520. *The Halides of Columbium (Niobium) and Tantalum. Part II. The Vapour Pressure of Tantalum Pentaiodide.*

By Kenneth M. Alexander and Fred Fairbrother.

Tantalum pentaiodide has been prepared by heating the metal in iodine vapour by means of high-frequency induction currents. It forms shiny black crystals which can be sublimed without decomposition; m. p. 496°; b. p. 543°. Measurements have been made, by a static method using a Bourdon-type sickle gauge, of its vapour pressure over a range of temperatures. It is not reduced by metallic tantalum at 550° but is thermally decomposed on the surface of incandescent tantalum.

The iodide of columbium, prepared by the action of heated columbium on iodine vapour, forms brass-like crystals which are instantly attacked on exposure to the air and which lose iodine on gentle heating.

The iodides of columbium and tantalum have received little attention. Unsuccessful efforts to obtain an iodide of tantalum were made both by Rose (*Pogg. Ann.*, 1856, **99**, 65, 575) and by Moissan (*Compt. rend.*, 1902, **134**, 211). Moissan stated briefly that tantalum powder does not react with iodine vapour at 600°. Van Haagen (*J. Amer. Chem. Soc.*, 1910, **32**, 729) prepared tantalum pentaiodide by repeated distillation of the pentabromide in a current of hydrogen iodide. The product was described as forming dark, nearly black lamellæ bearing a remote resemblance to iodine crystals, and could be distilled in a current of carbon dioxide without separation of iodine.

Barr (*ibid.*, 1908, **30**, 1668) stated that he had prepared from columbium bromide, an impure iodide which was quite stable but was freed from bromide with difficulty: it was apparently not analysed or examined further. Körösy (*ibid.*, **1939**, **61**, 838), as a corollary to a search for a metal which would be resistant to iodine vapour at high temperatures, investigated the direct reaction between iodine vapour and the heated metals: a coil of the metal wire was heated electrically, through molybdenum leads soldered to its ends, in an atmosphere of iodine. He states that both metals react with iodine vapour at a dull red heat, but it appears to have been necessary to heat the filaments to 1300—1600° for the completion of the reaction. He found that whereas tantalum pentaiodide was stable at least up to 500°, columbium pentaiodide easily dissociated at its sublimation temperature (about 400°) and appeared to be unstable at any temperature above 200°. In the present work we have confirmed this great difference in thermal stability of the two pentaiodides.

The use of a metal filament in the above manner has, however, obvious disadvantages as a method of preparation, chief among which is the limitation of the amount of iodide which can be prepared in a single experiment: any inequality in the wire leads progressively to a higher temperature and increased reaction of the thinner portions, with ultimate " burn-out " of the filament before it has completely reacted. We have now prepared these compounds in greater amount, and also avoided any impurities which might result from the action of iodine vapour on the electrical leads, by heating a coiled sheet of the metal in iodine vapour by high-frequency electrical induction currents.

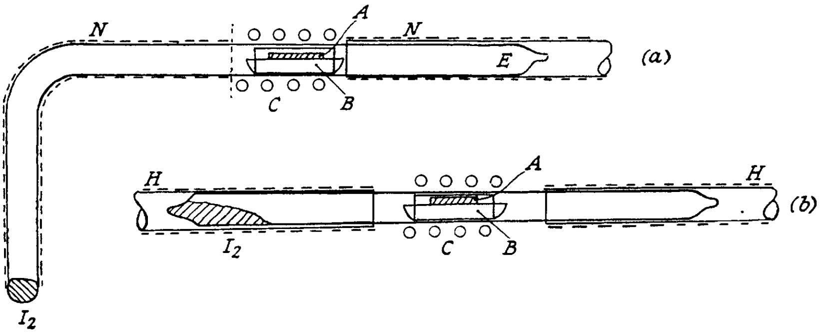
The resulting tantalum pentaiodide has been purified by fractional sublimation in a vacuum, and its vapour pressure determined over a range of temperatures: there is no evidence of any dissociation below its boiling point (543°/760 mm.). The pentaiodide vapour at the boiling point is not reduced by the metal, but is decomposed with evolution of clouds of iodine vapour on the surface of incandescent tantalum: this would appear to be a thermal decomposition. The pure tantalum pentaiodide solidifies to shiny black crystals.

