675. *The Halides of Niobium (Columbium) and Tantalum. Part III.* The Vapour Pressures of Niobium (Columbium) and Tantalum Pentafluorides.*

By Fred Fairbrother and William C. Frith.

Measurements have been made, by a static method using a Bourdon-type sickle gauge and by boiling-point determinations under a number of controlled pressures, of the vapour pressures of niobium† and tantalum pentafluorides: m. p.s: NbF_5, 80·0°; TaF_5, 95·1°; b. p.s (760 mm.): NbF_5, 234·9°; TaF_5, 229·2°. The tantalum pentafluoride, like the pentachloride and pentabromide, is more volatile than the corresponding niobium compound. The Trouton constants of all seven pentahalides examined are given and suggest some association in the liquid state.

A mixture of the fluorides prepared directly by fluorination of commercial ferrocolumbium is an excellent Friedel–Crafts-type catalyst.

The only previously reported estimates of the vapour pressures of these fluorides appear to be those derived from the boiling-point determinations carried out by Zedner and Schiller (*Ber.*, 1909, **42**, 492) and the vapour-pressure measurements by Ruff and Schiller (*Z. anorg. Chem.*, 1911, **72**, 329) carried out over a range of temperature of some 40—50° below the boiling point at 760 mm. The latter authors reported the boiling points of niobium† and tantalum pentafluorides at 760 mm. to be respectively 217—220° (corr.) and 229·2—229·5° (corr.), thus indicating that the niobium pentafluoride was more volatile than the tantalum pentafluoride. It was, however, shown in Part I of this series (*J.*, 1949, S 223) that niobium pentachloride and pentabromide were both less volatile than the corresponding tantalum compounds, and the present work shows that similarly it is the niobium pentafluoride which has the higher boiling point.

Direct measurements have now been made of the vapour pressures of both pentafluorides over a wider range of temperature by a static method using a sickle gauge, and confirmed and extended over the upper end of the temperature range by determinations of the boiling points at controlled pressures.

The measurement of the vapour pressures of these compounds presents some special difficulties on account of their extreme susceptibility to moisture and the reactivity of the hydrogen fluoride produced by hydrolysis. Ruff and Schiller (*loc. cit.*) attempted to overcome

* Part II, *J.*, 1949, 2472.

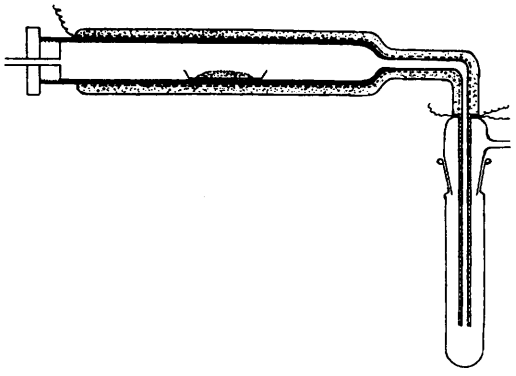
† The change from "columbium," as used in Parts I and II, to "niobium" in the present paper is in accord with a recent ruling of the Council of the Society.

these difficulties by using a copper vessel in the vapour-pressure method of Smith and Menzies (*J. Amer. Chem. Soc.*, 1910, **32**, 907). In this method the fluoride was introduced into a copper vessel with a narrow glass exit tube immersed in a bath of molten paraffin above which the pressure could be controlled and varied: the pressure at which the reference meniscus of paraffin near the tip of the glass tube neither rose nor fell was taken as the vapour pressure at the particular temperature. They observed that as the temperature was raised the halides were decomposed by the hot paraffin with the formation of brownish or black products. Moreover, as their method of introducing the fluoride into the copper vessel would probably not have excluded moisture, and as we have found with most of these solid halides, the hydrolysis by moist air is not instantaneous but occurs progressively on warming, probably through the decomposition of an intermediate hydrate, it is to be expected that in this method the vapour in the copper vessel would contain also some hydrogen fluoride, thus simulating a higher vapour pressure than the actual value. This source of error should have the most effect with the more easily hydrolysable niobium pentafluoride, and it may be seen that it is here that Ruff and Schiller's results show the greatest divergence from the present values.

