[CONTRIBUTION FROM THE DIVISION OF INORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

# Equilibria in Certain Tetrahalide Systems

BY P. A. BOND AND E. B. CRONE

Previous investigations have shown that the halides of many elements are appreciably soluble in liquid sulfur dioxide. In those cases where the melting points of the halides are low, systems of two liquid phases may be formed. Bond and Beach[1] studied systems of this type formed by carbon tetrachloride, stannic chloride and stannic bromide. Bond and Stephens[2] added those of titanium tetrachloride and of silicon tetrachloride. The last-named authors found also that the zirconium tetrachloride–sulfur dioxide system differed radically from the others mentioned, in that two liquid phases did not appear, and that a solvate $ZrCl_4 \cdot SO_2$ was formed. The purpose of the present work was to extend these investigations by a study of the behavior of titanium tetrabromide, germanium tetrachloride and lead tetrachloride in the same solvent.

The method of investigation used was developed by the previous workers mentioned,[1,2] and was essentially that first described by Alexejew.[3] It consists in sealing known weights of the two components in glass tubes, then rotating them in a bath whose temperature is controlled, and noting the temperature at which the two phases become one. From a series of such measurements the solubility curve may be constructed. The advantages of the method are that no chemical analyses of the solutions are required, and that it is applicable to volatile liquids above their boiling points.

## Experimental Part

Most of the tetrahalides of the elements of Group IV of the periodic system hydrolyze very rapidly with the formation of various hydrated compounds. Those to be described are not exceptional in this respect, for they fume even in ordinary air. This fact makes transfer of them in a moisture-free atmosphere imperative.

The apparatus used and the method followed in charging the specimen tubes with halide have been described by Bond and Beach.[1] In order to reduce to a minimum the chances of hydrolysis it was found best to maintain a current of dried air through the rotating receiver while the tubes were being filled, and to cool them to −25° in an acetone–solid carbon dioxide bath before they were sealed.

The sulfur dioxide was of the usual commercial grade obtained in small iron cylinders. It was purified by passing it successively through sulfuric acid, granular calcium chloride and phosphorus pentoxide. The gas was liquefied in a spiral glass condenser cooled by ice and salt, and the liquid received in a special Dewar flask. This receiver and the method of measuring liquid sulfur dioxide from it into the specimen tubes has been described fully by Bond and Stephens.[2]

The last-mentioned authors have also described in detail the method used in determining solution points, where the temperatures were below 0°. The same method was used in this work where the temperatures were low. Above 0° determinations were made in a water-bath, to which some sodium chloride was added at temperatures above 80°. Special carriers were provided to suspend the specimen tubes in the bath, and to enable them to be rotated.

For temperatures above 0° a mercury thermometer was used, and below 0° a pentane thermometer. Each was checked against a thermometer certified by the Bureau of Standards. It was necessary to apply corrections for emergence of the thermometer stem only at temperatures above 30°. At all lower temperatures the thermometer was immersed completely.

### Titanium Tetrabromide

As a check on its purity titanium tetrabromide was prepared by two methods. In the first, gaseous hydrogen bromide prepared by the action of liquid bromine on naphthalene at room temperature,[4] was allowed to bubble through titanium tetrachloride held at 50°. The titanium tetrachloride was a Kahlbaum product, perfectly clear and colorless. After the stream of hydrogen bromide had been passed into the reaction flask for twenty-four hours, it was interrupted and the reaction mixture allowed to cool. The product solidified at once to a mahogany-red mass of crystals.

In the second method C. P. titanium dioxide mixed with carbon was acted upon by bromine vapor at red heat, according to Hoffman.[5] The crude product had the same general appearance as that made by the first method.

The products from the two sources were purified separately, but by the same procedure, and were found to have identical properties and composition. They were first fractionally distilled six times. The first few cubic centimeters of each distillate were discarded, since they were darker in color than the subsequent fractions. Air dried by phosphorus pentoxide was drawn through the melted bromide to displace any dissolved hydrogen bromide, and it was then fractionally crystallized three times. The color of the final product was then transparent amber. It boiled at 230° (751 mm.) and melted at 38.2°. Other observers have noted the boiling points: 230° by Baxter and Butler[6] and by Young and Schumb,[7] and 229° (un-

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[1] Bond and Beach, THIS JOURNAL, **48**, 348 (1926).

[2] Bond and Stephens, *ibid.*, **51**, 2910 (1929).

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

[4] Kastle and Bullock, *Am. Chem. J.*, **18**, 105 (1896).