The reaction between columbium metal and an excess of iodine under similar conditions leads to the formation of well-defined crystals, sometimes several mm. long, with a marked metallic lustre, greatly resembling a mass of coarse brass filings. These cannot be distilled in a vacuum but fall to a dark powder with evolution of iodine when gently warmed. On opening the preparation tube, the product is immediately attacked by the atmosphere, with the disappearance of the brass-like lustre and with evolution of hydrogen iodide. Repeated attempts were made to analyse these brass-like crystals, with somewhat inconsistent results arising from the difficulty of separating them quantitatively from traces of metal and lower iodides and from the fact that they are so rapidly attacked on exposure to the air. The results, however, suggest that they are essentially crystals of CbI_5. When they are heated in a vacuum, iodine is given off at a low temperature, and on further heating sublimates and residues of variable composition are obtained, so that vapour-pressure measurements of the undissociated pentaiodide cannot be carried out. It is intended to make a further investigation of these iodides of columbium.

EXPERIMENTAL.

The essential feature of the preparation was the passage of iodine vapour at a pressure of 1—2 atm. in an otherwise evacuated tube, over a sheet of metal kept at the requisite temperature by radio-frequency

FIG. 1.



induction currents. Several forms of reaction vessel were tried. The two final forms are shown in Fig. 1: (*a*) was used for the preparation of the tantalum iodide, and (*b*) for the reaction with columbium.

The vertical limb of (*a*) enabled this to be cooled in liquid air during the evacuation of the tube. It was found later, however, that cooling by solid carbon dioxide was satisfactory, which enabled the simpler form of apparatus (*b*) to be used, and permitted the use of external heater tubes in place of the nichrome-tape windings on the reaction tube (*a*) itself. This form of apparatus would be equally suitable for the preparation of tantalum pentaiodide.

A sheet of pure metal, usually 0·004 inch to 0·006 inch thick, weighing from 2 to 2·5 g., was formed into a loose cylinder of about $\frac{3}{8}$-inch diameter, *A*, and placed in a silica combustion boat, *B*, which was in turn surrounded by a short length of clear silica tubing to protect the outer (Pyrex) vessel. These were then introduced into the reaction vessel together with a slight excess of A.R. iodine, the latter cooled in liquid air or solid carbon dioxide, and the reaction vessel evacuated (to about 10^{-4}—10^{-5} mm.) and sealed.

The portion of the reaction vessel containing the silica boat and metal cylinder was then enclosed by the output coil *C*, of a G.E.C. 1 kw. high-frequency induction heater operating at about 10^7 cycles per second : a variable transformer in one of the primary phases permitted a certain degree of control of the energy input to the metal. By this means the metals could be heated to any desired temperature up to their fusion points. In practice the metal, as observed by a " disappearing-filament " optical pyrometer, was heated to temperatures between 800° and 1500°, but in view of the high frequency of the heating current it is certain that the temperature of the surface, and therefore of the sphere of reaction was much higher. Loose powdered columbium was found to be unreactive in this method of preparation, as the energy absorption was inadequate to maintain the necessary temperature : $\frac{3}{16}$-inch diameter H.S. brand columbium rods were found to be little better with the power available. Both metals were therefore used in the form of a sheet coiled into a loose cylinder, with its axis parallel to that of the output coil. The diameter and number of turns of the latter were adjusted so as to give the required energy transfer. The nichrome windings *N* on tube (*a*), or the auxiliary heaters *H* around tube (*b*), were brought as near the reaction zone as the radio-frequency field of the output coil permitted. The radiation from the heated metal served to keep the reaction zone and the intervening spaces at a sufficiently high temperature to prevent condensation of iodine. In some early experiments the metal was heated intermittently, *e.g.*, 2—10 seconds " on," 5 seconds " off," to prevent undue heating of the Pyrex outer tube. It was found, however, that by directing an external air blast between the turns of the water-cooled output coil, on to the centre of the reaction zone, the metal cylinder could be maintained at a temperature of about 1200° for 30—40 minutes without collapse of the outer tube. By heating both ends of the reaction tube, the iodine atmosphere could be kept at any desired pressure, and by allowing one end to cool slightly, a stream of iodine vapour could be passed over the metal to sweep the product from the reaction zone : this became necessary from time to time to prevent the tube from becoming blocked by the solid iodide.

The rate of reaction appeared to depend greatly on the temperature of the metal and the pressure of the iodine vapour, both of which were difficult to adjust precisely. It was difficult to observe the exact temperature at which rapid formation of iodide took place, but it was apparent that a pressure of iodine in excess of 1 atm. was desirable. Moreover, in view of the temperature of the reaction it seems probable that the iodination is accomplished essentially by atomic iodine.

In some experiments the reaction was relatively rapid; in others it was very slow. In one experiment, for example, about 2·5 g. of tantalum at a temperature of 900—1500° in iodine vapour at about 1 atm. pressure, required a total of some 10—15 hours for complete reaction : in other experiments a similar amount of columbium reacted during the course of 10—15 minutes. In general, the reaction with columbium appeared to take place more readily than with tantalum. The induction heating became less efficient towards the end of the operation, as the metal cylinder began to disintegrate. The preparation was discontinued when the reaction zone, after cooling of the tube, no longer became warm on application of the high-frequency field.