Experimental.

Preparation of the Fluorides.—A few preliminary determinations were carried out with samples kindly prepared for us by Imperial Chemical Industries Limited, Alkali Division. Attempts were also made to fluorinate tantalum by heating it with silver bifluoride: these were unsuccessful, the silver bifluoride appearing to dissociate with loss of fluorine at temperatures at which the fluorination of the

Fig. 1.



metal was slow. The majority of the determinations were carried out with specimens made by direct fluorination of the pure metals in the apparatus shown in Fig. 1. Fluorine, generated by electrolysis at a rate of about 4 l. per hour, in a 10-ampere medium-temperature cell (I.C.I. Ltd.), was purified by passage through a tube containing sodium fluoride pellets at −80° to remove hydrogen fluoride, diluted with an approximately equal volume of dry oxygen-free nitrogen, and passed over 5—6 g. of pure metal in powder form, mixed with about 0·1 g. of aluminium powder and contained in a nickel boat in the heated Monel-metal reactor. The copper exit tube was heated electrically to about 150° to prevent obstruction by solidified fluoride, which was condensed in a conventional form of "trap" cooled at −80° and protected on the exit side by a drying tube. The reactor was heated initially to about 250° and the fluorination of the metal was usually completed in about 3 hours.

The trap, containing the crude product, was then quickly transferred into the wide end of a sublimation chain, as described in Part I (*loc. cit.*), which was then sealed by fusion. During this process a slow stream of dry nitrogen was passed through the sublimation chain, up to the final moment of the sealing process, in order to prevent any diffusion of atmospheric moisture into the fluoride. Fractional sublimation and transference to small hook-ended vacuum-opening ampoules then proceeded in substantially the same manner as described for the chlorides and bromides in Part I, the sublimation chain being tilted through an angle of 5—10° to the horizontal to reduce the risk of any molten fluoride flowing along the chain: melting usually occurred only in about the first four stages of fractionation, the solid subliming without melting in the later stages even though the external temperature of the tube was slightly above the m. p.

Vapour-pressure Measurements.—Measurements of the vapour pressure of tantalum pentafluoride, which were carried out first, were made in essentially the same manner as described in Part I, with the exception that corrections for pressure due to hydrolysis proved to be much more difficult. It has already been noted that it is not possible, even after careful out-gassing of the apparatus, to seal up the glass apparatus finally without disengaging a minute amount of water vapour from the molten

glass around the seal. But whereas in the case of the other halides this gives rise, on subsequent heating of the apparatus, to only a small amount of hydrogen halide which remains constant and can be easily allowed for, in the case of the fluorides the " residual pressure " observed on cooling the gauge appeared to increase steadily with both increase of temperature and time of heating. This increase, which is shown in Fig. 2, would appear to be due to the continuous formation of silicon tetrafluoride from the tantalum pentafluoride and the glass, in which the water acts as a catalyst, with the ultimate formation of tantalum entoxide with or without the intermediate formation of an oxyfluoride, *e.g.*,

$$4TaF_5 + 10H_2O = 2Ta_2O_5 + 20HF$$
$$20HF + 5SiO_2 = 5SiF_4 + 10H_2O$$

The formation of silicon tetrafluoride was confirmed by observing the temperature at which it could be condensed to a solid and the " residual pressure " removed. As may be seen from Fig. 2, the effect of this continuous hydrolysis may be very serious at the higher temperatures. It was taken into account in calculating the actual vapour pressures, by observing the rate of increase of " residual pressure " at the particular temperature of measurement and by cooling the gauge and contents as quickly as possible, after an observation, to room temperature, at which the hydrolysis is negligible. The additional correction for the effect of further hydrolysis during this cooling, which required about 10 minutes, was never more than 5 mm. and was negligible for measurements carried out at temperatures below 130°.

In an endeavour to reduce this progressive hydrolysis in the case of niobium pentafluoride, which as shown in Fig. 2 hydrolyses much more rapidly than tantalum pentafluoride, measurements of the

FIG. 2.

