methods, first, the change in $\Delta F^\circ$ in going from 25° to 327°, and then the further change in going to 498°, which gave $\Delta F^\circ$ at this latter temperature equal to —59,400 cal., corresponding to a decomposition potential of 1.285 v. The smooth line through our measured values for the pure lead chloride cuts this temperature at 1.272 v., corresponding to $\Delta F^\circ$ = —58,700 cal. The agreement lies well within the errors introduced by the uncertainties in the data used for making the calculation over the wide temperature range.

## Summary

1. The decomposition potential of fused lead chloride, diluted with varying amounts of potassium chloride, has been measured at various temperatures from 500° to 600°.

2. The relation between composition and activity coefficient of molten lead chloride has been determined at mole fractions of potassium chloride between 0 and 0.4, for 550° and 600°.

3. The results have been interpreted upon the assumption that the complexes $KPb_2Cl_5$, $K_2PbCl_4$ and $K_4PbCl_6$, which separate as solids, and perhaps others as well, also exist as partly ionized in the solutions along with un-ionized lead chloride.

4. The decomposition potential of pure, molten lead chloride corresponds to a free-energy value of —58,700 cal. at 498°, which is shown to be in substantial agreement with the value at 25° obtained by Gerke.

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

# SOLUBILITY. X. SOLUBILITY RELATIONS OF STANNIC IODIDE

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The solubility relations of stannic iodide are particularly appropriate for the further testing of the theories of solubility elaborated by the senior author and his collaborators.[1] Stannic iodide is relatively non-polar, and has a melting point sufficiently low to allow solubilities large enough for convenient measurement, and it has a high internal pressure, so that it was expected to show solubilities falling off regularly from the ideal value with decreasing internal pressures of the solvents used. A substance of intermediate internal pressure may show approximately equal solubilities in liquids of both higher and lower internal pressures, hence the relation be-

[1] (a) Hildebrand and co-workers, THIS JOURNAL, **38**, 1452 (1916); (b) **39**, 2297 (1917); (c) **41**, 1067 (1919); (d) **42**, 2180, (e) 2213 (1920); (f) **43**, 500, (g) 2172 (1921); (h) **45**, 682, (i) 2828, 2865 (1923); (j) *Phys. Rev.*, **21**, 46 (1923); (k) "Solubility," A. C. S. Monograph, Chemical Catalog Co., **1924**.

tween solubility and internal pressure is not given with such freedom from ambiguity.

The solvents considered were carbon disulfide, ethylene bromide, *m*-xylene, toluene, benzene, chloroform, carbon tetrachloride, ether, heptane, iodine and sulfur, which can all be regarded as of low polarity, and which cover a large range of internal pressures.

## Purification of Materials

The stannic iodide was prepared according to the method of McDermott[2] by heating C. P. tin powder and a solution of resublimed iodine in pure carbon tetrachloride, using a slight excess of tin. The stannic iodide was then recrystallized thrice from hot carbon tetrachloride, filtering through a carefully prepared asbestos mat on a Büchner funnel. In each case the filtrate was examined with a powerful light to detect the presence of insoluble matter. After each crystallization the crystals were rinsed free of mother liquor on a Büchner funnel without filter paper, loss of solid being prevented by the small size of the holes in the funnel. The crystals were finally dried by heating first under reduced pressure at 120°, and then for about 24 hours at the same temperature in a current of very dry air. The melting points of all preparations were found to lie between 143.3 and 143.5°, agreeing well with the value of 143.5° found by Reinders and de Lange.[3] The purity of each preparation was checked by analysis by conversion into stannic oxide by methods described later. The first lot of material amounted to 125 g. and the ratios of stannic iodide to stannic oxide found in four analyses were 4.153, 4.155, 4.157, 4.154; av., 4.155; calcd., 4.1565. Preparation 2, of 175 g., showed in three analyses ratios of 4.158, 4.156, 4.159; av., 4.158; and Preparation 3, of 1400 g., which furnished the material used in most of the solubility measurements, showed ratios of 4.160, 4.154, 4.159; av., 4.158. It is seen from the analyses that the material used was very pure. In addition, the absence of free iodine was shown by the starch test. The accuracy of these analyses proved to be much greater than that attained in the solubility determinations, due to the additional sources of error involved in the latter.