In the case of tantalum pentaiodide, at the conclusion of the reaction, the product was sublimed into one end of the reaction tube *E*, which was then cut off and sealed in a vacuum sublimation chain as described in Part I (this vol., p. S 223) but consisting only of some eight fractionation bulbs. Excess of iodine was removed by prolonged heating in a vacuum at 120—140°. The iodide was then sublimed at about 500°, at which temperature a dense brown vapour passed over and condensed to black crystals with a metallic lustre and which hydrolysed rapidly when exposed to the air (Found : I, 77·7±0·8. Calc. for TaI_5 : I, 77·8%). When all the pentaiodide had sublimed from the preparation tube, a small quantity of a brick-red powder (black when hot) remained. This was involatile at 600° and did not fume in moist air. Analysis showed it to contain less iodine than corresponds to TaI (Found : I, 38·5. Calc. for TaI : I, 41·2%). A similar brick-red powder was obtained by the action of incandescent tantalum on the pentaiodide vapour. 2 G. of purified pentaiodide (sufficient to give a saturated vapour) were sealed in an evacuated tube with a cylinder of sheet tantalum. The tube was kept at several temperatures up to 550°, the metal receiving no additional heating. On cooling, the tantalum pentaiodide condensed without apparent action on the metal, or liberation of free iodine, the metal remaining bright. This was then repeated, and the tantalum further heated by induction to 1000—1500° : a considerable amount of iodine was liberated, the metal was attacked, and a red deposit of a lower iodide formed in the immediate neighbourhood of the heated cylinder. This reaction would appear to be one rather of a thermal decomposition of the pentaiodide than a reduction by the metal. The further investigation of the reduction of the pentaiodide was deferred. It may be noted that Körösy (*loc. cit.*) reported the formation of products with less iodine than necessary for the monoiodide, by the action on the pentaiodide of a coil of tantalum wire heated electrically to 1300—1600°.

Analysis.—These compounds are insoluble in dilute nitric acid, though doubtless it will liberate most of the iodine as hydriodic acid; the desirable complete dissolution of the sample for analysis, however, is not easily accomplished in the open without loss of iodine. The compounds were therefore decomposed in a closed system by heating with potassium pyrosulphate. An evacuated bulb containing the sample of iodide (0·1—1·0 g.) was opened, and its contents rapidly transferred to a tared platinum crucible and immediately covered by a known weight (about 10 g.) of previously fused and powdered potassium pyrosulphate. The crucible and its contents were then re-weighed and transferred to the Pyrex fusion unit shown in Fig. 2.

The design of this apparatus was the result of a number of trials in which it was found that the narrow annular space shown by *S* (with resultant high-speed air flow) was necessary to prevent back-diffusion of the products of reaction. The crucible was heated by another output coil *C* operated by the same radio-frequency induction heater as used for the preparations. The liberated iodine, together with some sulphur trioxide was carried out of the top of the fusion unit in a current of air, and into a vertical absorption tube containing glass beads immersed in a solution of potassium hydroxide (8—10 g. in 250 c.c. of water). Most of the iodine was evolved within the first 5 minutes of heating, at a comparatively low temperature, and apparently ceased after 10—15 minutes, leaving a clear, faintly yellow liquid in the crucible. The temperature was then raised to incipient redness (about 700°), and heating continued for a further 10 minutes. Experiments showed that all the iodine was evolved and was collected by a single absorption column. The contents of this column were then acidified with dilute nitric acid, the iodate reduced by sulphur dioxide, and the iodine determined gravimetrically as silver iodide. A check on the iodine determinations was made by estimating the columbium or tantalum in the solidified pyrosulphate melt by dissolving it in concentrated sulphuric acid, diluting the solution, and estimating the columbium or tantalum either by Powell and Schoeller's tannin procedure (*Analyst*, 1925, **50**, 485) or by precipitation as hydroxide, filtration, and ignition.

FIG. 2.