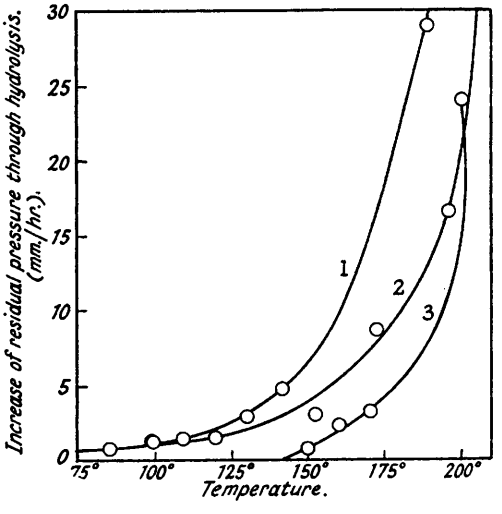
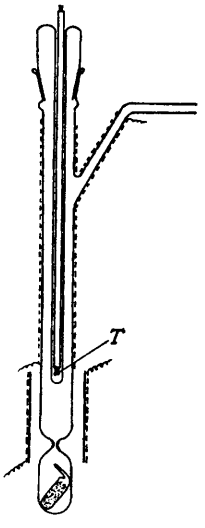


FIG. 3.



1. NbF_5 (*bare-glass gauge*). 2. TaF_5. 3. NbF_5 (*nickel-plated gauge*).

vapour pressure near the b. p. were carried out in an apparatus of similar construction but in which the whole of the interior of the gauge chamber and sickle were plated with a thin film of nickel. The purified specimen of halide, in its hook-ended container, was introduced into, and distilled from, an unplated kind of ante-chamber, which was then sealed off, so that in the end the only bare glass in contact with the fluoride vapour was the few mm. length in the neighbourhood of the final glass seal. This procedure greatly reduced, but did not entirely prevent, progressive hydrolysis : its advantages were more apparent at the lower temperatures. The thin film of nickel, deposited on the glass by the thermal decomposition of nickel tetracarbonyl, was on the average about 10^{-4} mm. thick and did not diminish the sensitivity of the gauge.

Further precautions and minor changes in design of the gauge were necessary in the case of niobium pentafluoride in order to prevent any solidification of the molten fluoride in narrow spaces or where the glass was thin.

The polymorphism of solid niobium pentabromide and pentachloride has already been noted in Part I : these are obvious since they involve visible changes in colour and crystalline form as well as, at all events in the case of the chloride, detectable changes in the vapour pressure–temperature relation. There is also some evidence of polymorphism in the case of solid niobium pentafluoride which is less easy to demonstrate since the solid remains white throughout and its vapour pressure is too small for any transition to be detected by the present method. On the other hand, it was repeatedly observed that when a mass of niobium pentafluoride which had been melted and allowed to solidify was heated, loud cracks could be heard when the temperature was still some distance below the m. p., the glass tube in which it was contained being itself not infrequently broken : much trouble

was experienced on this account. Also, when a sample was allowed to solidify in a melting-point tube, the tube was suddenly shattered on re-heating to about 20° below the m. p., whilst loose crystals in a melting-point tube seemed to become more translucent above about 60°.

Boiling-point Method.—Owing to the difficulties caused by hydrolysis of the fluorides, as noted above, measurements of the vapour pressures near the b. p. and for some distance below were confirmed and extended by determinations of the actual b. p. s at a number of different pressures. In this method, some 10 g. of purified halide were sublimed *in vacuo* into the boiling-point apparatus (Fig. 3) through the lower end, which was then sealed off, and the upper part of the apparatus was filled with dry nitrogen. The halide was heated electrically and allowed to reflux gently over the thermocouple well T which contained the same double-junction chromel–alumel thermocouple used in the measurements with the sickle gauge. The upper part of the apparatus was heated to about 110° to prevent solidification of the condensed fluoride, and connected to the same manometer and pressure-adjusting device as used for the pressure balance with the sickle gauge. Owing to the large volume of this part of the system, there was no difficulty in maintaining a constant pressure over the boiling halide: any hydrogen fluoride or silicon tetrafluoride produced by hydrolysis simply replaced part of the nitrogen as supernatant gas and was excluded from the rest of the pressure system by a trap cooled in liquid nitrogen. Boiling was continued under a given pressure until a constant temperature was reached and maintained. This method was limited to temperatures above about 160°, since below this temperature much vigorous " bumping " of the boiling halide took place. Niobium pentafluoride, once having been melted in the apparatus, was not allowed to solidify again between measurements on account of the risk of fracture of the tube on re-melting, mentioned above.

