202. *Niobium and Tantalum Pentachlorides and Their Binary System.*

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The boiling points of niobium and tantalum pentachlorides have been measured over a range of pressures. At 760 mm. pressure they were found to be 247·4° ± 0·1° and 232·9° ± 0·1° respectively, and the heats of vaporisation were calculated as 12·6 and 13·1 kcal. mole^{-1} respectively. The triple points have been determined as 203·4° ± 0·2° and 215·9° ± 0·1° respectively. The liquid–vapour equilibrium in the system niobium pentachloride–tantalum pentachloride has been examined and the relative volatility ($TaCl_5$: $NbCl_5$) at atmospheric pressure found to be 1·36 over the whole range of mixture compositions.

PREVIOUS investigations of the vapour pressure of niobium pentachloride, all of which gave different boiling points, have been reported.[1, 2, 3] Schäfer, Bayer, and Lehmann[4] combined the published vapour-pressure data with a measurement of the melting point made by Schäfer and Pietruck,[5] and obtained a boiling point of 250° for niobium pentachloride.

The relative volatilities of the pentachlorides have been studied theoretically by Geldart and Steele.[6]

EXPERIMENTAL

The halides were prepared by direct chlorination of the metals at 450° by use of chlorine which had been dried by bubbling through sulphuric acid. Oxide, present as an impurity in the metals, led to the formation of oxychloride, the amount of which could be greatly reduced by adding carbon tetrachloride to the pentachloride whilst it was gently refluxed under an air condenser, and then pumping off volatile products after cooling. The pentachlorides were purified by fractional distillation through a 60-cm. electrically-heated column packed with glass Fenske helices. A magnetically-operated swinging funnel was used to deliver about 1/50th of the total reflux to the receiver. One of the fractions of niobium pentachloride was further purified by vacuum sublimation at 100°, the pentachloride subliming much more rapidly than the oxychloride: at 190° no separation was possible. This material was used for the boiling-point and triple-point determinations (Found: Ta, 50·2 ± 0·5; Nb, 0·19. Calc. for $TaCl_5$: Ta, 50·50) (Found: Nb, 34·7 ± 0·3; Ta, 0·015. Calc. for $NbCl_5$: Nb, 34·38%).

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[1] Opichtina and Fleischer, *Zhur. Obshchei. Khim.*, 1937, **7**, 2016.

[2] Tarasenkow and Komandin, *ibid.*, 1940, **10**, 1319.

[3] Alexander and Fairbrother, *J.*, 1949, S223.

[4] Schäfer, Bayer, and Lehmann, *Z. anorg. Chem.*, 1952, **268**, 268.

[5] Schäfer and Pietruck, *ibid.*, 1951, **267**, 174.

[6] Geldart and Steele, Paper No. 16, Presented at an Institution of Mining and Metallurgy Symposium, March, 1956.

Attempts to prepare the white modification of niobium pentachloride described by Alexander and Fairbrother [3] were unsuccessful. A white material, similar in appearance to that obtained by us by burning niobium trichloride in oxygen, was sometimes found with the unsublimed but never with the sublimed pentachloride and could always be explained as niobium oxychloride present as impurity.

Boiling-point Apparatus.—Boiling points were taken in a glass tube, electrically heated at the bottom and lagged over the lower 10 cm. of its length. It was connected to a manometer and a pressure regulating system in which fluctuations were damped to ±2 mm. by a 750 ml. flask. To obtain pressures above atmospheric, dry nitrogen was blown into the apparatus and allowed to escape through a mercury bubbler, the head of mercury thus determining the excess of pressure. Pressures below atmospheric were obtained by slowly evacuating the apparatus and admitting dry air through the bubbler.