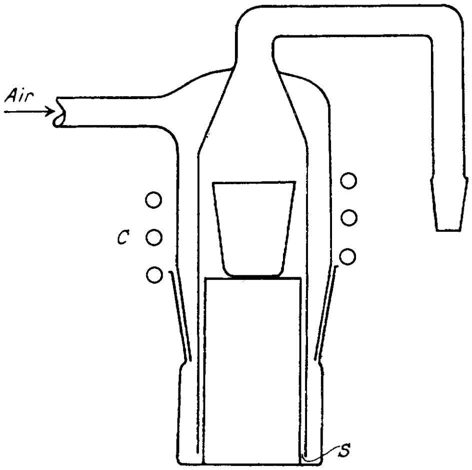
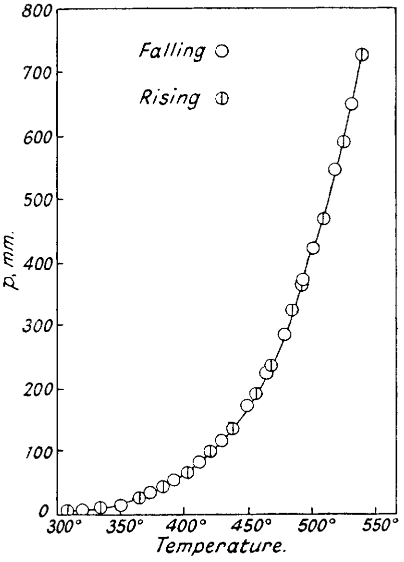


FIG. 3.



The Vapour Pressure of Tantalum Pentaiodide.—These determinations were carried out in substantially the same manner as is described for the pentachlorides and pentabromides in Part I of this series (*loc. cit.*). A sample (about 10 g.) of tantalum pentaiodide, purified by sublimation in a vacuum, was re-sublimed in a vacuum into a hook-ended tube and transferred to the Bourdon-type sickle gauge. No trace of permanent distortion of this gauge could be observed even after its repeated use at 500—540°, the pointer always returning to the same zero on cooling. Pressure measurements were made at fixed temperatures, approached both from above (falling temperature) and from below (rising temperature) as previously described. Vapour pressures, in mm. of Hg., at 15° are given in the table and in Fig. 3.

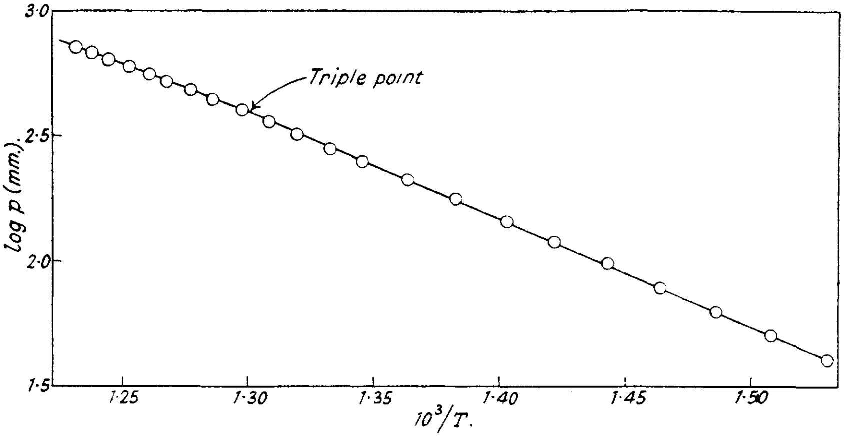
Vapour pressure of tantalum pentaiodide.

Temp.:			Temp.:			Temp.:		
Rising.	Falling.	V. p. (mm.).	Rising.	Falling.	V. p. (mm.).	Rising.	Falling.	V. p. (mm.).
307·7°	—	5·8	419·5°	—	95·6	485·4°	—	322·4
—	320·0°	7·6	—	428·7°	117·5	492·1	—	362·1
334·3	—	9·9	437·9	—	138·1	—	493·0°	373·1
—	350·3	16·0	—	449·4	172·6	—	500·4	421·2
363·7	—	25·7	455·8	—	192·3	509·0	—	469·4
—	372·7	35·1	—	464·3	226·2	—	518·5	547·3
382·8	—	44·0	466·8	—	236·6	524·5	—	590·4
—	391·7	54·5	—	478·5	288·7	—	531·0	650·4
402·5	—	67·2				539·1	—	727·4
—	411·1	81·4						

Triple pt.	B. p. (760 mm.).	L_s, kcals.	L_v, kcals.	L_f, kcals.
496° ± 2°	543° ± 0·5°	19·7	18·1	1·6

Estimates of the latent heats of change of state were calculated by the Clausius–Clapeyron equation from the log p–$1/T$ relation (Fig. 4); L_s, L_v, and L_f (the last by difference) refer, respectively, to the molar heats of sublimation, volatilisation, and fusion. Owing to the small heat of fusion, the triple point is not sharply defined, but estimates from both a large-scale p–t curve and the log p–$1/T$ relation indicate a triple point of 496° ± 2°. A short extrapolation of the p–t curve gives the boiling point at 760 mm. as 543° ± 0·5°.

Fig. 4.



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