Discussion.

The vapour-pressure measurements (in mm. of Hg at 15°) are given in the accompanying table and in the curves of Figs. 4 and 5. Values of log p against $1/T$ have also been plotted

Table I.

r.: Bourdon-type sickle gauge; temp. approached from below.
f.: ,, ,, temp. approached from above.
Ni: Nickel-plated Bourdon-type sickle gauge.

Niobium pentafluoride				*Tantalum pentafluoride*			
Temp.	V. p. (mm.)	Temp.	V. p. (mm.)	Temp.	V. p. (mm.)	Temp.	V. p. (mm.)
67·5°	1·0 (f.)	190·8°	205·8 (r.)	80·0°	1·0 (f.)	182·1°	191·4 (r.)
75·4	2·0 (r.)	192·5	236·7	80·0	2·0 (r.)	183·3	214·4
83·0	3·1 (f.)	199·3	289·1	84·5	1·7 (r.)	187·3	237·7 (f.)
99·2	7·3 (r.)	201·2	294·4 (r., Ni)	89·8	3·6 (f.)	192·1	282·7
108·8	11·4 (f.)	205·8	340·3	99·7	7·8 (r.)	196·4	307·3 (r.)
118·2	17·9 (r.)	210·5	390·9	109·1	14·6 (f.)	199·1	337·7
129·7	27·6 (f.)	215·0	451·2	120·9	20·7 (r.)	200·9	334·6 (f.)
142·1	43·1 (r.)	219·0	506·4	136·5	38·0 (f.)	203·9	393·1
152·2	57·7 (r., Ni)	222·4	563·7	147·5	61·3 (f.)	206·4	410·4
160·3	81·6 (f., Ni)	225·0	614·3	152·3	67·2 (r.)	208·5	417·3 (r.)
170·7°	118·8 (r., Ni)	228·6	660·3	160·7	99·5	212·2	491·0
181·8	176·7 (f., Ni)	232·0	723·9	162·2	105·3 (f.)	223·4	642·0
184·3	192·1	—	—	172·5	143·4 (r.)	228·2	733·7
				175·9	165·0	228·8	741·9

Compound	M. p.	B. p. (760 mm.)	L_v, kcals.	Vapour pressure
NbF_5	80·0°	234·9°	12·9	$\log p_{mm.} = 8·439 - 2·824/T$
TaF_5	95·1	229·2	13·0	$\log p_{mm.} = 8·524 - 2·834/T$

in Figs. 6 and 7: from these the latent heats of volatilisation have been calculated by the Clausius–Clapeyron equation. Owing to the low volatility of the solid fluorides and the short range of vapour-pressure measurements over the solids it was not possible to derive accurate values for the molar heats of sublimation by this method. The values obtained by Ruff and Schiller (*loc. cit.*) have been included for comparison in Figs. 4 and 5, and the corresponding values of log p and $1/T$ calculated from them in Figs. 6 and 7.

It may be observed that the vapour pressures of these two fluorides are very close over much of the temperature range up to their boiling points, but that at any particular temperature the vapour pressure of niobium pentafluoride is *less* than that of tantalum pentafluoride. The separation, however, is so small in the lower ranges of temperature as to make it very difficult to represent them on a common diagram.

The difference between the physical properties of the corresponding halides of these two elements becomes therefore progressively less as the halogen becomes smaller, in all cases, however, the niobium halide being the less volatile, except perhaps in the case of the iodides for which no comparison can be made since that of niobium is too unstable to sublime. The

FIG. 4.