In all distillations for the purification of the solvents a flask with a long fractionating column was used. The distilling apparatus was so constructed that the vapor and liquid came into contact with glass only, except for the tin foil used to cover the stopper. Only middle fractions were used. The neutrality of the liquids was tested with litmus paper.

C. P. carbon tetrachloride, marked free from acids, non-volatile matter, carbon disulfide and chlorine, was purified by the method of Hildebrand and Jenks.[1f,1g] It was shaken with concd. sodium hydroxide solution to remove acidic constituents, and distilled from phosphorus pentoxide. Practically all distilled within less than 0.1°.

[2] McDermott, THIS JOURNAL, **33**, 1963 (1911).

[3] Reinders and de Lange, *Z. anorg. Chem.*, **79**, 230 (1912).

Thiophene-free benzene was tested with concd. sulfuric acid, frozen twice and distilled from phosphorus pentoxide, practically all distilling within 0.1°.

The toluene used was previously purified material which had been preserved over sodium wire. It was redistilled, and the large middle fraction distilling within less than 0.1° was preserved over sodium wire until used.

The heptane was purified by the method previously used in this Laboratory.[11] All distilled within 0.2° and most of it within 0.1°.

The ethylene bromide was Eastman material which was shaken with sodium carbonate solution to remove acidic constituents, washed with water, shaken with phosphorus pentoxide and distilled. All distilled within 0.3° and the large middle fraction within less than 0.1°.

Kahlbaum *m*-xylene was shaken with phosphorus pentoxide and distilled. All distilled within 0.6° and the large middle fraction within 0.2°. The melting point of this fraction was found to be —53.5°. This agrees with the values given in the literature, —53.5° to —54°. *Ortho*- and *p*-xylenes, which cannot be separated from the *meta* form by distillation alone, due to the closeness in boiling points, melt at —28° and 15°, respectively; hence the observed melting point indicates their absence, since otherwise the melting point of the *meta* form would be considerably lowered.

Baker's C. P. chloroform, marked free from phosgene, alcohol, chlorine and hydrochloric acid, was distilled from phosphorus pentoxide. The large middle fraction distilled within 0.05°.

Baker's C. P. carbon disulfide, marked free from non-volatile matter, sulfur, sulfides and mercaptans was distilled from phosphorus pentoxide. All distilled within 0.1°, and did not darken clean, bright mercury, over which it was preserved in a dark bottle and used as soon as possible. The odor of the purified material was not unpleasant.

Baker's C. P. anhydrous ether, distilled over sodium, marked free from water, peroxides, acids, alcohols and aldehydes, was allowed to stand in contact with sodium wire for several days and then was distilled from sodium wire. All distilled within less than 0.1°. The very sensitive iodoform test indicated the absence of alcohol.

C. P. nitric acid and ammonium sulfate were used and tested for the absence of non-volatile matter. The ammonium hydroxide was prepared by passing ammonia gas into distilled water.

## Apparatus and Procedure

The apparatus used was essentially that of Hildebrand and Jenks.[11] It consisted of a bulb and a weight pipet, which fitted with the neck of the bulb by a ground-glass joint. The lower bulb was shaken in the thermostat. Since it is very difficult to grind a stopper to fit the same seat that the pipet fits into, a hole was bored in a cork stopper which was split and wired around the outlet tube of the bulb. A glass cap was then fitted tightly over the cork and both were sealed with paraffin. An unground-glass stopper, which fitted fairly well, was inserted in the ground-glass seat. The cap, in addition to preventing vapor from escaping, prevented any foreign matter from getting into the solution through the glass stopper.

When the solution had come to equilibrium, the pipet fitted with a ground-glass cap was weighed and filled with air saturated with the vapor of the liquid at the temperature of the determination, so as to prevent any of the entering solution from evaporating. The bulb was then tilted so that the outlet tube was almost vertical, the cap and stopper were re-

moved, the pipet was inserted and some of the solution forced up by blowing air saturated with the vapor of the solvent through the stopcock. The air was saturated by first drying with concd. sulfuric acid and then passing it through a large wash tower of the pure liquid which was immersed in the thermostat. If ordinary air were used, the evaporation would cool the more volatile solutions over half a degree. With solvents such as ethylene, bromide and xylene, whose vapor pressures are small at the temperatures involved, dry air was used. The pipet was then removed, wiped clean with filter paper, weighed and the contents washed into a flask for analysis. The construction of the apparatus and the high density of stannic iodide, 4.7, eliminated the danger of solid entering the pipet.

