1. The proportion of pyrosulfate used in the fusion mixture and the time of heating have little or no effect on the solubility of the product formed.
2. Concd. sulfuric acid is a more effective differentiating solvent for the tantalum and columbium than hydrofluoric acid.
3. A complete separation of tantalum and columbium may be obtained with concd. sulfuric acid if the fusion has been made at 835–875°.
4. The solution of columbium is unaffected by cold 6 *N* sulfuric acid but is almost completely precipitated in a hot solution.
5. The compounds formed by the fusion are probably tantalates and columbates rather than sulfates or double sulfates.
6. A method of procedure is given for the separation of tantalum and columbium.

RENO, NEVADA

[CONTRIBUTION FROM THE LABORATORY OF INORGANIC CHEMISTRY, STATE UNIVERSITY OF IOWA]

THE SYSTEMS FORMED BY CERTAIN INORGANIC COMPOUNDS WITH LIQUID SULFUR DIOXIDE

BY P. A. BOND AND HOWARD T. BEACH[1]

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In 1920 Waddell, in this Laboratory, while determining the solubilities of inorganic substances in sulfur dioxide, found that tin tetrabromide was soluble in all proportions above 49°, while below that temperature two liquid layers were obtained. The writers have investigated other tetrahalogen compounds of the same periodic group and have found that in several other cases the double layers may occur. The present investigation is concerned with those formed when stannic bromide and chloride and titanic chloride are treated with anhydrous sulfur dioxide.

The most common method for determining the mutual solubilities in binary systems was introduced by Alexejew.[2] It consists in sealing known weights of the two components in glass tubes, raising their temperature slowly while they are being agitated, and noting the temperature at which the mixture becomes clear. If the process be repeated with a series of concentrations, the complete solubility curve may be obtained. In thermostatic methods the temperature is maintained constant and the composition of the two layers is determined by analysis. The former of the two methods was used in our work.

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[1] Adapted from a dissertation presented by Howard Thomas Beach to the Graduate Faculty of the State University of Iowa in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Alexejew, *Wied. Ann.*, **28**, 305 (1886).

Experimental Part

Preparation of the Materials.—The chief difficulty encountered both in the preparation of the anhydrous salts and in their transfer to the tubes used was the very great ease of hydrolysis and the extreme affinity for water which they manifest. When brought into contact with air, all of these substances fume with the formation of various hydrated compounds. The following procedure was arranged in order to overcome the difficulty.

The tin compounds were made by the direct union of the elements and for the other compounds the ordinary commercial products were taken as starting material. The preparation and purification of these materials will be described later. The purified fraction in each case was then transferred to another distilling flask provided with a fractionating column, and from this flask the liquid was distilled into a rotating receiver. The nature of this receiver is indicated by the accompanying diagram. Quantities of the compound as it distilled were caught in the compartment A and from here the material could be distributed to the receivers as the flask F was rotated at the ground-glass joint E. To avoid the use of stopcocks, for the stopcock grease would be a possible source of contamination, the outlet from A was closed by a glass rod B which worked through the mercury seal C and fitted into a ground-glass socket at D. The flask F was made from an ordinary 250cc. Pyrex flask. Around the bottom in a circle were eight outlets, two of which are shown in the diagram at G,G, to which receivers of any type desired could be attached. The desired quantities of the purer fractions were caught in tubes of the type shown in Fig. 2. Each of these tubes was made from three pieces of glass tubing, the two larger having an outer diameter of about 11 mm. and the longer central tube an outer diameter of about 6 mm. They were labeled as indicated and a file mark was made around the central part to facilitate the opening of the tube after it had been sealed. The tubes were carefully weighed and after the liquid had been run into them they were sealed off near the top of the stem. By weighing the two parts of the tube the weight of the material in the tube could be determined.

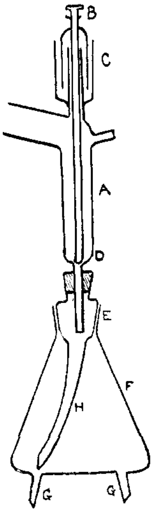

Fig. 1.