[5] Hoffman, *Proc. Roy. Soc.* (London), **8**, 42 (1857).

[6] Baxter and Butler, THIS JOURNAL, **50**, 408 (1928).

[7] Young and Schumb, *ibid.*, **52**, 4233 (1930).

corr.) by Thorpe.[8] The following melting points are noted: "about 40°" by Thorpe,[8] 39° by Biltz and Keunecke[9] and by Ruff and Eisner,[10] and 38.5° by Falciola.[11]

The results of the determination of solubility points are contained in the data in Table I, and are shown graphically in Fig. 1. At temperatures above 29° two liquid phases occur, which have a critical solution temperature of 103.8°. The separation of the solution into two liquid layers is sharp, and the temperature at which the change occurs can be determined easily. Solutions whose concentrations are near the critical solution point exhibit an opalescence just above their solution temperatures. However, because the solutions are amber in color, it is not particularly noticeable.

At concentrations greater than 96% and less than 9% of titanium tetrabromide the binary liquid miscibility curve is metastable. It could be followed to temperatures below 29° only by slow and careful cooling. If the solutions were cooled rapidly crystallization resulted, and the points found lay on the stable melting point curve. At low temperatures the solubility of titanium tetrabromide in sulfur dioxide is very slight, for which reason the eutectic point could not be determined exactly.

TABLE I

MISCIBILITY OF $TiBr_4$ WITH $SO_2$

| $TiBr_4$, % | Soln. pt. | M. p., °C. | $TiBr_4$, % | Soln. pt. | M. p., °C. |
|---|---|---|---|---|---|
| 100.00 | | 38.2 | 48.58 | 98.9 | |
| 99.10 | | 35.4 | 42.28 | 94.1 | |
| 98.07 | | 33.1 | 36.06 | 87.6 | |
| 97.03 | 23.5 | 30.8 | 32.46 | 83.3 | |
| 95.95 | 34.5 | | 29.33 | 79.7 | |
| 95.14 | 45.3 | | 26.28 | 74.9 | |
| 94.10 | 53.4 | | 24.22 | 70.8 | |
| 93.20 | 57.8 | | 21.06 | 64.7 | |
| 91.96 | 67.6 | | 19.24 | 61.2 | |
| 91.43 | 72.0 | | 15.92 | 50.8 | |
| 88.73 | 81.4 | | 12.52 | 44.0 | |
| 88.05 | 84.5 | | 11.47 | 40.3 | |
| 84.23 | 92.6 | | 10.66 | 36.1 | |
| 80.82 | 97.8 | | 9.88 | 33.8 | |
| 78.54 | 100.8 | | 9.20 | 31.6 | |
| 74.90 | 102.9 | | 8.94 | 29.0 | 29.4 |
| 73.57 | 103.2 | | 7.45 | 22.0 | 26.2 |
| 71.97 | 103.3 | | 7.05 | 18.8 | 24.4 |
| 71.08 | 103.5 | | 6.36 | 16.0 | 23.5 |
| 70.05 | 103.7 | | 4.98 | | 18.5 |
| 68.87 | 103.8 | | 4.06 | | 14.0 |
| 65.22 | 103.8 | | 3.00 | | 8.2 |
| 64.53 | 103.8 | | 2.54 | | 3.5 |
| 63.78 | 103.3 | | 1.79 | | − 1.0 |
| 60.63 | 103.0 | | 1.22 | | −12.8 |
| 57.20 | 102.4 | | 1.14 | | 13.2 |
| 53.18 | 101.4 | | 1.08 | | 17.0 |
| 52.24 | 100.8 | | 0.80 | | 21.7 |
| 51.61 | 100.4 | | .00 | | 75.5 |

### Germanium Tetrachloride

The germanium used was extracted from germanite by the method of Dede and Russ,[12] and recovered in the form of the dioxide. To obtain the chloride the general method of Bauer and Burschkies[13] was followed but the reaction between germanium dioxide and concentrated hydrochloric acid was carried out in sealed tubes heated to 165° in a bomb furnace. The colorless liquid product was dehydrated by distillation from concentrated sulfuric acid. Air was bubbled through the liquid at −15° in order to displace any dissolved hydrogen chloride. It was then distilled from anhydrous sodium carbonate, and fractionated twice. It boiled sharply at 84.0° (756 mm.), and melted at −51.8°. Other observers have recorded the boiling point as: 86.5° by Dennis and Hance,[14] 85.5° by Pugh and Thomas[15] and by Bauer and Burschkies,[13] 83.1° by Laubengayer and Tabern,[16] and 83.0° by Dede and Russ.[12] Melting points of −49.5° by Dennis and Hance[14] and of −50° by Laubengayer and Tabern[16] are noted.