The saturation point was approached both from above and below. In the former case, the liquid was shaken in a thermostat for three days. In the latter case, the liquid in contact with solid was heated considerably above the temperature at which the determination was to be carried out. The bulb was then shaken in the thermostat and observed. The separation of crystals indicated that the solution had been supersaturated. The bulb was then shaken in the thermostat for three days. In the carbon disulfide determinations at 40°, and those of ether at 30°, the solutions were supersaturated by raising the temperature of the thermostat four degrees in each case and shaking for about a day. The temperature was then lowered again, crystals were observed to separate and the bulb was shaken for three days.

## Methods of Analysis

It was thought at first that by treatment with concd. nitric acid the stannic iodide could be quantitatively converted into hydrated stannic oxide, which could be filtered through a Gooch crucible, ignited and weighed as stannic oxide. This proved quite successful for test determinations. However, in attempting to apply this method to solubility measurements, it was found that the two phases, the nitric acid and the organic liquid, in spite of all precautions, could not be boiled without bumping and spattering. Consequently, the solutions were not boiled but simply kept at about 70°; this procedure did not yield consistent results, however, so was abandoned. It appears that soluble stannic nitrate is stable in concd. nitric acid at lower temperatures, although decomposed at 100°.[4] The fact that the solubility, as indicated by these measurements, was lower in every case than the value obtained later from consistent measurements, supports this conclusion.

In the next method used, the stannic iodide was hydrolyzed by treating with concd. ammonium hydroxide, and allowing to stand at 70°. The disappearance of the orange color in the organic layer indicated that the

[4] Roscoe and Schorlemmer, "A Treatise on Chemistry," Macmillan and Co., London, **1913**, vol. 2, p. 868.

hydrolysis was complete. The solution was then neutralized with dil. nitric acid, using methyl orange as an indicator, so that any hydrated stannic oxide that may have been dissolved would be reprecipitated. The precipitate was filtered through a Gooch crucible, ignited to constant weight and weighed. The absence of tin from the filtrate was shown each time by passing in hydrogen sulfide. Under these conditions, less than 0.5 mg. of tin will give a precipitate. This method gave consistent results but the fine condition of the hydrated stannic oxide made filtration very slow. Recourse was finally had to a procedure described by Fresenius, whereby the hydrolysis is brought about by ammonium hydroxide in the presence of sodium sulfate, except that we used ammonium sulfate in place of the latter. After standing with these reagents, followed by neutralization with dil. nitric acid, the precipitate could be easily filtered and treated as before. In the case of carbon disulfide, ammonium sulfide is formed by this treatment, which acts upon the hydrated stannic oxide to form stannic sulfide. However, when ignited in air, this is converted quantitatively into the oxide.

## Results

Table I gives the results obtained. Four independent determinations for each liquid were carried out at each temperature. The first two values listed for each case were obtained by approaching the saturation point from above, and the last two by approaching from below. The solvents are arranged in order of increasing solubility expressed in mole fractions.

