

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 stated⁶ 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 $\approx 0.3^\circ$ 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 $\approx 0.1^\circ$. 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 $\text{TiI}_{4(l)} \rightleftharpoons \text{TiI}_{4(g)}$ ⁶

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

$$\log p_{(\text{atm.})} = (3054/T) + 4.696$$

$$\Delta H = 13,975 \text{ cal./mole}$$

$$\text{B. p.} = 377.2 \pm 0.2^\circ$$

$$\Delta F^\circ = 13,975 - 21.49 T$$

$$\Delta S = 21.49 \text{ E.U.}$$

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

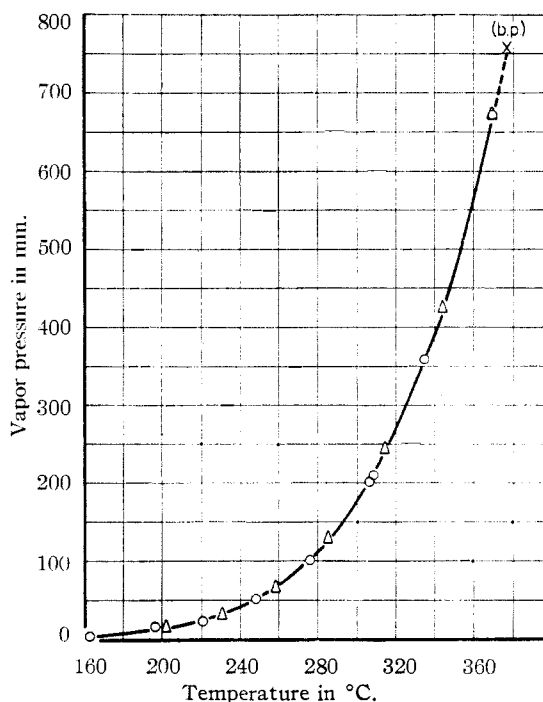


Fig. 3.—O, Ascending points; Δ , descending points.

It is believed that the temperature measurements are good to $\approx 0.2^\circ$ and the accuracy of the pressure measurements limited by the uncertainty (≈ 1 mm.) in the "head" correction.

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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 $377.2 \pm 0.2^\circ$ 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.