Fig. 2.

The sulfur dioxide used in this work was purchased in cylinders and was purified by bubbling through concd. sulfuric acid and then through sodium bisulfite solution. From the washing cylinders the gas was passed through 1.8 meters of calcium chloride and 3.6 meters of phosphorus pentoxide and into a condenser. The condenser was of the spiral type and contained 13 meters of 10mm. glass tubing. A freezing mixture of ice and salt was used and the condensed liquid was caught in an unsilvered Dewar flask closed with a rubber stopper. The sulfur dioxide was led into the flask through a tube extending through the rubber stopper and which was connected to the lower end of the condenser by a mercury seal. Two other tubes ran through the stopper, one extending to the bottom of the flask and serving as a siphon through which the liquid could be forced out when the other tube was closed. When a sufficient quantity of liquid had been condensed, the tubes containing the halogen compound were cooled with the ice-and-salt mixture and opened by means of a hot Nichrome wire held along the file mark. A quantity of liquid sulfur dioxide was forced into the tubes through the siphon tube when the other outlet into the Dewar flask was closed, the liquid vaporizing in the Dewar flask furnishing a pressure sufficient to force the liquid over. Then by means of an oxygen flame the tube was sealed off as close as possible to the lower end of the 6mm. tubing. The bulb with its contents, the piece of tubing cut off by the torch and the piece cut off by the hot wire were weighed and from these weights the quantity of sulfur dioxide in the bulb could be determined. From this and the weight of the halogen compound in the mixture the percentage composition was calculated.

Determination of Solubility Points

The method used in the determination of solubility points depended somewhat upon the temperature at which the complete solubility took place. The critical solution temperature for stannic bromide was about 49° and for determining the solubility temperatures from that point down to 0°, an ordinary constant temperature water-bath was used. For temperatures below 0° mixtures of carbon dioxide and acetone or carbon dioxide and ether in a vacuum flask were substituted. Since these mixtures showed considerable turbidity when first made up, it was necessary to filter them rapidly through a folded filter.

Temperature measurements were made by means of low-temperature thermometers. When determinations were carried out in a water-bath the thermometer was totally immersed; in freezing mixtures part of the stem was exposed at times and stem corrections were necessary. At most, these never amounted to more than 0.4° and it is improbable that there was any considerable error from this source. Methods were checked by determining the freezing points of various substances which solidified between 0° and —75°.

Tin Tetrabromide.—The tin tetrabromide was made by adding liquid bromine to a good quality of tin shot in a flask fitted with a reflux condenser. Considerable heat was evolved in the course of the reaction, and it was necessary to add the bromine slowly and to cool the reaction flask in running water. When the addition was completed and the mixture ceased to evolve heat when shaken, it was heated until most of the bromine was driven out. When the liquid was allowed to cool to room temperature it crystallized in well-defined crystals. It was found advisable to keep the compound in round-bottomed flasks which were less than half filled in order to avoid breakage due to the expansion of the solid when it became necessary to melt it.

The liquid was purified by fractional distillation, using a fractionating column about 30 cm. long. The purified compound boiled sharply and without decomposition at 205.05° (734 mm.), and melted at 29.45°. Other observers note the following boiling points: 201° (uncorr.) by Carnelley and O'Shea,[3] 203.3° by Preis and Rayman.[4] The following melting

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[3] Carnelley and O'Shea, *J. Chem. Soc.*, **33**, 55 (1878).

[4] Preis and Rayman, *Ann.*, **223**, 324 (1884); *Jahresber.*, **37**, 436 (1884).

points are noted: 39° by Boedeker,[5] 33° by Preis and Rayman,[4] 29.45° by Garelli,[6] 29.9° by Tolloczko and Meyer.[7] Tin tetrabromide hydrolyzes slowly in comparison with the other substances investigated, fuming being scarcely visible unless the liquid is warm.

