121. *The Halides of Niobium and Tantalum. Part VIII.** *The Densities, Viscosities, and Self-ionisation of Niobium and Tantalum Pentafluorides.*

By Fred Fairbrother, Kenneth H. Grundy, and Alan Thompson.

The densities and viscosities of molten niobium and tantalum pentafluorides have been measured over a range of temperatures. The densities at the melting points are: NbF_5, $d_4^{80\cdot0} = 2\cdot6955$; TaF_5, $d_4^{95\cdot1} = 3\cdot8800$. The dynamic viscosities at the melting points are, respectively, 91·41 and 70·31 centipoises. The results, in conjunction with previously reported conductivities, indicate self-ionisation of the melt of less than 1% and an association of the molecules into polymeric units.

In Part IV,[1] measurements were reported of the conductivities of molten niobium pentafluoride and tantalum pentafluoride. No experimental data were then available regarding their viscosities, and of the densities only that of niobium pentafluoride was known,[2] so that it was necessary to rely on estimated values.

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* Part VII, Copley, Fairbrother, and Thompson, *J.*, 1964, 315.

[1] Fairbrother, Frith, and Woolf, *J.*, 1954, 1031.

[2] Junkins, Farrar, Barber, and Bernhardt, *J. Amer. Chem. Soc.*, 1952, **74**, 3464.

The viscosities and densities of these pentafluorides have now been measured directly. The density values for niobium pentafluoride agree well with those reported by Junkins *et al.*[2] and those for tantalum pentafluoride with those computed in Part IV [1] from a consideration of the density of molten niobium pentafluoride and the ratio of the densities of the solids. On the other hand, the viscosities are greater than was estimated from a rough visual comparison with those of other liquids.

The results confirm the existence of an association of molecules or formation of polymeric units in the melts, as suggested by the high Trouton constants,[3] and, combined with the previous conductivity measurements, indicate that the self-ionisation of these pentafluorides is less than 1%.

EXPERIMENTAL

The pentafluorides were prepared and purified as already described by the action of gaseous fluorine on the pure metals, followed by fractional sublimation in a vacuum and transfer into small ampoules.[3] NbF_5, m. p. 80·0°; TaF_5, m. p. 95·1°.

The viscosities of the molten fluorides were measured in a sealed glass viscometer similar to that described by Greenwood and Wade.[4] The viscometer was totally immersed in a large oil-filled unsilvered Dewar vessel, the oil being electrically stirred and maintained at the temperature of measurement to ±0·02°. The temperature was measured to ±0·02° by an N.P.L. calibrated thermometer, and the time of efflux by a stop-watch to ±0·1 sec. The viscometer was calibrated by use of 40% (w/w) sucrose solution,[5] and the kinematic viscosity, ν, found to be related to the efflux time, t, by the equation: $\nu = 9\cdot962 \times 10^{-2}t - 3\cdot433t^{-1}$. The fluorides were introduced into the viscometer under a vacuum, in the molten state and through a sintered glass disc. The efflux times of the pentafluorides in the viscometer varied between 80 and 350 sec., the average of six readings at each temperature being taken.

Densities were measured in a sealed glass dilatometer consisting of a capillary tube of diameter 0·1903 cm. and a bulb of volume, to an etch mark on the capillary, of 3·6535 c.c.; the dilatometer was calibrated with mercury. The pentafluoride was introduced into the dilatometer, under a vacuum, from a previously weighed ampoule. The dilatometer was sealed off and mounted vertically in the oil thermostat and the level of the meniscus above the etch mark read to ±0·01 mm. by means of a cathetometer. The usual corrections for buoyancy in weighing and thermal expansion of the glass were applied.

TABLE 1.

Densities of (*a*) niobium pentafluoride (m. p. 80°) and (*b*) tantalum pentafluoride (m. p. 95·1°).

