phases separated, the heavier flowed to the lower end of the tube and exerted a torque which rapidly displaced the reading on further lowering of temperature. The intersection of the two lines drawn through the points was sharp to within 0.1°. The points on the solubility curve given in Table II and plotted in Fig. 1 were all determined in this manner. The maximum of this curve gives t_c = 160.5° and the corresponding composition as about 67 mole per cent. of iodine. Both figures agree with the prediction as accurately as could be expected.

TABLE II

MUTUAL SOLUBILITY OF LIQUID IODINE AND CARBON TETRACHLORIDE

Wt. % of iodine	44.8	63.0	67.0	76.0	80.8	81.7	86.6
Mole % of iodine	33.0	50.8	55.1	65.7	71.8	73.1	79.7
Solution temp.	129.8	155.0	158.1	160.6	160.1	159.9	153.5

We may express this correlation in terms of D^2. Substituting the experimental values of T_c and

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[11] T. Nayder, *Bull. Intern. Acad. Polonaise, Classe Sci. Math. Nat.*, 231 (1934A); *cf. C. A.*, **29**, 976 (1935).

N_2 in Equation 3 gives $D^2 = 18.3$. We take from the curve the values of N_2 and N_2' given in Table III, and substitute them in the formula,[2] p. 144,

TABLE III

t	N_2	N_2'	v_1	v_2	D^2
150	0.450	0.820	116	66.0	19.6
154	.494	.796	117	66.2	19.2
158	.550	.760	118	66.4	17.5

$RT \ln (N_2'/N_2) = v_2 (\mathfrak{V}_1^2 - \mathfrak{V}_1'^2) D^2$, getting the figures in the last column of the table. Table IV,

TABLE IV

t, °C.	0	25	35	50	150	154	158	161
D^2	32.3	30.5	30.1	28.7	19.6	19.2	17.5	18.3

plotted in Fig. 2, summarizes all the values of D^2 calculated in this paper from the experimental data. The decline toward high temperatures is very similar to that encountered with the systems previously investigated. It will be worth while to re-examine this system as soon as a more reliable figure for the heat of fusion of iodine can be obtained. Meanwhile, it is evident that the methods here illustrated are again successful in correlating the solubility of a substance in its solid and liquid forms, in spite of the difference of 100° between the two sets of data.

In conclusion, it is interesting to compare the heat of solution of iodine in carbon tetrachloride, as measured by Blair and Yost,[12] 5990 ± 60 cal. per mole of iodine in very dilute solutions, about 0.1 mole per cent., at 25°. The figures in Table I correspond to a free energy of solution in excess of the ideal free energy, $\bar{F}_2 - \bar{F}_2^i = 1790$ cal. at 25° when $N_2 = 0.015$. Dividing this by $(1 - N_2)^2$ gives 1845 cal. for an infinitely dilute solution. If these solutions are completely "regular," in the sense of having ideal entropy of solution, this figure should represent the heat absorbed in mixing liquid iodine with carbon tetrachloride, or, added to the heat of fusion, which we have taken to be 3725 cal., we get 5570 cal., which agrees with the 5990 cal. of Blair and Yost as closely as could be expected.

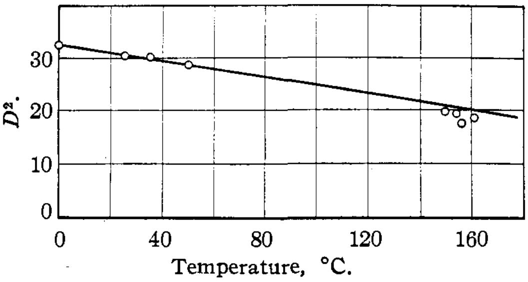

Fig. 2.

Summary

The predicted existence of a two liquid phase system in the case of iodine and carbon tetrachloride has been verified, the critical solution temperature being 160.5° and the corresponding composition, 0.68 mole per cent. of iodine. The correlation between the solubility of iodine in the solid and liquid states has been discussed.

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[12] C. M. Blair and D. M. Yost, THIS JOURNAL, 55, 4489 (1933).

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The Molecular Structures of Boron Trimethyl, Trifluoride, Trichloride, and Tribromide. The Covalent Radius of Boron

BY HENRI A. LÉVY AND L. O. BROCKWAY

The molecular structures of the compounds of boron are of special interest because the unusual number of electrons occurring in many of them suggests that their structures may be different from those of corresponding compounds of the other non-metallic elements of the first row of the periodic table. Because of the anomalous electronic structures of the stable hydrides due to the lack of enough electrons to form electron-pair bonds throughout the respective molecules, other compounds of boron were chosen in the hope of determining a characteristic single bond covalent radius for comparison with the radii of other elements. Although boron in its normal valence compounds (in which it is coördinated with three univalent atoms or groups) has only six electrons around it in place of the octet found in the normal valence compounds of the following first row elements, the number of electrons in the BX_3 compounds is sufficient for the formation of electron pair bonds. In particular, boron trimethyl was investigated because the methyl derivatives