In transferring the purified liquid to the flask for distillation it was only necessary to draw a current of air dried by phosphorus pentoxide through the apparatus and then pour the liquid into the flask. Since the melting point of this substance is slightly above room temperature, it was necessary to warm the condensing apparatus slightly with a free flame to prevent solid from accumulating. Samples of this substance sealed in the tubes remained colorless for a considerable length of time when free from impurities; when contaminated, however, or when heated too strongly as the tubes were sealed off, the product became colored upon standing for a few hours. No samples were used that showed any tendency to color on standing.

When sulfur dioxide was added to the tin tetrabromide in the manner previously described it was found that some mixtures showed two phases at ordinary temperatures while others were homogeneous.

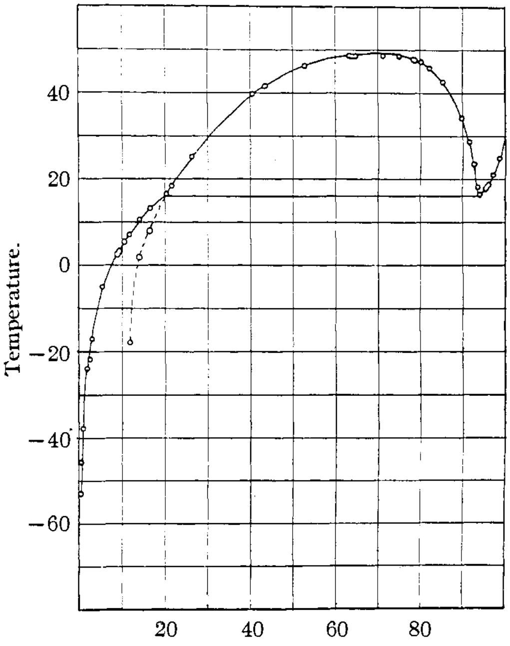

Fig. 3.

The results of the determination of the solubility points are shown in the data of Table I and in the temperature-concentration diagram (Fig. 3). It will be noted that two stable liquid phases were possible at temperatures above 16.3° and that the critical solution temperature was placed at 48.6°. Owing to the large difference in densities of the two layers, solubility points were sharp and temperature determinations were easily made. In regions immediately above and around the critical solution temperature the familiar phenomenon of opalescence was observed: the solutions showed a bluish turbidity which faded

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[5] Boedeker, *Jahresber.*, **13**, 17 (1860).

[6] Garelli, *Gazz. chim. ital.*, [2] **28**, 253 (1898).

[7] Tolloczko and Meyer, *Chem. Centralbl.*, [ii] **81**, 1025 (1910).

slowly with increase in temperature and which was sometimes noticeable at temperatures 4° above the solubility point. The opalescent solutions were easily distinguished from the partially miscible mixtures, however, and the solubility points were sharp.

Stable two-liquid systems are not possible in the case of mixtures with a tin tetrabromide content of less than 20%, but when the mixtures were cooled carefully, metastable two-phase systems could be obtained in some cases, and in this way the binary-liquid curve was followed for a distance of about 35° into the metastable region. When the mixtures were cooled strongly, solidification resulted and the solubility points obtained were points on the solid-liquid solubility curve.

At temperatures below —45° the solubility of tin tetrabromide in sulfur dioxide was so slight that the eutectic point could not be located readily.

Table I

Stannic Bromide Mixtures

% $SnBr_4$	100.00	99.96	98.74	98.68	97.30	96.24	95.71	95.70	95.62	95.42
M. p., °C	29.45	28.50	24.90	24.86	21.15	18.80	18.23	18.23	18.00	17.80
% $SnBr_4$	94.12	94.07	93.67	92.75	91.65	89.81	85.54	82.49	82.38	80.31
M. p., °C	16.60	16.55[a]	...	...	...	...	...	...	...	...
Soln. p.	..	...	18.33	23.60	28.70	34.25	42.60	45.75	45.80	47.25
% $SnBr_4$	78.97	78.44	75.14	71.38	64.77	64.00	63.30	52.83	43.60	43.34
Soln. p.	47.70	47.20	48.60	48.60	48.48	48.50	48.50	46.30	41.67	41.45
% $SnBr_4$	40.63	26.33	26.09	21.67	20.39	16.55	14.08	11.88	10.61	9.45
M. p., °C	...	...	...	16.3[a]	...	13.2	10.7	7.1	5.45	3.25
Soln. p.	39.75	25.22	25.00	18.42	16.60	8.00	1.8	−17.8	...	...
% $SnBr_4$	8.93	6.29	5.37	2.97	2.41	1.88	0.92	0.58	0.39	0.00
M. p., °C	2.5	−3.5	5.0	17.1	21.8	24.00	37.7	45.7	53.05	...