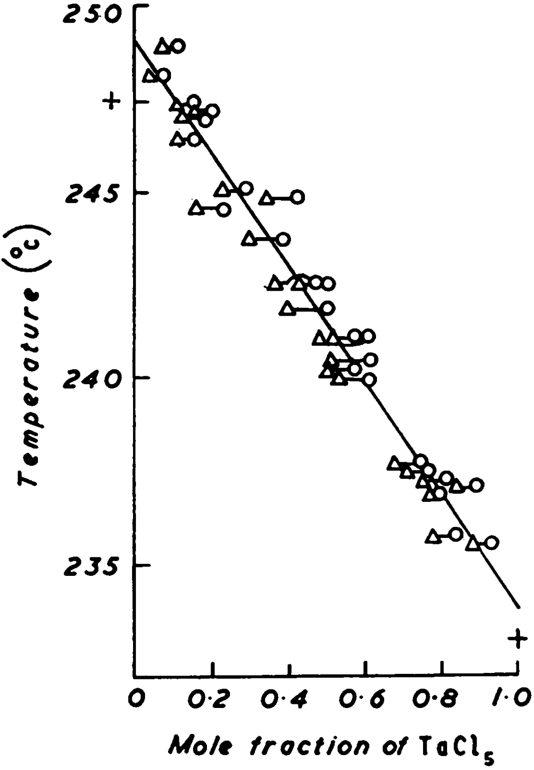

FIG. 1. *Liquid–vapour equilibrium for the niobium pentachloride–tantalum pentachloride system.*

△ liquid phase, ○ vapour phase, + boiling points of the pure components.

About 60 g. of pentachloride were distilled into the apparatus which was evacuated and then filled with dry nitrogen. The charge was melted and the heater adjusted so that refluxing took place just above the lagging. A calibrated bare thermocouple (Pt/Pt–13% Rh), so arranged that the junction could not be cooled by condensate running down the leads, was used to measure temperature. The thermocouple E.M.F. was measured on a millivolt potentiometer which could be read to the nearest microvolt, corresponding to 0·1° at 200°. The thermocouple junction was usually placed in the vapour, though some of the measurements with tantalum pentachloride were made with it in the liquid. Pressure and temperature readings were taken and when three consecutive temperature readings at 5-min. intervals, at the same pressure, agreed within 0·1° they were taken as the boiling point at that pressure.

Triple-point Apparatus.—The triple point was measured by plotting the cooling curve of the liquid, under its own vapour, in a glass bulb fitted with a bare thermocouple. After introduction of about 60 g. of pentachloride the bulb was evacuated and sealed off. The charge was melted with a flame and the bulb placed in an electrically heated Dewar vessel and covered with asbestos wool. When the temperature in the bulb reached about 240° the heater was switched off and temperature readings taken, at intervals of about 1 min., from which the cooling curve was drawn.

The Equilibrium Still.—The still was of a recirculating type, based on that described by Othmer.[7] It was charged with a mixture of the pentachlorides and set up in an oven maintained at about 230°. The still heater was adjusted to give continuous boiling, the pressure adjusted to 760 mm., and the temperature measured at regular intervals. Equilibrium was assumed to have been attained when the boiling point was constant to 0·1° over a period of 20 min. The vapour sample present as condensate in a U-tube was collected by solidification by rapidly cooling the tube with a jet of air, and the liquid sample was taken in a side arm on the boiler in the same way. Care was taken, when collecting the liquid sample, that the initial solidification occurred close to the boiler, thus minimising the effects of any change of composition during solidification. The sample tubes were drawn off under vacuum and their contents analysed for niobium and tantalum.

Results.—Fourteen measurements of the boiling point of niobium pentachloride were made at pressures between 680 and 900 mm. Over this range the b. p. can be related to the pressure by the equation $\log p$ (mm.) $= 8{\cdot}201 - 2{\cdot}770 \times 10^3/T$, which corresponds to b. p. 247·4° ± 0·1° at 760 mm. The greatest deviation of any point from this line corresponds to an error of $2{\cdot}5 \times 10^{-3}$ in $\log p$.