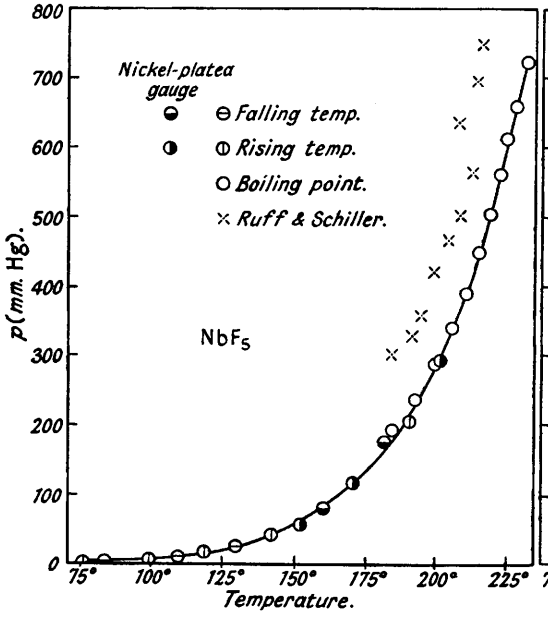


FIG. 5.

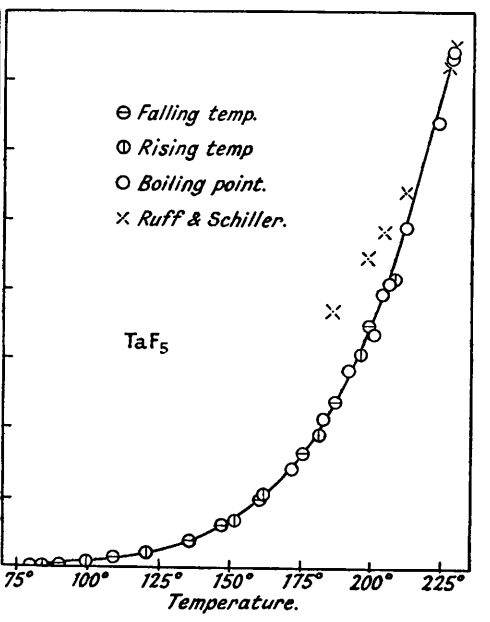


FIG. 6.

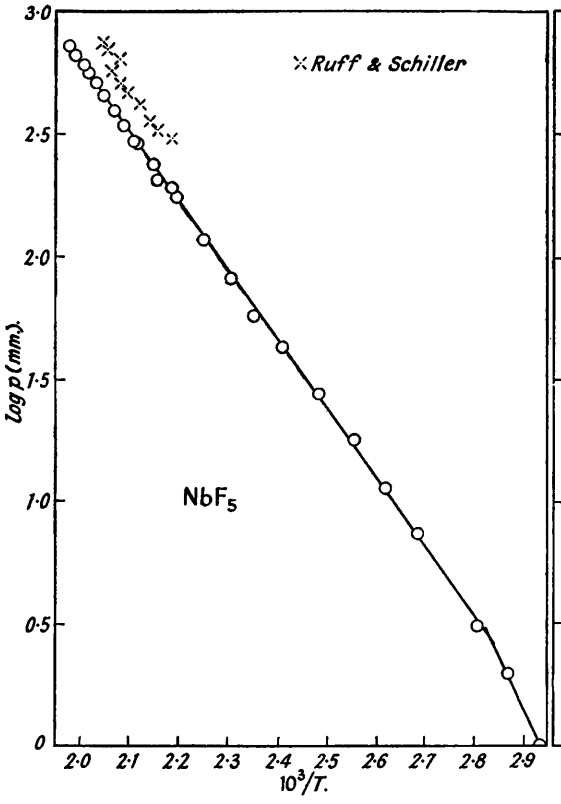
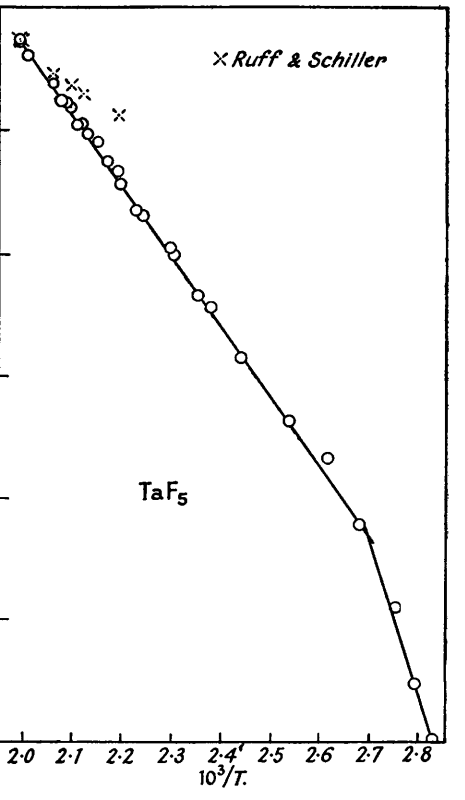