[a] Quadruple point.

Carbon Tetrachloride.—A good grade of carbon tetrachloride, taken as starting material, was allowed to stand for several days over sodium hydroxide and then over metallic sodium for two or three days. It was next subjected to repeated fractionation, using a fractionating column about 60 cm. long. Other methods of purification were tried, but the product obtained in this way was of the best quality; it boiled sharply at 75.8° (745.7 mm.). It was kept in the dark in well-stoppered flasks until it was needed for use.

The methods of preparing mixtures of this substance with sulfur dioxide were practically the same as the methods used with other compounds. At temperatures above the melting point of carbon tetrachloride (—24.8°) the mixtures were homogeneous solutions and consequently all investigations with this substance were made in a bath of carbon dioxide and acetone.

Accurate determinations of freezing points were not always easily made with this pair of components. When two liquid phases were obtained they seemed to be of about the same index of refraction and as a result solubility points could not be seen clearly. When solid phases appeared they were of a waxy character and solubility points were not sharp.

The curve obtained was of very much the same type as the tin tetrabromide curve. The critical solution temperature was at —29.3° and both liquids were stable phases down to about —45°. It was impossible to trace the binary-liquid curve into the metastable region.

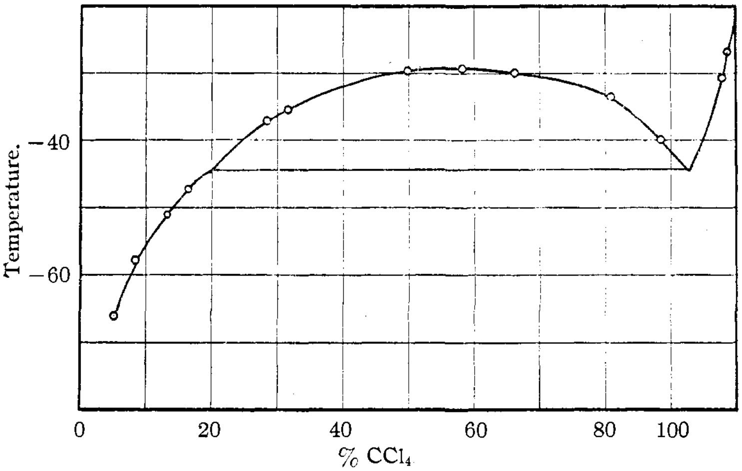

Fig. 4.

Table II

Carbon Tetrachloride

% CCl_4	98.79	97.81	97.44	95.43	88.44	82.56	80.83	70.89	66.26	58.98
M. p., °C	−26.78	30.58	34.90	44.63	...	...	...	...	...	...
Soln. p	...	...	...	...	−39.80	34.9	33.57	...	29.8	29.37
% CCl_4	58.19	49.93	42.66	31.66	28.36	16.44	15.31	13.33	8.42	5.24
M p., °C	...	...	...	...	...	47.2	47.5	50.9	57.9	66.1
Soln. p	29.27	29.68	...	35.2	37.2	...	...	...	...	...

Tin Tetrachloride.—Tin tetrachloride was prepared from tin shot and from chlorine obtained from cylinders. The gas was passed into a retort containing the tin and the heat of reaction was sufficient to cause the compound to distil out of the retort and through a water-cooled condenser. The liquid obtained in this way was colored with chlorine and it fumed strongly when brought into contact with moist air. It was allowed to stand over metallic tin and was then subjected to fractional distillation. The fractions were caught in a rotating receiver, all precautions being taken to keep the liquid away from moist air. The resulting product boiled at 112.1° (750 mm.) and solidified at —32.7°. Other observers record the following boiling points: 112° (754.9 mm.) by Haagen,[8]

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[8] Haagen, *Pogg. Ann.*, **131**, 117 (1867).

