

S 48. *The Halides of Columbium (Niobium) and Tantalum. Part I. The Vapour Pressures of Columbium (Niobium) and Tantalum Pentachlorides and Pentabromides.**

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Measurements have been made, by a static method using a Bourdon-type sickle gauge, of the vapour pressures of carefully purified specimens of the pentachlorides and pentabromides of columbium and tantalum, and the latent heats of change of state calculated. M. p.s: CbCl_5 , 209.5°; TaCl_5 , 220.0°; CbBr_5 , 267.5°; TaBr_5 , 280.0°. B. p.s (760 mm.): CbCl_5 , 254.0°; TaCl_5 , 239.3°; CbBr_5 , 361.6°; TaBr_5 , 348.8°. The tantalum halides, especially in the liquid state, are more volatile than the corresponding columbium compounds. Solid CbCl_5 is dimorphous: white (α) \rightarrow yellow (β), transition temperature 183°.

The pentachlorides of columbium and tantalum have been reported (Grosse and Ipatieff, *J. Org. Chem.*, 1937, **1**, 559; Dermer and Billmeier, *J. Amer. Chem. Soc.*, 1942, **64**, 464) to be effective as catalysts in the ethylation of benzene and the alkylation of toluene. These experiments indicate that their catalytic activity in other reactions may be very good, but the possibilities of these chlorides as Friedel-Crafts-type catalysts have not been fully investigated. The catalytic activities of the bromides do not appear to have been examined.

The present work was undertaken in the first place as part of a study of the chemical and physical properties of these substances which may be relevant to their behaviour as catalysts, and with a further view to examining the possibilities of methods of achieving the difficult separation of columbium and tantalum, alternative to the fractional crystallisation of the salts of the fluoro-acids. As a first step, accurate measurements have been made, by a static method, of the vapour pressures of pure specimens of these halides, and the corresponding heats of change of state calculated. In the course of this work we have been able to demonstrate the existence of two enantiotropic modifications of CbCl_5 , with a transition temperature of 183°.

Apart from isolated estimates of the boiling points, only two previous investigations of the vapour pressures of CbCl_5 and TaCl_5 have been reported. In the first, by Opykhtina and Fleisher (*J. Gen. Chem. Russia*, 1937, **7**, 2016), a dynamic method was used, a current of chlorine being streamed over the substances. In the second, by Taresenkov and Komandin (*ibid.*, 1940, **10**, 1319), the vapour pressures of the solids were measured by a simple mercury tensimeter in which the vapours were in contact with the mercury meniscus, and above the melting points by the determination of the boiling points at various pressures. The results of these determinations differ somewhat from one another and from the present results. We can find no recorded measurements of the vapour pressures of the pentabromides.

EXPERIMENTAL.

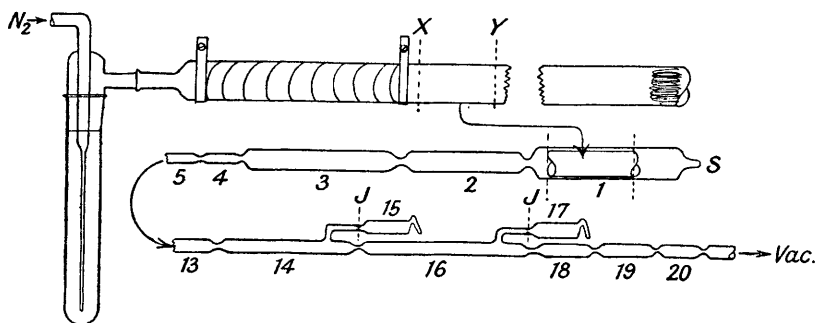
The halides were prepared by direct halogenation of the pure metals. The arc spectra of the sheet tantalum (from Messrs. Johnson, Matthey & Co., Ltd.) and of the columbium powder (from Fansteel Metallurgical Corporation) were compared with those of "H.S." samples by means of a Hilger Type E2 quartz spectrograph, and the plates enlarged 8 diameters; no lines additional to those of the spectrographic standards were observed. Cylinder chlorine was dried with sulphuric acid, liquefied, and the most volatile fraction used. "A.R." Bromine was treated with pure anhydrous calcium bromide and further dried with phosphoric oxide. The nitrogen used as a carrier gas was freed from traces of oxygen by hot copper turnings, and after a preliminary drying was finally dried by alternately heating to 300° (to remove any fog) and cooling in liquid air.