TABLE I

SOLUBILITIES OF STANNIC IODIDE

| Solvent | Temp., °C. | G. of $SnI_4$ per 100 g. of soln. | | | | Av., g. | Mole % |
|---|---|---|---|---|---|---|---|
| Heptane | 10.00 | 2.05 | 2.00 | 2.03 | 2.01 | 2.02 | 0.329 |
| | 25.00 | 3.34 | 3.35 | 3.36 | 3.37 | 3.36 | .553 |
| | 40.00 | 5.21 | 5.26 | 5.24 | 5.25 | 5.24 | .877 |
| Ether | 10.00 | 3.61 | 3.63 | 3.65 | 3.66 | 3.64 | .445 |
| | 20.00 | 4.77 | 4.80 | 4.81 | 4.82 | 4.80 | .593 |
| | 30.00 | 6.35 | 6.38 | 6.36 | 6.35 | 6.36 | .797 |
| Carbon tetrachloride | 10.00 | 3.54 | 3.54 | 3.57 | 3.58 | 3.56 | .898 |
| | 25.00 | 5.70 | 5.68 | 5.67 | 5.69 | 5.69 | 1.459 |
| | 40.00 | 9.06 | 9.02 | 9.03 | 9.05 | 9.04 | 2.382 |
| Chloroform | 10.00 | 4.93 | 4.92 | 4.95 | 4.95 | 4.94 | 0.981 |
| | 25.00 | 8.30 | 8.27 | 8.28 | 8.27 | 8.28 | 1.692 |
| | 40.00 | 12.90 | 12.89 | 12.93 | 12.91 | 12.91 | 2.747 |
| Benzene | 10.00 | 9.75 | 9.74 | 9.76 | 9.78 | 9.76 | 1.330 |
| | 25.00 | 15.19 | 15.16 | 15.15 | 15.18 | 15.17 | 2.181 |
| | 40.00 | 23.00 | 23.04 | 23.02 | 23.01 | 23.02 | 3.593 |
| Toluene | 10.00 | 9.96 | 9.98 | 10.02 | 10.01 | 9.99 | 1.605 |
| | 25.00 | 14.86 | 14.90 | 14.89 | 14.91 | 14.89 | 2.507 |
| | 40.00 | 21.90 | 21.92 | 21.96 | 21.95 | 21.93 | 3.967 |

TABLE I (*Concluded*)

| Solvent | Temp., °C. | G. of $SnI_4$ per 100 g. of soln. | Av., g. | Mol. % |
|---|---|---|---|---|
| *m*-Xylene | 10.00 | 8.60 8.58 8.64 8.63 | 8.62 | 1.572 |
| | 25.00 | 13.44 13.41 13.42 13.40 | 13.42 | 2.558 |
| | 40.00 | 19.98 19.97 20.04 20.02 | 20.00 | 4.062 |
| Ethylene bromide | 10.00 | 9.10 9.09 9.12 9.13 | 9.11 | 2.915 |
| | 25.00 | 14.16 14.15 14.16 14.18 | 14.16 | 4.714 |
| | 40.00 | 20.93 20.90 20.88 20.94 | 20.91 | 7.347 |
| Carbon disulfide | 10.00 | 48.99 49.00 49.04 49.02 | 49.01 | 10.46 |
| | 25.00 | 58.50 58.53 58.55 58.54 | 58.53 | 14.64 |
| | 40.00 | 67.51 67.57 67.59 67.55 | 67.56 | 20.20 |
| Sulfur | 130 | 90.8 | | 80.2 |
| | 104 | 76.2 | | 56.7 |

We also made two determinations of the solubility of stannic iodide in molten sulfur by the aid of cooling curves. The mixture was contained in a test-tube surrounded by a larger tube immersed in a bath of glycerol. By slow cooling, stirring and seeding at the proper time, the initial break in the curve was obtained with an accuracy of 1°. The results are included in Table I.

McDermott[2] has given values for the solubility of stannic iodide in carbon tetrachloride, chloroform and benzene; Retgers[5] has given a single value for the solvent methylene iodide. There exist data by Arctowski[6] for carbon disulfide between —58° and —114.5° but they appear to be rather inaccurate and we shall not further consider them.

Reinders and de Lange[3] and also van Klooster[7] have determined melting points for the system stannic iodide-iodine. The two sets of data agree well. All these data are given in Table II.

TABLE II

SOLUBILITIES OF STANNIC IODIDE, BY OTHER OBSERVERS

| Solvent | Temp., °C. | $SnI_4$, % | Mole % |
|---|---|---|---|
| Carbon tetrachloride | 22.4 | 5.25 | 1.34 |
| | 50.0 | 12.50 | 3.39 |
| Chloroform | 28.0 | 8.21 | 1.68 |
| Benzene | 20.2 | 12.65 | 1.77 |
| Methylene iodide | 10 | 19.3 | 9.26 |
| Iodine | 133 | 92.9 | 82.2[a] |
| | 127 | 90.0 | 78.5 |
| | 108.4 | 80.0 | 61.8 |
| | 102.5 | 76.6 | 57.0[a] |
| | 89.8 | 70.0 | 48.7 |
| | 83.5 | 65.0 | 42.9 |

[a] Values by van Klooster.