112.5° (752 mm.) by Andrews,[9] 113.89° (760 mm.) by Thorpe,[10] 114° (765 mm.) by Walden.[11] A melting point of —33° is recorded by Besson.[12]

When the tubes were to be filled, tin tetrachloride was distilled from the main supply into the flask which was part of the apparatus for filling the tubes by distillation. The air in this apparatus had been previously dried by passing it over phosphorus pentoxide. When the sealed tubes had been weighed they were cooled with ice and salt and opened for the introduction of the liquid sulfur dioxide. At low temperatures there is very little vaporization of the tetrachloride and when the sulfur dioxide is run into the tubes rapidly no contamination is observed. In case contamination was observed the tube was rejected.

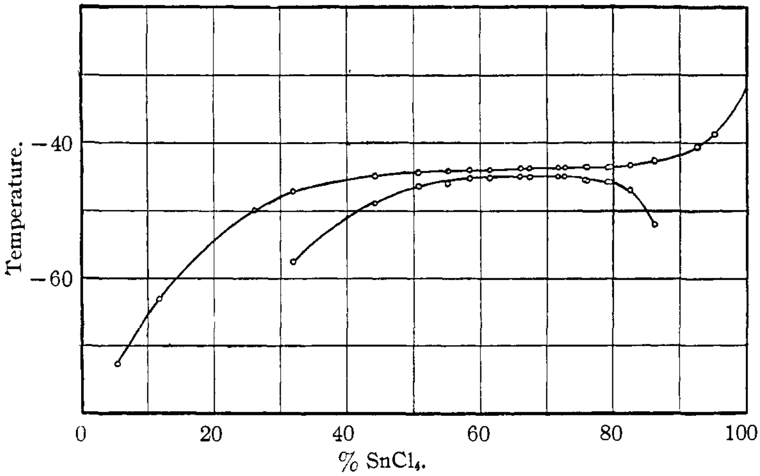

Fig. 5.

Since tin tetrachloride melts at —32.7° it would be expected that the solubility curve would be confined to lower temperatures and such was found to be the case. Unlike tin tetrabromide, however, this compound when mixed with sulfur dioxide gave no stable binary-liquid curve; but by carefully cooling the mixtures it was possible to obtain metastable

Table III

Stannic Chloride

$SnCl_4$, %.....	100.00	95.23	92.66	86.16	82.41	79.43	79.05	76.07	75.76	72.62	71.75	67.47
M. p., °C....	−32.7	38.7	40.6	42.6	43.25	43.6	43.6	43.4	43.4	43.6	43.7	43.8
Soly. p. (meta)	...	...	...	−52.0	46.8	45.7	45.7	45.6	45.4	44.9	44.9	45.0

$SnCl_4$, %.....	66.06	61.54	61.35	58.54	55.24	50.76	44.27	31.96	26.29	11.78	5.40
M. p., °C....	43.8	43.9	43.9	44.0	44.1	44.3	44.8	47.1	49.8	63.0	72.7
Soly. p. (meta)	45.0	45.1	45.1	45.3	45.9	46.3	48.8	57.5			

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[9] Andrews, *Chem. News*, **25,** 61 (1847).

[10] Thorpe, *J. Chem. Soc.*, **37,** 331 (1880).

[11] Walden, *Z. physik. Chem.*, **70,** 581 (1910).

[12] Besson, *Compt. rend.*, **109,** 940 (1889).

binary-liquid systems, the binary-liquid curve lying completely below the solid-liquid solubility curve.