The arrangement of the halogenation chain is shown in Fig. 1. Dry nitrogen was passed through liquid chlorine or bromine, suitably cooled or warmed respectively, and led over some 5–10 g. of the metal: the latter was heated initially to 300–350° for chlorination and to 500–550° for bromination, but the heat of the reaction caused the metal to glow. On completion of the halogenation, the portion of the tube X–Y containing the solid halide was quickly cut off and slipped into the wide end of the fractionation chain S, which was then immediately sealed: this was the only exposure of the halide to the atmosphere, and the quantities used and the subsequent fractionation were such as to remove completely any hydrolysis products. Immediately after the crude halide had been sealed in the first bulb, the fractionation chain, consisting of 18 bulbs in series and two appendices (15 and 17), was evacuated and bulb 2 well out-gassed. The halide was then sublimed into bulb 2, leaving a slight residue in the first bulb, which was then sealed off. Bulb 3 was then out-gassed, the halide sublimed into it, and bulb 2 removed. These initial sublimations served to eliminate occluded gases, including excess of halogen, and any hydrolysis products. Bulbs 4–20, including the appendices, were baked in a vacuum for an hour each at the softening temperature of the Pyrex glass, and the thickened

* The authors prefer the name columbium which was given to this element in 1801 by the English chemist Charles Matchett, to the name niobium given by H. Rose in 1844.

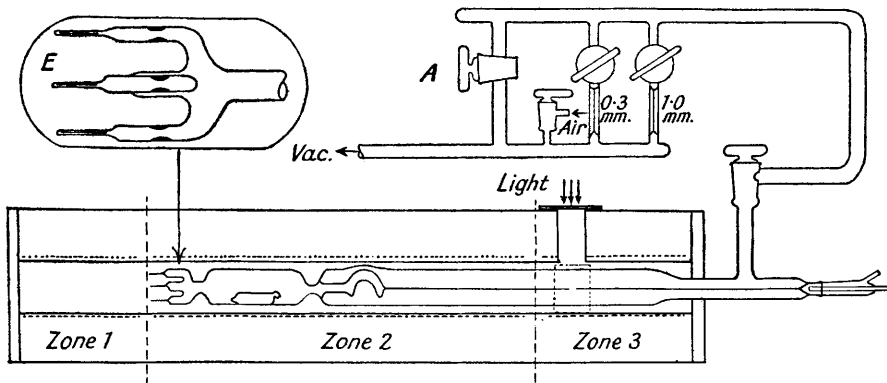
constrictions between the bulbs heated to dull redness. The halide was then slowly fractionated along the chain by means of a movable temperature-controlled electric-tube furnace. The most volatile fraction was sublimed right through the chain into the three terminal bulbs 18—20, and the main middle fraction finally divided between bulbs 14 and 16. Each of the latter was sealed from the chain and its contents (still in a vacuum) sublimed into the appendix and sealed off. Each appendix was provided with a flattened hook end of a shape which many trials had shown was best for the subsequent breaking. The appendices had been weighed empty before attachment to the main line at *J, J*. Since the latter joint was always visible as a thin line along which the glass could be sealed off, it was possible, by reweighing after filling, to make a close estimate of the amount of halide in the tube—a necessary provision since the large molecular weights of the halides (270.5 to 581) mean that a large weight of halide is required for complete saturation of the vapour at the higher temperatures. Yields of the pentahalides of the order of 97—99% (calc. from the weight of metal used) were obtained.

FIG. 1.



Vapour-pressure Measurements.—The salient features of the apparatus were as follows. A very sensitive Bourdon-type sickle gauge, selected from some scores made for the purpose, was sealed into the all-Pyrex apparatus shown in Fig. 2. The sickle was provided with a 5" pointer whose tip moved 0.18 mm. per mm. of mercury change of pressure: this movement was magnified $\times 35$ by a reading telescope, so that the pressures on the outside and inside of the sickle could easily be equalised to ± 0.1 mm. Hg. The balancing air pressure, controlled by the coarse, medium, and fine adjustment at *A*, was observed by means of a wide-bore mercury manometer read by a cathometer with an Invar scale.

FIG. 2.