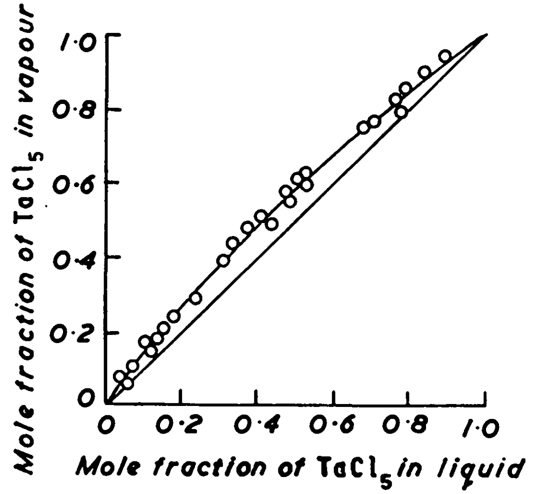

FIG. 2. *Liquid–vapour equilibrium for the niobium pentachloride–tantalum pentachloride system.*

Nineteen measurements of the boiling point of tantalum pentachloride were made with the thermocouple in the vapour over the same pressure range. These measurements fit the equation $\log p$ (mm.) $= 8{\cdot}543 - 2{\cdot}865 \times 10^3/T$, giving b. p. at 760 mm. pressure of 232·9° ± 0·1°. The maximum deviation of any point from this line corresponds to an error of 3×10^{-3} in $\log p$. Other measurements with the thermocouple in the liquid, though self-consistent, were about 1° higher than those measured in the vapour: this was probably due to superheating. From the vapour-pressure equations, which were obtained by the method of least squares, the heats and entropies of vaporisation (ΔH_v and ΔS_v) were calculated.

Cooling curves were drawn for each of the pentachlorides. Projection of the plateaux of these curves back to the portions representing cooling of the liquids gives the triple point of tantalum pentachloride as 215·9° ± 0·1°, and of niobium pentachloride as 203·4° ± 0·2° (203·0° ± 0·2° before sublimation).

The mole fractions of the components in the binary mixture were calculated from the results of the analyses of the liquid and vapour samples from the equilibrium still, and their values normalised so that the sum for any sample was unity. The sum calculated directly from the analytical figures always lay between 0·97 and 1·04. Results are shown in the Figures. The

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[7] Othmer, *Ind. Eng. Chem.*, 1928, **20**, 743.

relative volatility appeared to be constant over the whole range of mixture compositions and a mean value of 1·36 was calculated from the experimental values lying between 1·20 and 1·48 (two values below 1·1 being rejected). The probable error in a single observation was 0·04.

DISCUSSION

Phase Relations of the Pure Compounds.—A comparison between this and other published work is shown in the Table. The boiling and triple points reported here are 4—6° lower than those obtained by Alexander and Fairbrother [3] but the triple points are only 1° lower than values given by Schäfer *et al.*[4, 5] Examination of Alexander and Fairbrother's work permits a possible explanation of these discrepancies, in that their pentachlorides may have been contaminated with oxychlorides. The present work has shown that at 200°, the temperature used by Alexander and Fairbrother,[8] it is not possible to separate niobium oxychloride and pentachloride by vacuum sublimation and any oxide in the original metal would be carried through the purification as oxychloride.

	Niobium pentachloride			Tantalum pentachloride		
	Present work	Alexander and Fairbrother	Schäfer *et al.*	Present work	Alexander and Fairbrother	Schäfer *et al.*
Boiling point °	247·4 ± 0·1	254·0 ± 0·1	250	232·9 ± 0·1	239·3 ± 0·1	—
Triple point °	203·4 ± 0·2	209·5 ± 0·5	204·7	215·0 ± 0·1	220·0 ± 0·5	216·5
ΔH_v (kcal. mole^{-1}) ...	12·6 ± 0·1	13·2	13·1	13·1 ± 0·4	13·6	—
ΔS_v (cal. deg.$^{-1}$ mole^{-1})	24·3 ± 0·3	—	25·1	25·9 ± 1·3	—	—

The Binary System.—It can be seen that there is a considerable scatter of points in Fig. 1, whereas in Fig. 2 the scatter is much less, suggesting that most of the errors must have been in the measured temperatures. The calculated boiling points of the pure components are also shown in Fig. 1 and all the temperature measurements lie above the line joining these points. It is probable that, in spite of the treatment with carbon tetrachloride, there was contamination by oxychloride which raised the b. p. The mean value of the relative volatility is 1·36 : if mixtures of the pentachlorides behaved ideally the relative volatility would be 1·42 and 1·44 at the tantalum and niobium ends of the range respectively.

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[8] Fairbrother, personal communication.