(*a*) t (°c)	87·1	93·8	99·0	104·3	108·3	125·6
d_4^t	2·6781	2·6616	2·6487	2·6360	2·6255	2·5851

$$d_4^t = 2\cdot6955 - 2\cdot490 \times 10^{-3}(t - 80)$$

(*b*) t (°c)	109·2	114·3	120·9	125·4	130·4
d_4^t	3·8223	3·8026	3·7765	3·7580	3·7370

$$d_4^t = 3\cdot8804 - 4\cdot035 \times 10^{-3}(t - 95\cdot0)$$

TABLE 2.

Kinematic viscosity, dynamic viscosity, and fluidity.

Niobium pentafluoride				Tantalum pentafluoride			
t (°c)	ν (cs.)	η (cp.)	ϕ (p.$^{-1}$)	t (°c)	ν (cs.)	η (cp.)	ϕ (p.$^{-1}$)
82·7	31·23	83·97	1·191	102·7	15·45	59·47	1·682
87·2	28·23	75·60	1·323	110·4	13·43	51·26	1·955
93·2	24·76	65·94	1·517	116·0	11·93	45·29	2·216
102·0	20·15	53·23	1·879	121·1	10·68	40·31	2·480
107·9	17·29	45·42	2·203	126·2	9·719	36·49	2·740
114·2	15·23	39·76	2·515	130·3	9·100	34·02	2·940
119·0	13·85	35·98	2·779	136·1	8·158	30·30	3·299

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[3] Fairbrother and Frith, *J.*, 1951, 3051.

[4] Greenwood and Wade, *J. Sci. Instr.*, 1957, **34**, 288.

[5] Bingham and Jackson, *Bull. Bur. Stand.*, 1918, **14**, 59.

The densities are given in Table 1, and the values of the kinematic viscosity, ν (centistokes), dynamic viscosity, η (centipoises), and fluidity, ϕ, in Table 2, the relationship between these being $\eta = \nu d = 1/\phi$. The graphs of log η against $1/T$ are linear, and the activation energies of viscous flow, E_η, calculated from the slopes of the lines, are 6·58 and 6·13 kcal. mole^{-1} for NbF_5 and TaF_5, respectively.

Batschinski [6] showed that the temperature variation of the viscosity of a large number of organic liquids could be expressed by the equation $v = b + B\phi$, in which v is the specific volume $(1/d)$, ϕ is the fluidity $(1/\eta)$, and b and B are constants. This relationship has been shown to hold also for a number of molten salts [7] and for other inorganic liquids and fused complexes.[8]

In the present work, the plots of v against ϕ show, over the whole temperature range studied, a slight divergence from the linearity demanded by the Batschinski relationship, in the sense that B decreases with increasing temperature. The mean slopes over the temperature range studied give the following values of b and B: NbF_5, $b = 0{\cdot}364$ c.c. g.$^{-1}$, $B = 0{\cdot}749$ c.c. cp. g.$^{-1}$; TaF_5, $b = 0{\cdot}251$, $B = 0{\cdot}544$.

DISCUSSION

In Part IV [1] the electrical conductivities were reported over the ranges 78·9—154·1° for molten niobium pentafluoride and 92·9—154·1° for molten tantalum pentafluoride, and an attempt was made to ascertain whether these results indicated that a self-ionisation, possibly of the form $[MF_5]_2 \rightleftharpoons MF_6^- + MF_4^+$, was involved in the association of these pentafluorides which is implied by their high Trouton constants.[3]

The activation energies of specific electrical conductance, E_κ, calculated from the variation of specific conductance with temperature, $\kappa = \kappa_0 \exp(-E_\kappa/\mathbf{R}T)$, were 7·52 and 6·42 kcal. mole^{-1} for niobium pentafluoride and tantalum pentafluoride, respectively. The corresponding activation energies for the molar conductances, E_μ, involved a knowledge of the densities of the molten fluorides, since $\mu = M\kappa/d$. The only experimental data then available were those [2] for the densities of niobium pentafluoride. The (interpolated) value [2] for d_4^{100} of 2·6429 is in excellent agreement with our present interpolated value, $d_4^{100} = 2{\cdot}6457$. In order to calculate E_μ in the case of tantalum pentafluoride, it was assumed that its density was 1·44 times that of niobium pentafluoride, this being the ratio of the densities of the solids.[9] Again, this is confirmed by the present determinations which give the ratio of the densities of the molten pentafluorides at their respective melting points as 1·44.