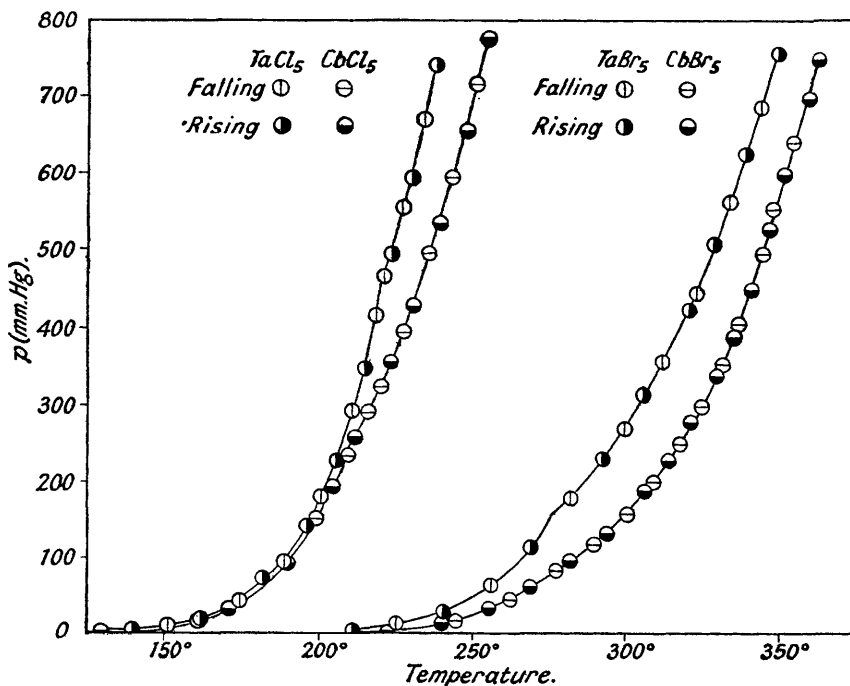
The gauge specimen chamber was provided with a 5-tube end *E*; one tube served for initial evacuation and four for subsequent re-evacuation (see later). The entire gauge was enclosed, as shown, in the high-temperature thermostat and inclined at an angle of about 20° to the horizontal, with the specimen chamber uppermost. This inclination was sufficient to prevent convection current disturbance following the admission of cold air to the gauge but small enough to prevent molten halide from running into the sickle.

The constant-temperature enclosure, on the control of which the final accuracy largely depended, was constructed from $2\frac{1}{4}$ " diam. brass tube, 32" long, and was provided with two orthogonally situated mica-covered tubular observation ports, for the illumination and observation respectively of the indicating pointers. The tube was well lagged with kieselguhr in a 6" diam. asbestos-cement tube. The nichrome-tape heater windings around the tube were divided into three zones, each of which was controlled by a Cambridge Instrument Co. thermocouple temperature regulator. These windings, together with appropriate series-parallel resistances were so arranged that the "on-off" operation of the regulator only involved a small change of current in the windings.

The two outer zones (1 and 3) served to buffer the effects of room temperature on the central zone (2) and enabled temperature gradients within it to be minimised. A sliding thermocouple was used in all experiments to check the temperature gradient in the tube and to permit corrections to be made for individual variations in the zero deflections of the control galvanometers. When finally adjusted, the temperature gradient in the centre 18" of the tube—which contained all of the gauge except the tip of the sickle pointer—could be reduced to less than $\pm 0.5^\circ$ at 300° , and the temperature variation of a given point within this centre zone to $\pm 0.15^\circ$. The temperatures of the halides were measured by a fifth, double-junction chromel–alumel thermocouple, fixed alongside the specimen chamber. This thermocouple was calibrated against the freezing points of tin, lead, and zinc and the boiling point of water, and the calibration was used to construct an individual correction to the standard temperature–E.M.F. relation for chromel–alumel thermocouples. The sliding temperature-gradient thermocouple and the fixed double-junction thermocouple were used in conjunction with a six-dial vernier potentiometer, permitting the equilibrium temperature of the halide to be measured directly to $\pm 0.1^\circ$.

The halide specimen tube was sealed inside the gauge specimen chamber, and the gauge evacuated and out-gassed at a temperature somewhat higher than any reached during a vapour-pressure determination. The gauge was then sealed off at the centre outlet tube of the end *E*, cooled, the halide tube broken by gentle shaking, and the gauge fixed in position in the constant-temperature oven. Vapour-pressure measurements were made after adjusting the temperature to the required point and holding it constant to $\pm 0.15^\circ$ for about an hour whilst the sickle pointer was kept in the zero position by adjusting the external pressure, from which the measurements were taken.

FIG. 3.



The measurements with a given specimen extended over some weeks, only a few equilibrium determinations being possible during a single day: in the intervals between the measurements the gauge was returned to room temperature. The equilibrium temperatures were approached both from above (falling temperature), the gauge being first heated to a slightly higher temperature, and from below. Measurements were made with each halide between zero pressure and atmospheric at approximately 10° intervals in the lower regions of the P - t curves, and at intervals of about 50 mm. pressure in the higher regions, where the pressure was rising rapidly with temperature. Observations were so arranged that points approached from above alternated on the curve with those approached from below: both sets of measurements fell on the same smooth curve. Reproducible results were obtained with different specimens of the same compound, with different gauges and furnaces, and also in repeated "runs" with the same specimen and apparatus.