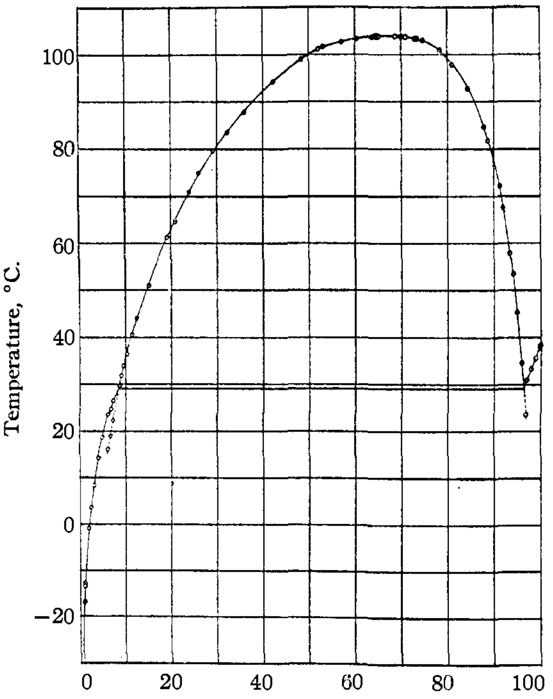

Fig. 1.—Miscibility of titanium tetrabromide with sulfur dioxide.

Above 0° solutions of germanium tetrachloride with sulfur dioxide in any concentration form a single liquid phase. Hence all determinations of solubility points were made in an acetone bath cooled to a low temperature. Between the limits of 6 and 97% of germanium tetrachloride two binary liquid phases were stable above −56°. The critical solution temperature was −4.7°. Separation of the solution into two liquid phases was extremely sharp, and solution temperatures could be determined very accurately. A bluish opalescence appeared in the region of the critical solution point, but persisted over a temperature range of less than 1.0°. Below −56° the binary liquid miscibility

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(8) Thorpe, *J. Chem. Soc.*, **47**, 126 (1886).

(9) Biltz and Keunecke, *Z. anorg. Chem.*, **147**, 179 (1925).

(10) Ruff and Eisner, *Ber.*, **41**, 2250 (1908).

(11) Falciola, "Int. Crit. Tables," Vol. IV, p. 214.

(12) Dede and Russ, *Ber.*, **61**, 2451 (1928).

(13) Bauer and Burschkies, *ibid.*, **66**, 277 (1933).

(14) Dennis and Hance, THIS JOURNAL, **44**, 299 (1922).

(15) Pugh and Thomas, *J. Chem. Soc.*, **129**, 1051 (1926).

(16) Laubengayer and Tabern, *J. Phys. Chem.*, **30**, 1047 (1926).

curve could be followed far into the metastable region. The solutions undercooled so persistently that points on the melting point curve could be obtained only by removing the specimen tubes momentarily from the cooling bath and chilling them in liquid air, in order to start crystallization.

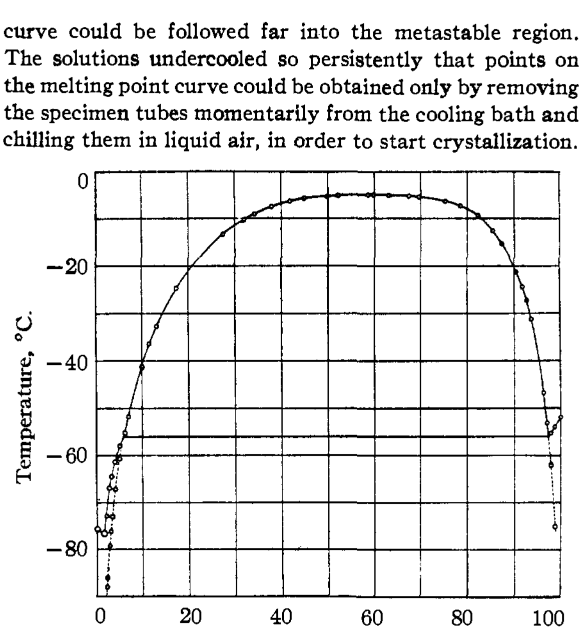

Fig. 2.—Miscibility of germanium tetrachloride with sulfur dioxide.

