The Halides of Niobium (Columbium) and Tantalum. Part IV. The Electrical Conductivities of Niobium and Tantalum Pentafluorides.*

By Fred Fairbrother, William C. Frith, and Alfred A. Woolf.

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The conductivites of liquid niobium and tantalum pentafluorides have been measured over a range of temperatures. The specific conductivities at the melting points are respectively, NbF_5, $1{\cdot}63 \times 10^{-5}$ ohm^{-1} cm.$^{-1}$ at 80·0°; TaF_5, 1·56 ohm^{-1} cm.$^{-1}$ at 95·1°, and the activation energies of the molar conductivites 8·1 and 6·7 kcal. mole^{-1}. The results indicate a partial ionisation of these compounds, probably into MF_6^- and MF_4^+.

In Part III of this series * it was noted that niobium and tantalum pentafluorides possessed marked catalytic properties in a number of Friedel–Crafts type reactions, and entropies of vaporisation of the liquids (Trouton constants) higher than normal. These results suggested some degree of association of the molecules in the liquid state and possibly a partial self-ionisation of the form $(NbF_5)_2 \rightleftharpoons NbF_6^- + NbF_4^+$. The latter point has now been examined by the measurement of the electrical conductivities of the fused pentafluorides. The temperature coefficients of these conductivities are positive. The activation energies of the specific conductivities, calculated from the slope of the $\log_{10} \kappa$–$1/T$ curve, are 7·52 kcal. mole^{-1} for NbF_5 and 6·42 kcal. mole^{-1} for TaF_5. The corresponding activation energies for the molar conductivities ($\kappa M/d$) involve a knowledge of the densities of the molten fluorides. If we assume that the densities of molten NbF_5 are as given by Junkins *et al.* (*J. Amer. Chem. Soc.*, 1952, **74**, 3464) and that the densities of TaF_5 (for which no experimental data are available) are 1·44 times greater, which is the ratio of the densities of the solids (Ruff and Schiller, *Z. anorg. Chem.*, 1911, **72**, 329) and also roughly that of their molecular weights, the activation energies of the molar conductivities are 8·1 kcal. mole^{-1} for NbF_5 and 6·7 kcal. mole^{-1} for TaF_5. It may also be noted, in connection with this assumption regarding the densities of TaF_5, that the molecular dimensions in the gas phase of the pentachlorides and of the pentabromides are almost identical (Skinner and Sutton, *Trans. Faraday Soc.*, 1940, **36**, 668).

It is known (Bloom and Heymann, *Proc. Roy. Soc.*, 1946, *A*, **158**, 392) that in many cases the variation with temperature of the specific conductivity (κ) of molten salts of a predominantly ionic character can be represented by a simple exponential equation, $\kappa = \kappa_0 e^{-E_\kappa/RT}$ where E_κ is the activation energy of ionic migration, deviations from this equation being sometimes found for partially covalent compounds, *e.g.*, $ZnCl_2$, $PbCl_2$. It

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* Part III, *J.*, 1951, 3051.

may be observed that in the case of niobium and tantalum pentafluorides, although these are predominantly covalent, the exponential relation holds over the entire range of measurement.

Bloom and Heymann (*loc. cit.*) also note that the energy of ionic migration (E_κ) is always smaller than the activation energy of viscous flow. The relationship between these two magnitudes has been discussed at length by Greenwood and Martin (*J.*, 1953, 1427) who have shown that, for a large number of molten picrates and boron trifluoride co-ordination compounds, the ratio of the activation energies of viscous flow (E_η) and of ionic migration (E_μ)—the latter being calculated from the *molar* conductivities—is very close to unity. In the case of some high-melting inorganic solids, *e.g.*, the alkali-metal halides and silver halides, where there is a considerable disparity between the radii of anion and cation, and where different structural processes may be involved in viscous flow and in ionic migration, the ratio E_η/E_μ may be greater than unity, with an average value of 4·0. The present work suggests that in the case of niobium and tantalum pentafluorides the ratio E_η/E_μ is *less* than unity.

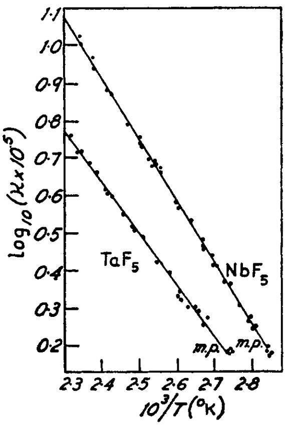
No experimental data are available for the viscosities of these fluorides (though visual comparison with other liquids suggests that they are of the order of 20 centipoises), but an estimate of the activation energies of viscous flow may be obtained from thermodynamic data. Kincaid, Eyring, and Stern (*Chem. Reviews*, 1941, **28**, 301) have put forward evidence to show that the activation energy of viscous flow is related to the energy of vaporisation and cite a large number of experimental figures to show that in general it lies between one-third and one-quarter of this magnitude. The latent heats of vaporisation as determined by Fairbrother and Frith (Part III) being used, the activation energy of viscous flow for both compounds should lie between 3 and 4 kcal. On this basis, therefore, the ratio E_η/E_μ for niobium pentafluoride and tantalum pentafluoride, is at the most about 0·5 and 0·6 respectively. Such data as are available (Woolf and Greenwood, *J.*, 1950, 2200) indicate that in the case of antimony pentafluoride and arsenic trifluoride also, the value of this ratio is less than unity.