In each case, at the end of the first "run" with a given specimen and gauge, the pressure, which had been zero at the beginning, did not return to zero but remained at a minimum of from 1 to 3 mm. of mercury. After re-evacuation of the specimen chamber through one of the multiple ends (*E*, Fig. 2) and repetition of the run, the same result was obtained; a residual pressure of 1 or 2 mm. of mercury at room temperature persisted even after the gauge had been re-evacuated and heated three times. This residual pressure developed during the first "run" after the sealing, and did not increase thereafter. Its origin was finally identified, in the case of TaBr_5 , by the temperature at which the residual

vapour condensed, as due to a trace of hydrogen halide, possibly due to a minute trace of water vapour liberated from the glass in the sealing-off process; the amount involved was estimated to be only of the order of a few hundredths of a milligram. This residual hydrogen halide was assumed to obey the gas laws and its partial pressure at each temperature subtracted from the total pressure indicated by the gauge.

DISCUSSION.

The vapour-pressure measurements (in mm. of Hg at 15°) are given in Table I and in the curves of Fig. 3. Values of $\log p$ against $1/T$ have also been plotted (Fig. 4) by taking equal small intervals from the $p-t$ curves when plotted on a large scale: from these the latent heats of change of state have been calculated by the Clausius-Clapeyron equation. These heats are given in Table II, together with the triple points and boiling points of the halides; L_s , L_v , and L_f (the last by difference) refer respectively to the molar heats of sublimation, volatilisation, and fusion.

TABLE I.

Temp.			Temp.			Temp.		
Rising.	Falling.	V.p. (mm.)	Rising.	Falling.	V.p. (mm.)	Rising.	Falling.	V.p. (mm.)
<i>Columbium pentachloride.</i>								
129.6°		4.3	204.7°		192.6	230.6°		430.0
150.1		11.3		209.1°	234.9		236.0°	497.7
	160.6°	19.7	212.1		258.4	239.3		537.5
170.6		32.7		216.3	290.5		243.3	595.6
	181.5	61.9		220.1	324.4	248.0		659.1
190.1		93.6	223.5		357.4		251.0	718.8
	199.0	151.9		227.4	395.6	254.6		778.5
<i>Tantalum pentachloride.</i>								
139.1		4.8	196.0		141.1	223.4		498.4
	150.8	11.3		200.7	180.2		227.4	558.5
161.1		20.4	205.9		228.8	230.1		595.7
	173.6	42.9		210.7	291.2		234.3	671.5
181.5		67.3	214.8		348.4	238.1		741.7
	188.6	97.6		218.7	418.6			
				221.1	468.5			
<i>Tantalum pentabromide.</i>								
211.0		4.1	292.2		228.3	328.7		507.8
	225.5	12.9		299.3	267.6		333.4	560.3
240.3		28.5	305.5		311.0	338.7		624.4
	256.2	62.5		311.6	354.7		343.4	683.9
269.1		112.9	320.0		421.2	348.8		756.9
	282.0	176.8		322.4	443.5			
<i>Columbium pentabromide.</i>								
207.5		0.5	293.6		130.2	334.2		385.5
	222.3	1.8		299.9	154.9		336.4	402.5
239.9		13.9	306.5		185.5	340.0		447.3
	244.1	17.6		308.5	198.3		343.1	491.7
255.7		32.4	313.5		223.5	345.5		525.6
	262.1	43.9		317.2	246.5		347.3	550.4
268.7		60.5	321.2		274.6	351.1		596.7
	276.8	81.6		324.1	293.6		353.5	639.3
281.8		93.8	329.1		336.4	358.3		697.8
	289.5	116.7		330.7	350.4	361.7		747.6