[5] Retgers, *Z. anorg. Chem.*, **3**, 343 (1893).

[6] Arctowski, *ibid.*, **11**, 272 (1896).

[7] van Klooster, *ibid.*, **79**, 223 (1912).

All of the foregoing data are represented graphically in Fig. 1, according to the method previously employed in these studies, by plotting log $N$ against $1/T$, where $N$ is the mole fraction of the stannic iodide.

## Discussion

The relative positions of the curves in Fig. 1 correspond to the internal pressures of the substances[1k] as determined by the various methods, and is essentially the same as found with iodine and with sulfur.[1e,1g,1k] The similarity between this and the sulfur group is particularly close, extending even to the slight discrepancy with the internal pressure series in the reversal of benzene, toluene and xylene.

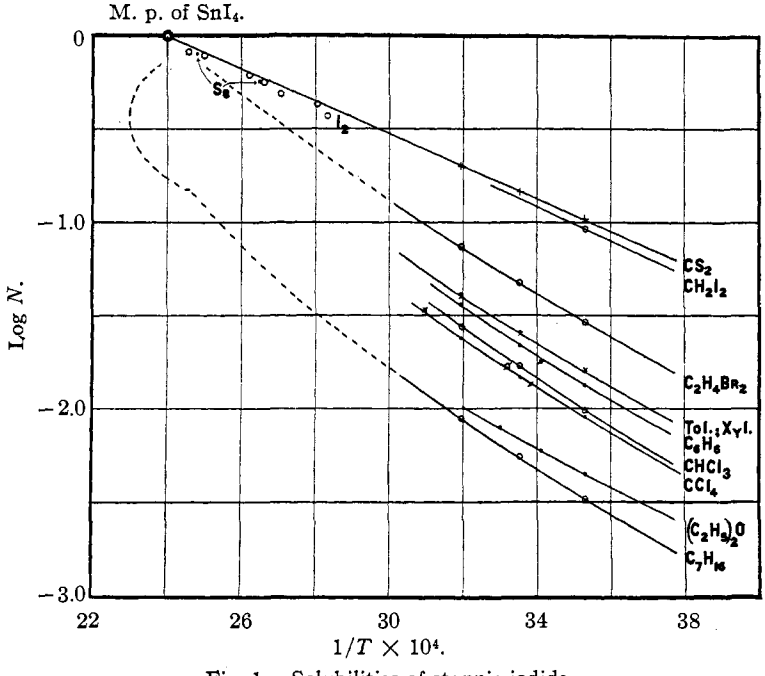


Fig. 1.—Solubilities of stannic iodide.

In order to estimate the internal pressure of stannic iodide apart from solubility data it was necessary to determine its molal volume in the liquid form. This was done by the aid of a volumenometer made of Pyrex and

TABLE III

OBSERVED SPECIFIC VOLUMES OF STANNIC IODIDE

| Temp., °C. | Spec. vol. | Temp., °C. | Spec. vol. | Temp., °C. | Spec. vol. |
|---|---|---|---|---|---|
| 145 | 0.2639 | 180 | 0.2701 | 225 | 0.2788 |
| 155 | .2656 | 185 | .2715 | 250 | .2835 |
| 160 | .2668 | 205 | .2739 | 260 | .2855 |
| 165 | .2678 | 210 | .2760 | 275 | .2885 |

immersed in a bath allowing good temperature control. The accompanying Table III gives the observed values for the specific volume, using 13.165 g. of stannic iodide, and corrected for the expansion of the glass.

These figures were plotted on a large scale, giving a straight line within the limit of error, from which was obtained a specific volume of 0.2368 at 0° and 0.2405 at 20°, a molal volume at 20° of 150.7 cc. and a coefficient of expansion 0.00079. The specific volume between 145° and 275° is given by the expression $v = 0.2368\ (1 + 0.00079t)$.

The boiling point of stannic iodide is 340°; hence, applying the expression for relative internal pressure previously derived $(5200 + 30\ t_b)/V$, we get 102, a value near that for ethylene bromide, 106.