FIG. 7.



entropy change accompanying volatilisation of each of the liquid halides is high, as is shown by their respective Trouton constants given below :

Trouton constants (cals./°K.)

	$NbBr_5$ ..... 29·5	$NbCl_5$ ..... 25·0		NbF_5 ..... 25·4	
TaI_5 ..... 22·2	$TaBr_5$ ..... 24·0	$TaCl_5$ ..... 26·5		TaF_5 ..... 25·9	

It would appear in consequence that some degree of association occurs in the liquid state of these halides. This may possibly take the form of a partial dimerisation into double molecules, in which the halogen atoms are arranged about the two metal atoms in the form of two octahedra sharing an edge. Such a behaviour would be consistent with the " acidic " or electron-acceptor properties of these halides and with the sixfold co-ordination around the metal atoms, common in their complex compounds. It is, moreover, probable, especially as the ions $[MX_6^-]$ must be involved in the Friedel–Crafts catalyses (see below), that a number of the dimeric molecules $[MX_5]_2$ undergo an ionisation into $[MX_4^+][MX_6^-]$ pairs. It is hoped to examine this point by conductivity measurements.

In Part I of this series it was pointed out that the experiments of Grosse and Ipatieff (*J. Org. Chem.*, 1937, **1**, 559), on the ethylation of benzene with niobium and tantalum pentachlorides and those of Dermer and Billmeir (*J. Amer. Chem. Soc.*, 1942, **64**, 464) on the acylation of toluene with the niobium compound suggested that several other of these halides might be very good Friedel–Crafts-type catalysts. No experiments in this connection appear to have been reported in which the fluorides have been used.

The relatively high cost of the pure metals or their compounds, consequent to some extent upon the difficulties associated with their separation from one another, precludes any extensive use of the pure halides as catalysts. Since, however, the physical properties of these two fluorides are so closely similar, it is to be expected that a mixture of the two will not behave very differently as a catalyst from either in the pure state. Accordingly we have carried out several typical Friedel–Crafts-type reactions, using a mixture containing about 70% of NbF_5 and 30% of TaF_5, which we may call tantalo-niobium fluoride, and which was made by the action of fluorine gas in a similar manner to that described above, on a commercial powdered ferrocolumbium containing about 52% of niobium and 22% of tantalum, as used in the manufacture of stainless steels. As a consequence of the relative involatility of ferric fluoride and of most of the fluorinated impurities, a mixture of the fluorides of niobium and tantalum, containing little else, can be obtained in a single operation from ferrocolumbium, which thus forms a very convenient starting material for the preparation of this catalyst.

The Friedel–Crafts-type reactions examined included the alkylation and acylation of benzene with benzyl chloride and acetyl chloride, respectively, the ethylation of benzene in the presence of hydrogen chloride, and the polymerisation of *iso*butene in hexane solution at −80°. The last reaction was found to require a co-catalyst, for which trichloroacetic acid was used (cf. Plesch, *J.*, 1950, 543), and gave a polymer under the particular conditions of the experiment, with an estimated molecular weight of about 10,000. In all the experiments the tantalo-niobium fluoride proved to be an excellent catalyst.

We are indebted to Imperial Chemical Industries Limited, Alkali Division, for their help, especially for the provision of the fluorine cell, and to the Derbyshire County Education Committee for a grant to one of us (W. C. F.).

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