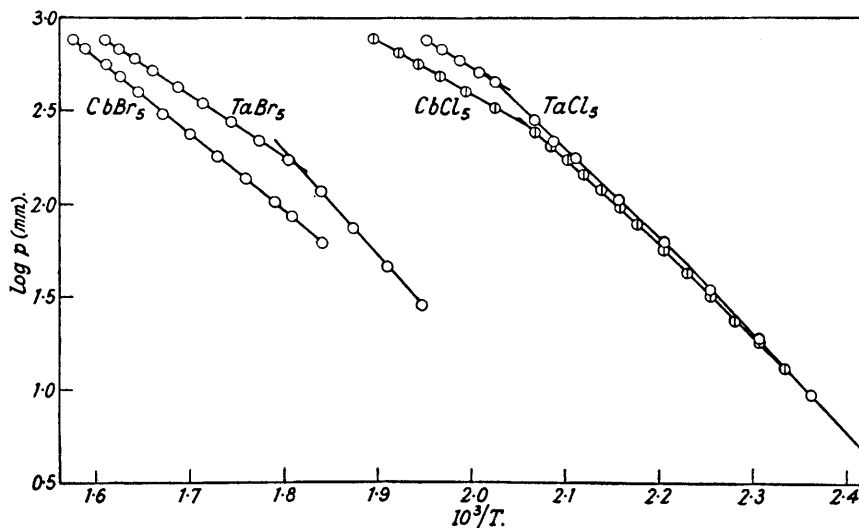
TABLE II.

Com- pound.	Temp. range.	L_s , kcal.	L_v , kcal.	Com- pound.	Temp. range.	L_s , kcal.	L_v , kcal.	Com- pound.	Temp. range.	L_s , kcal.	L_v , kcal.
CbCl ₅	155—183°	22.5	—	TaCl ₅	140—175°	24.0	—	CbBr ₅	270—360°	—	18.7
	183—209	20.9	—		175—220	22.0	—	TaBr ₅	250—280	25.8	—
	210—254	—	13.2		220—240	—	13.6		290—350	—	14.9
Com- pound.	L_f , kcal.	Triple pt.	B. p. (760 mm.).	Com- pound.	L_f , kcal.	Triple pt.	B. p. (760 mm.).				
CbCl ₅	7.7	209.5° ± 0.5°	254.0° ± 0.1°	CbBr ₅	—	267.5° ± 1.0°	361.6° ± 0.1°				
TaCl ₅	8.4	220.0 ± 0.5	239.3 ± 0.1	TaBr ₅	10.9	280.0 ± 1.0	348.8 ± 0.1				

Transition temperature, CbCl₅(α) → CbCl₅(β): 183°.

The graphs of CbCl_5 , TaCl_5 , and TaBr_5 clearly show breaks at the triple points, the positions of which were also confirmed by direct m. p. determinations in vacuum; CbCl_5 also shows a break in the solid-vapour equilibrium at 183° . This is probably the transition temperature, for solid CbCl_5 is quite clearly dimorphous. The high-temperature modification, which we will call $\text{CbCl}_5(\beta)$, and which is formed when the liquid solidifies or the compound is rapidly sublimed in a vacuum, crystallises as clear, well-formed, lemon-yellow prisms—probably orthorhombic (parallel or symmetrical extinction). The low-temperature modification, $\text{CbCl}_5(\alpha)$, often crystallises as white or colourless transparent needles, which grow out from the faces of the yellow prisms. A quantity of the compound sealed in a vacuum could be repeatedly and completely changed from one form to the other by heating at 160 – 180° or around 200° : the change from the yellow to the white modification is very slow at lower temperatures. Under a microscope, both modifications may frequently be seen together.

FIG. 4.



The $\log p-1/T$ relation for solid TaCl_5 shows a perceptible curvature or change of slope with a mid-point about 175° , but there is no clear evidence of dimorphism as in the case of CbCl_5 . Values of L_s have been calculated for both ranges of temperature. It may be noted that the difference between the m. p. and the b. p. of TaCl_5 is only about 20° , and the vapour pressure at the triple point is 450 mm. All specimens of TaCl_5 were pure white.

In the case of CbBr_5 , owing to the low volatility of the solid, the pressure at the triple point being only some 50 mm. (as compared with 450, 240, and 170 mm. for TaCl_5 , CbCl_5 , and TaBr_5 , respectively), and the lower branch of the $\log p-1/T$ curve being correspondingly short, it was not possible to derive a reliable value for the molar heat of sublimation of CbBr_5 : for the same reason it was difficult to observe the triple point. The matter is further complicated by the fact that visual examination of solid CbBr_5 shows that, like the chloride, it is polymorphic.

It is noteworthy that in both cases the heavier tantalum halide, especially in the liquid state, is more volatile at a given temperature than the lighter columbium compound.

The vapour-pressure curves of Fig. 3 show that a separation of columbium and tantalum by the fractional sublimation of their chlorides or bromides is not practicable, but above the melting points the differences of vapour pressure suggest that with an efficient heated fractionating column, a separation might be effected.

We are indebted to the D.S.I.R. for a maintenance grant to one of us (K. M. A.) during the course of this work.