parallel or symmetrical extinction. There is a tendency to form twins. It has low birefringence, less than 0.01 and a positive sign of elongation.

The Ternary System $MgCl_2$–KCl–H_2O

Table IV, Fig. 3.—Even with increased temperature the area of existence of $MgCl_2 \cdot 6H_2O$ has not increased appreciably. It still represents a very small portion of the entire diagram. Since potassium chloride was determined directly on a sample of saturated solution, the values obtained for the isothermally invariant composition of solutions in equilibrium with carnallite and $MgCl_2 \cdot 6H_2O$ are slightly lower than those reported at nearby temperatures.

Acknowledgment.—The authors wish to thank Dr. R. L. Barrett for his assistance in the identification of the crystalline and optical properties of the substances encountered in the experimental portion of the study.

Summary

1. The isotherms for the ternary systems at 75° are given.

2. The ternary compound $2KCl \cdot CaCl_2 \cdot 2H_2O$ has been found to exist at 75°.

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[Contribution from Battelle Memorial Institute]

The Vapor Pressure of Liquid Titanium Tetraiodide

By John M. Blocher, Jr., and Ivor E. Campbell

The literature is fairly complete with respect to the vapor pressures of zirconium,[1] thorium,[2] and tin[3] tetraiodides. However, no data are available for titanium tetraiodide. All references to its volatility and boiling point stem from the original work of Hautefeuille,[4] who simply states that it has a sensible vapor pressure at room temperature, melts at 150° and boils at a little above 360°, distilling without decomposition.

The present work represents the first determination of its vapor pressure. Titanium tetraiodide is extremely hygroscopic as well as being easily oxidized in air. Hence a suitable technique was developed for its preparation, purification, and transfer *in vacuo*.

Materials and Procedure

Titanium tetraiodide was prepared by the direct iodination of crude titanium (98%) containing 1.6% iron and some calcium as the principal impurities. Twenty grams of titanium (100% excess), having been previously washed with dilute hydrofluoric acid, distilled water, and absolute alcohol and dried, was placed in the middle bulb e of the glass apparatus in Fig. 1 which was sealed at f, stoppered at a, evacuated with flaming to 10^{-3} mm., and then let down to dry air. One hundred grams of dry resublimed iodine was liquefied in the funnel at a and allowed to run into the end bulb at c. A seal was made at b and the funnel was pulled off at that point. With bulb c cooled in Dry Ice, the system was again evacuated and sealed off at i. The middle bulb was maintained at 525° while the end bulbs were alternately heated and cooled in air in such a way as to drive the iodine slowly back and forth across the hot titanium. After three passes, the conversion was apparently complete. With bulb c cooled in Dry Ice, about one-half of the titanium tetraiodide in h was distilled into c which was then sealed off at d. One-third of the remaining material was distilled in a like manner into e, a seal made at g and bulb h pulled off. This left about 30 g. of iodine-free titanium tetraiodide in bulb h. To provide for the breaking of this ampoule, the flame of an oxygen torch was touched to the glass wall, whereupon a concave thin glass "bubble" was formed. This operation required some care and practice. The ampoule containing the titanium tetraiodide was sealed into the vapor-pressure apparatus as indicated in Fig. 2.

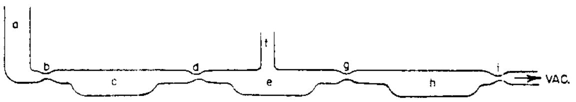

Fig. 1.

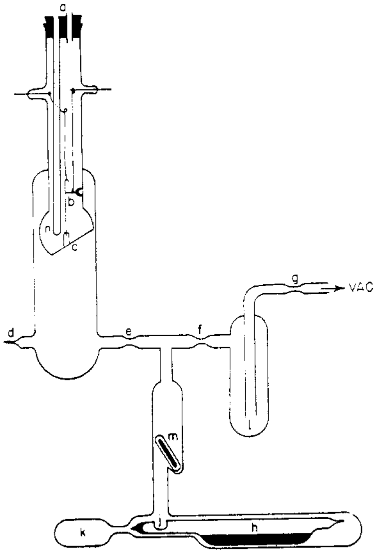

Fig. 2.

The differences in the boiling points of iodine (b. p. 184°), titanium tetraiodide (b. p. 377°), and calcium iodide (b. p. 718°) are such as to permit separation by distillation. A qualitative thiocyanate test for iron in the sample used was negative.

The vapor-pressure measurements were carried out in an all-glass manometer of the type described by Daniels[5]

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[1] Rahlfs and Fischer, *Z. anorg. allgem. Chem.*, **211**, 349 (1933).

[2] Fischer, Gewehr and Wingschen, *ibid.*, **242**, 161 (1939).

[3] Negishi, This Journal, **58**, 2293 (1936).

[4] Hautefeuille, *Bull. Soc. Chim.*, [2] **7**, 202 (1867).

[5] F. Daniels, This Journal, **50**, 1115 (1928).

in which the unknown vapor pressure on one side of a thin glass diaphragm (c) provided with electrical contacts (b) was balanced by a measured pressure on the other side (communicated through a). In the present work the contacts were connected to an electronic relay and indicating light.