Thereafter the melting points could be determined in the usual way without great difficulty. The data obtained are given in Table II, and the results shown graphically in Fig. 2.

TABLE II

MISCIBILITY OF $GeCl_4$ WITH $SO_2$

| $GeCl_4$, % | Soln. pt. | M. p., °C. | $GeCl_4$, % | Soln. pt. | M. p., °C. |
|---|---|---|---|---|---|
| 100.00 | | −51.8 | 41.86 | −6.2 | |
| 98.80 | −75.0 | 53.9 | 37.78 | 7.4 | |
| 97.97 | 61.9 | 55.0 | 34.22 | 9.0 | |
| 97.07 | 53.0 | | 31.95 | 10.1 | |
| 96.41 | 46.6 | | 27.52 | 13.1 | |
| 93.72 | 31.0 | | 17.52 | 24.6 | |
| 92.72 | 27.2 | | 13.16 | 32.7 | |
| 91.76 | 24.2 | | 11.31 | 36.4 | |
| 90.58 | 21.1 | | 10.07 | 41.2 | |
| 87.42 | 15.0 | | 7.00 | 51.5 | |
| 85.54 | 12.3 | | 6.26 | 55.2 | |
| 82.24 | 9.2 | | 5.15 | 60.5 | −58.0 |
| 78.62 | 7.1 | | 4.21 | 67.1 | 61.2 |
| 75.36 | 6.1 | | 3.48 | 73.0 | 64.5 |
| 69.42 | 5.2 | | 3.07 | 76.1 | 66,0 |
| 68.78 | 5.2 | | 2.71 | 79.2 | 66.8 |
| 67.59 | 5.0 | | 2.17 | 86.0 | 71.8 |
| 63.98 | 4.9 | | 2.07 | 88.0 | 72.8 |
| 63.06 | 4.9 | | 1.55 | | 76.5 |
| 59.87 | 4.7 | | 1.48 | | 76.5 |
| 58.81 | 4.7 | | 0.94 | | 76.1 |
| 52.37 | 4.9 | | 0.72 | | 75.9 |
| 49.92 | 5.1 | | .00 | | 75.5 |
| 45.00 | 5.5 | | | | |

### Lead Tetrachloride

Lead tetrachloride was prepared by the method of Friedrich.[17] This compound is so unstable above 0° that solutions of known concentration cannot be prepared and examined satisfactorily by the method used for the other halides. Hence the results reported here are qualitative only.

Lead tetrachloride dissolves readily in liquid sulfur dioxide. The solutions are colored a pale yellow. If kept above 0° for more than a few minutes, decomposition begins and lead dichloride is deposited. If the solutions are cooled, they show no signs of forming a binary liquid system, but instead deposit lemon-yellow crystals. An analysis of these crystals showed that they consisted of unsolvated lead tetrachloride. The removal of adhering sulfur dioxide from the crystals preparatory to analysis was accomplished by pressing them on a porous plate in a desiccator, which was kept at a temperature below their melting point by means of solid carbon dioxide. Dry air was circulated through the desiccator to carry away the sulfur dioxide and carbon dioxide evolved.

## Conclusions

Previous work in this Laboratory, to which reference has been made, has shown that the tetrachlorides of carbon, silicon, titanium and tin form with sulfur dioxide systems of two liquid phases, and that these observations are in accord with the principles expressed by Hildebrand[18] and by Mortimer.[19] Each of these chlorides has a low dielectric constant (they range between 2.3 and 3.2) and their limited miscibilities with sulfur dioxide may be correlated with the considerably higher value of 15.6 for the latter. Their internal pressures, where calculations could be made, were found to be of the same general magnitude as that of sulfur dioxide.

The dielectric constant of germanium tetrachloride is given by Lear[20] as 2.6. This value would place it between silicon and titanium tetrachlorides in the series given above. In this investigation its miscibility with sulfur dioxide was found to resemble more closely that of silicon tetrachloride. This is in harmony with the fact that the melting and boiling points of germanium tetrachloride are closer to those of silicon tetrachloride than to those of titanium tetrachloride.

The solubility behavior of titanium tetrabromide with sulfur dioxide should be compared with that of the previously studied tin tetrabromide rather than with those of the chlorides mentioned. The dielectric constant of neither bromide is known, but their relative miscibilities as determined harmonize with the fact that the melting

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(17) Friedrich, *Ber.*, **26**, 1434 (1893).

(18) Hildebrand, "Solubility," The Chemical Catalog Co., New York, 1924.