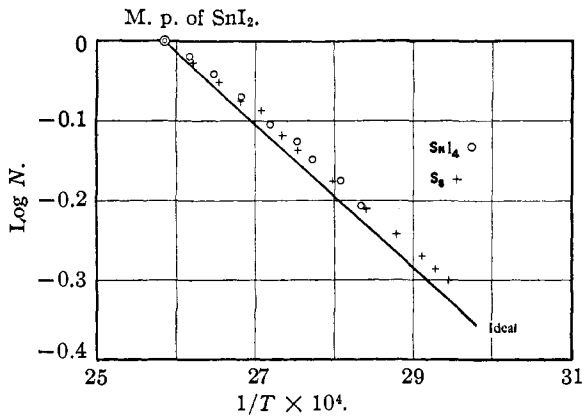


Fig. 2.—Solubilities of iodine in stannic iodide and in sulfur.

Estimating the van der Waals $a$ by the method of van Laar gives for $a/V^2$ the value $833 \times 10^{-8}$, which is between the value for bromine, 730, and sulfur monochloride, 850; iodine is 860.

The solubility curves themselves indicate that the internal pressure of stannic iodide is greater than that of ethylene bromide, for its maximum solubility seems to be reached in carbon disulfide, sulfur, iodine and methylene iodide. The evidence is very striking that stannic iodide, iodine and sulfur all form solutions with each other which obey Raoult's law very closely. We see from Fig. 1 that stannic iodide is equally soluble in the other two, but since we have no figure for its heat of fusion we cannot prove directly that this curve corresponds to Raoult's law. It has previously been shown,[1d,1g] however, that iodine and sulfur, whose heats of fusion are known, obey Raoult's law closely, and the figures of Reinders and de Lange[3] for the system iodine-stannic iodide indicate that the solubility of the latter in the former follows Raoult's law. Fig. 2 gives the ideal solubility curve for iodine together with its solubilities in sulfur and stannic

iodide, which are seen to agree well with the ideal curve. It can easily be shown that if one component obeys Raoult's law through a considerable range of concentration, the other must also.[8] We can, therefore, conclude with considerable assurance that the top line in Fig. 1 represents the ideal solubility rather closely and, further, that the heat of solution calculated from it is also the heat of fusion of the pure solid. This we have calculated to be 4000 cal. per mole.

It is interesting to note that not all of the curves in Fig. 1 would converge to the melting point. We found that decane and stannic iodide melt to two liquid phases which become completely miscible only above 160°. Although heptane, on account of its lower boiling point, volatilizes in an open tube before the melting point of the stannic iodide is reached, there can be no doubt that under pressure in a sealed tube two liquid phases would be obtained, as in the case of sulfur with various liquids.[9] We have accordingly indicated by the dotted portion in Fig. 1 the type of curve that would be found.

We may mention finally that although the order of internal pressures agrees well with the relative solubilities, there is not strict proportionality, and the curves are not spaced quite the same for sulfur, stannic iodide and iodine. Furthermore, although these three substances form ideal solutions with each other, and although stannic iodide obeys Raoult's law in carbon disulfide, iodine and sulfur do not. We have given evidence ealier,[10] both theoretical and experimental, that the difference in internal pressure is not the sole factor determining deviations from Raoult's law, even with substances of low polarity.

## Summary

1. The solubilities of stannic iodide have been determined in carbon disulfide, ethylene bromide, *m*-xylene, toluene, benzene, chloroform, carbon tetrachloride, ether, heptane and sulfur at temperatures ranging from 10° to 40° (for sulfur, 104° to 143°).

2. The data obtained, together with solubilities to be found in the literature for iodine and methylene iodide, are shown to be in good accord with the relative internal pressures of the substances, thus giving further confirmation of the theories of solubility contained in previous publications from this Laboratory.

3. The specific volume of liquid stannic iodide between 145° and 275° is given by the expression $v = 0.2368\ (1 + 0.00079t)$.

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[8] Ref. 1 k, p. 46.

[9] Ref. 1 g; 1k, p. 152.

[10] Ref. 1 k, pp. 67, 153.