Normally the contacts of the manometer are set to close with a slight positive pressure above the diaphragm. It has been stated[5] that the zero setting or "head" of the manometer does not change sensibly over a wide temperature range. In contrast, one manometer used in preliminary work had a sensitivity of ±0.5 mm., while its "head" varied from 4 mm. at room temperature to about 20 mm. at 230°. The manometer used in obtaining the present data had a sensitivity of better than ±0.2 mm. Its variation of "head" with temperature was determined before the run. The "head" changed from 2.0 mm. at 160° to 4.0 mm. at 360°. A ±1 mm. uncertainty was assigned to this "head" correction in view of the tension placed on the contacts and diaphragm during subsequent glass-blowing operations, despite the fact that the "head" returned after the glass blowing to within 0.5 mm. of its initial value at room temperature.

In order to fill the manometer, the system was evacuated on both sides of the diaphragm to 10^{-3} mm. and heated by a soft flame. With bulb k and trap l cooled in Dry Ice, the "bubble" j on the sample ampule was broken with the magnetically operated, glass-enclosed striker m. The bulb containing the sample ampoule was heated and about one-third of the sample distilled into the trap and bulb k. The trap was then sealed off at f, a seal made at i, and about one-half of the remaining sample distilled into the manometer. Then with bulb h cooled in Dry Ice, the manometer was heated and about one-third of the sample driven out prior to making a seal at e and pulling off the auxiliary apparatus at that point. No free iodine was observed in any part of the apparatus during the above operations.

In the system connected with a were included a vacuum pump, mercury manometer, Pirani gage and a device for the controlled admission of air to raise the pressure above the diaphragm. A coil heater extended down into the well n above the diaphragm to keep its temperature above that of the liquid pool in order to prevent condensation on the diaphragm. During the vapor-pressure measurements the manometer was immersed to a point about 2 inches above the ring seal in a well-insulated, well-stirred salt-bath which was electrically heated and maintained within ±0.3° of the equilibrium temperature. The temperature of the bath was recorded by a double junction copper–constantan thermocouple calibrated against the freezing and boiling points of water and the melting points of standard samples of tin, lead and zinc.

At the completion of a run, a piece of rubber tubing with two clamps along its length was slipped over the fragile tip *d* which was crushed inside the tubing. The rate of admission of air to the bulb could be regulated so as to equalize the pressure on the diaphragm as the system was let down to air.

Results

The data are given in Fig. 3. Each point represents the average of two or three readings at equilibrium temperature. The maximum deviation from the mean of the pressure readings was ±1 mm. at high pressures and ±0.5 mm. at low pressures. The maximum deviation from the mean of the temperature measurements was ±0.1°. The data fit the equation $\log p$ (mm.) = $-(3054/T) + 7.5773$ to an average deviation of ±0.7 mm. and a maximum deviation of ±1.5 mm. Calculations from the data give the following for $TiI_{4(l)} \rightleftarrows TiI_{4(g)}$[6]

$$\log p_{(\text{atm.})} = (3054/T) + 4.696$$
$$\Delta H = 13{,}975 \text{ cal./mole}$$
$$\text{B. p.} = 377.2 \pm 0.2^\circ$$
$$\Delta F^\circ = 13{,}975 - 21.49\,T$$
$$\Delta S = 21.49 \text{ E.U.}$$

No heat capacity data are available with which to expand the thermodynamic functions.

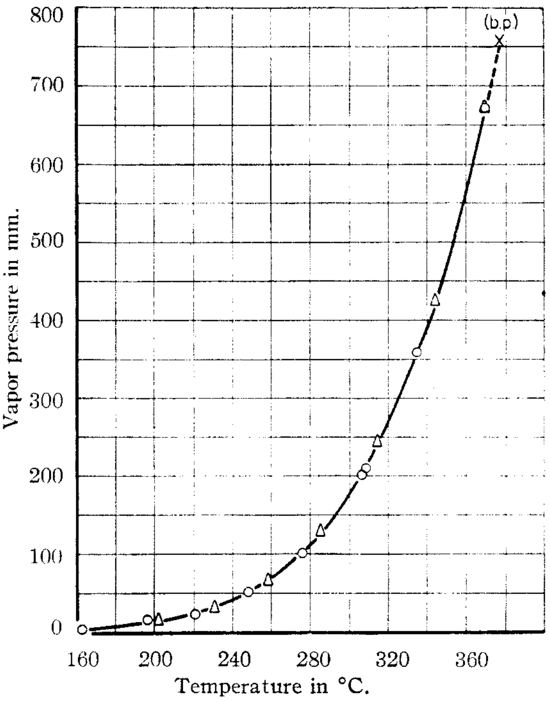

Fig. 3.—O, Ascending points; △, descending points.

It is believed that the temperature measurements are good to ±0.2° and the accuracy of the pressure measurements limited by the uncertainty (±1 mm.) in the "head" correction.

Acknowledgment.—The authors wish to acknowledge the financial aid of the Iodine Educational Bureau, Inc., in carrying out the vapor-pressure measurements.

Summary

The vapor pressures of liquid titanium tetraiodide have been found to fit the equation $\log p$ (mm.) = $-(3054/T) + 7.5773$ to within ±1.5 mm. from 4 to 670 mm. The boiling point has been established at 377.2 ± 0.2° and the heat of vaporization of 13,975 cal./mole has been calculated.

Difficulties with the temperature stability of the Daniels-type all-glass manometer have been noted.

A suitable technique has been described for the preparation, fractionation, and transfer of titanium tetraiodide *in vacuo* which should have general application to very reactive volatile materials.

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(6) Vapor phase consists of TiI_4 molecules at 400° according to density measurements of Hautefeuille.[4]