The ionisation of niobium and tantalum pentafluorides has been formally represented as that of a definite dimeric species, *viz.*, $(NbF_5)_2 \rightleftharpoons NbF_6^- + NbF_4^+$. The nature of the association in the molten fluorides may, however, be less that of a simple dimerisation than of a more generalised interaction between one fluoride molecule and its neighbours resulting from the strong electron-acceptor character of the molecules—as indicated by their Friedel–Crafts activity—and the negative character of the fluorine atoms. It does, however, seem probable that the ions involved in the conduction process are the hexafluoro- and tetrafluoro- anion and cation respectively.

EXPERIMENTAL

The pentafluorides were prepared and purified as already described (Part III, *loc. cit.*) by the action of gaseous fluorine on the pure metals, followed by repeated fractional sublimation in a vacuum and transfer to small hook-ended ampoules. The same trouble was experienced, as previously noted, of the cracking of the glass apparatus on attempting to remelt a specimen of niobium pentafluoride which had been allowed to melt and solidify, a consequence of the polymorphic expansion which takes place below the melting point.

The conductivity cell was constructed of Pyrex glass, the platinum electrodes being silver-soldered to stout tungsten leads. The carefully purified fluoride, contained in a sealed ampoule, was sealed *in vacuo* in a side arm of the cell, which had been previously thoroughly out-gassed. The ampoule was broken, and the fluoride melted and allowed to cover the electrodes. At no stage after the initial transfer into the purification line were the fluorides allowed to come into contact with the atmosphere. The conductivity measurements were carried out in the sealed cell immersed in an oil-thermostat which could be maintained at any desired temperature to $\pm 0{\cdot}2°$. Measurements were made, with 1000-cycle A.C., during 3 days (the fluoride not being allowed to solidify) at a series of temperatures from near the m. p.s to about 160°. Higher temperatures were not used, since experiments had shown that these fluorides attack Pyrex glass with a rapidity which increases very quickly with rise of temperature and is very marked above about 160°. In the present work the negligible amount of attack on the glass was shown by the smallness of the variation of the conductivity over 72 hr. The cell constant changed by little more than 1% over the entire series of measurements: in the calculation of specific conductivity, the mean cell constant (0·277) was used. Both liquid fluorides could be supercooled considerably, so that specific conductivites at the m. p.s could be obtained by interpolation. These (in ohm^{-1} cm.$^{-1}$) were $1{\cdot}65 \times 10^{-5}$ and $1{\cdot}56 \times 10^{-5}$ for NbF_5 at 80° and for TaF_5 at 95·1°, respectively. The specific conductivities are tabulated below and the plots of $\log_{10} \kappa$ against $1/T$ are given in the Figure.



Niobium pentafluoride.

t	$10^5\kappa$	Time, hr.		$10^5\kappa$	Time, hr.	t	$10^5\kappa$	Time, hr.	t	$10^5\kappa$	Time, hr.
78·9°	1·54	0·5	102·0°	2·90	—	126·5°	5·37	—	119·1°	4·70	—
79·1	1·51	—	101·8	2·88	—	132·2	6·16	—	118·8	4·60	—
79·0	1·51	—	111·4	3·68	—	141·1	7·60	—	112·2	3·80	—
79·2	1·52	—	121·6	4·76	—	147·1	8·73	—	106·8	3·40	—
78·8	1·51	—	123·0	4·96	—	153·4	10·15	35·0	107·2	3·41	—
84·3	1·76	—	79·4	1·55	—	126·5	5·49	50·0	102·2	3·01	59·0
84·2	1·78	—	79·5	1·56	20·0	154·1	10·55	—	98·7	2·74	—
88·7	2·01	—	120·4	4·90	—	148·0	9·29	—	92·5	2·31	—
93·8	2·33	4·0	120·1	4·82	—	139·4	7·54	—	85·1	1·88	—
97·6	2·57	—	119·9	4·80	24·0	127·1	5·66	—	85·6	1·89	72·0
97·4	2·57	—									

Tantalum pentafluoride.

t	$10^5\kappa$	Time, hr.	t	$10^5\kappa$	Time, hr.	t	$10^5\kappa$	Time, hr.	t	$10^5\kappa$	Time, hr.
111·0°	2·15	4·5	119·7°	2·64	—	149·3°	4·88	—	104·3°	2·00	39·5
110·2	2·11	—	129·8	3·26	—	154·1	5·23	24·0	103·8	1·97	—
107·7	2·01	—	129·6	3·24	—	152·9	5·22	—	100·3	1·83	—
101·6	1·81	—	141·2	4·08	—	153·1	5·25	—	92·3	1·52	—
101·8	1·81	—	140·7	4·04	—	145·6	4·59	—	92·3	1·52	—
110·8	2·20	—	139·1	3·99	—	134·0	3·57	—	92·5	1·51	—
110·9	2·21	—	158·0	5·75	—	125·7	3·10	—	92·6	1·53	72·0
119·7	2·64	—	149·3	4·88	—	114·7	2·48	—	92·9	1·52	—

Attempts were also made to determine the decomposition potentials of the two pentafluorides. This, however, was found to be impracticable on account of a considerable polarisation at the electrodes. Application of a constant potential to the electrodes gave a current which decreased with time, and on reversal of the potential, the back E.M.F. then manifested itself by a current which was greater than that corresponding to the potential and the A.C. resistance of the cell.

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