Titanium Tetrachloride.—The titanium tetrachloride used in this work was obtained by the purification of a crude grade of that compound. This crude liquid, which is colored reddish-yellow by ferric chloride and by other chlorides, is purified only with considerable difficulty. A lemon-yellow product boiling over a range of 0.2° is obtained without difficulty, but further purification is effected only by repeated careful fractionation. The yellow color is said to be due to the presence of vanadyl chloride which boils at 126° while titanium tetrachloride boils at 136°. By repeated fractionation a product boiling at 136.0° (750 mm.) and having no trace of color was obtained. Thorpe[13] records a boiling point of 136.35° at 753.28 mm. and others report the boiling point to be "about 136°." It was perfectly stable when kept away from the air and showed no tendency to become colored upon long standing.

The work on the system titanium tetrachloride-sulfur dioxide has not been completed. Data obtained place the critical solution temperature at 11.9° with 55.80% of titanium tetrachloride in solution.

Conclusions

The marked solubility of the tetrahalogen compounds of carbon, titanium and tin corresponds with what would be expected according to the views of Hildebrand[14] and Mortimer.[15] The polarities of the compounds are low, and, according to the rule that liquid compounds of nearly equal polarity are likely to be miscible in all proportions, we should expect the tetrahalogen compounds to be very soluble in sulfur dioxide which itself has a very low polarity. If the polarities change unequally with change in temperature, we may find incomplete solubility above or below certain temperatures. Other factors such as the relative change in internal pressures with change in temperature must also be taken into account for a more perfect understanding of the results.

In no case has compound formation been apparent. It does not seem to occur at temperatures above the melting point of sulfur dioxide (—72°), and if it does occur below this temperature, certainly the compounds are not conspicuous. With compounds of low polarity we should hardly expect to find the striking examples of compound formation that we find in the case of sulfur dioxide with the highly polar potassium iodide. It should be admitted, however, that there is a possibility of compound formation within the region made up of solid phases, though the probability of this is not great.

[13] Thorpe, *J. Chem. Soc.*, **47**, 108 (1885).

[14] Hildebrand, "Solubility," Am. Chem. Soc. Monograph, Chemical Catalog Co., **1924**.

[15] Mortimer, THIS JOURNAL, **44**, 1416 (1922); **45**, 633 (1923).

In the system tin tetrachloride-sulfur dioxide we have a rather unusual case. A curve for the two-liquid phase system was obtained, and over the same composition range a curve for the solubility of the solid tin tetrachloride in sulfur dioxide was obtained, the first curve lying completely below the latter. However, the fact that such curves exist need not be unexpected, and several such systems are known.

It is interesting to note that in determining the solubility of the solid in liquid at concentrations where the two curves ran close together, opalescence was observed after the solid had completely dissolved. This would seem to indicate that opalescence may occur at times other than those at which the mixtures are caused to transform from the binary-liquid state to the homogeneous state.

Summary

1. Sulfur dioxide in contact with the liquid tetrahalide compounds forms mixtures which are but partially miscible at lower temperatures.

2. The relative positions of the critical mixing temperatures are such as might have been predicted from the polarities, internal pressures and the melting points of the compounds involved.

3. In the case of the system sulfur dioxide-tin tetrachloride a metastable binary-liquid system was found.

4. Compound formation was not apparent at temperatures above the melting point of sulfur dioxide.

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[Contribution from the Bureau of Mines, United States Department of Commerce]

ADJUSTED VAPOR PRESSURES OF ZINC AND CADMIUM[1]

By Charles G. Maier

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During recent experimental determinations of certain reduction equilibria of zinc oxide, carried out at the Berkeley station of the Bureau of Mines, need arose for data on the free energy and heat of vaporization of zinc and cadmium, from both the solid and liquid state. For both of these metals experimental vapor-pressure determinations of solid and liquid metal, as well as values for the heat of fusion, are available. It was found, however, that direct calculation of the heat and free energy from these values does not lead to entirely consistent results unless some adjustment of the data is made. This is especially true when one attempts to extrapolate to ordinary temperature, in order to calculate the standard free-energy change.

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[1] Published by permission of the Director of the Bureau of Mines, Department of Commerce.