(19) Mortimer, This Journal, **44**, 1416 (1922); **45**, 633 (1923).

(20) Lear, *J. Phys. Chem.*, **28**, 889 (1924).

and boiling points of titanium tetrabromide are the higher.

That lead tetrachloride does not appear to form a system of two liquid phases with sulfur dioxide is not surprising in view of the metastable nature of the system formed by tin tetrachloride.[1]

In none of the three systems investigated was evidence of compound formation with the solvent discovered. With substances of such low polarity as those in question we should hardly expect to find compounds of as great stability as those which are formed by the highly polar alkali iodides with sulfur dioxide.

## Summary

1. The solubility relations of the partially miscible systems formed by titanium tetrabromide and by germanium tetrachloride with liquid sulfur dioxide have been investigated over the entire range of composition.
2. These relations are such as may be expected from considerations of polarity, internal pressure, and melting and boiling points.
3. Lead tetrachloride does not form such a partially miscible system.
4. No evidence of compound formation was discovered.

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[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF HARVARD UNIVERSITY]

# The Induced Decomposition of Acetaldehyde[1]

BY AUGUSTINE O. ALLEN AND DARRELL V. SICKMAN

It recently has been shown[2] that the kinetics of various organic decompositions including that of acetaldehyde can be explained by supposing them to be chain reactions, with free methyl and other organic radicals carrying on the chains. It seemed important to determine whether such chains actually can exist, and whether methyl radicals will react with molecules, such as those of acetaldehyde, with the proper activation energy. This test has been made by heating a mixture of acetaldehyde and azomethane to temperatures around 300°, where the aldehyde is inert, while the azo compound decomposes at a measurable rate, presumably giving free methyl as the initial step in its decomposition.[3]

## Experimental

The azomethane was made by the method of Ramsperger[4] and fractionated carefully to remove dissolved air and other impurities. Acetaldehyde (Eastman best grade) was purified by fractionating several times before using. The vapors of these compounds were let through stopcocks into an evacuated one-liter bulb, and allowed to stand overnight to ensure thorough mixing. It was found that if any traces of air were present a reaction, presumably polymerization of the aldehyde, would occur resulting in the formation of a reddish water-soluble tar; but with greater precautions to exclude air, the mixture could be kept indefinitely. In making runs, a portion of the mixture would be let into another bulb, connected to the reaction vessel through a three-way stopcock, its other lead connecting the reaction vessel directly to the pump. The gas would then be admitted to the evacuated reaction flask, and pressure allowed to equalize before closing the stopcock again; the reaction could be followed on a mercury manometer connected to the reaction flask, while another manometer on the admission bulb gave the initial pressure. The reaction vessel was a 200-cc. Pyrex bulb. Another bulb of the same size was also used, packed with short pieces of 4 mm. (o. d.) Pyrex tubing, with ends fire-polished; the surface was increased 12- or 13-fold. Between runs the reaction bulb would be evacuated to $10^{-4}$ mm. or less. A mercury diffusion pump backed by an oil pump was used. The oil in the latter had to be changed frequently, acetaldehyde dissolving readily in it and eventually preventing the attainment of a good vacuum. The reaction bulb was in an electrically heated air-bath, whose temperature was kept spatially uniform by separate adjustments of heating units at its ends, and temporally constant to ±0.5° by a de Khotinsky bimetallic regulator. Temperatures were measured by an iron–constantan thermocouple calibrated in boiling sulfur.

In a preliminary experiment, acetaldehyde was found to show no pressure change on standing overnight at 300°. To test the effect of mercury vapor, a drop of mercury was introduced into the reaction bulb together with the aldehyde, but once the mercury had distilled out again it was seen that no aldehyde had decomposed. The mercury catalyzed decomposition of aldehyde reported by Kassel[5] was thus not observed; Kassel's pressure increases are probably to be explained simply by the rather slow evaporation of the mercury droplets which are introduced in his experiments. The azomethane was found to decompose at rates agreeing with those of Ramsperger.[4]

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(1) A preliminary notice of this work appeared as a Communication to the Editor, THIS JOURNAL, **56**, 1251 (1934).

(2) F. O. Rice and Herzfeld, *ibid.*, **56**, 284 (1934).

(3) Kassel, "The Kinetics of Homogeneous Gas Reactions," p. 199.

(4) Ramsperger, THIS JOURNAL, **49**, 912 (1927).

(5) Kassel, *J. Phys. Chem.*, **34**, 1171 (1930).