An estimate of the actual degree of electrolytic dissociation in the melts requires a knowledge of their viscosities. No experimental data were available in Part IV and it was assumed, from visual comparison with other liquids, that the viscosities of the molten fluorides were of the order of 20 centipoises. The present work shows that they are in fact 91·41 and 70·31 cp. for niobium pentafluoride and tantalum pentafluoride, respectively, at their melting points; the values of E_η now calculated from experimental data are, respectively, 6·58 and 6·13 kcal. mole^{-1}, and, correspondingly, the values of E_η/E_μ are 0·827 and 0·905, which are much closer to unity than previously supposed.

The relationship between these two activation energies was discussed at length by Greenwood and Martin [10] who concluded that, if E_η/E_μ lies close to unity, the product $\mu\eta$ may be taken as a measure of the percentage of ionic self-dissociation in the melt. It emerges from the present work that the values of $\mu\eta$ for niobium pentafluoride and tantalum pentafluoride at their melting points are 0·104 and 0·078, respectively.

The estimation of the degree of electrolytic dissociation in the melt from these data involves the assumption of an average value for the mobilities of the ions in a solvent of unit viscosity and that the conductance is primarily viscosity-controlled. They cannot,

[6] Batschinski, *Z. phys. Chem.*, 1913, **84**, 643.
[7] Harrap and Heymann, *Chem. Rev.*, 1951, **48**, 45.
[8] Greenwood and Martin, *Quart. Rev.*, 1954, **8**, 1.
[9] Russ and Schiller, *Z. anorg. Chem.*, 1911, **72**, 329.
[10] Greenwood and Martin, *J.*, 1953, 1427.

therefore, be taken as a precise measure of the degree of ionic dissociation, but they give an order of magnitude of the concentration of kinetically free ions.

Niobium pentafluoride and tantalum pentafluoride have been shown,[11] by a complete crystal-structure determination, to exist in the solid state as tetramers with the metal atoms at the corners of a square and linked by linearly-bonded fluorine atoms. They are isostructural with molybdenum pentafluoride, in contrast to niobium and tantalum pentachlorides which exist in the solids as dimers.[12] It seems probable that the high viscosities and high Trouton constants of these pentafluorides are due to polymer formation through fluorine-bridging, and this is reflected in the magnitudes of B in the Batschinski equation, which is related to the size of the flow unit, and which decreases with increasing temperature. The actual viscosities of the present pentafluorides are also very high, being exceeded among inorganic fluorides only by those of vanadium pentafluoride (124·2 cp. at 25°) [13] and antimony pentafluoride (460 cp. at 25°).[14] The latter has been shown by ^{19}F n.m.r. to contain fluorine-bridged polymers in the melt.[15]

A further indication that molten niobium and tantalum pentafluorides contain polymeric units comes from the observation that the relationship between the values of E_η and ΔH_{vap} does not follow that predicted fom the theory of absolute reaction rates of Kincaid, Eyring, and Stern, who showed that for many liquids the values of E_η are between one third and one quarter of the values for ΔH_{vap}.[16] The heats of vaporisation of niobium and tantalum pentafluorides have been shown to be 12·9 and 13·0 kcal. mole^{-1}, respectively; the values of E_η are approximately half these values, which would be expected for compounds which are highly associated in the liquid state.

TABLE 3.

Physical properties of vanadium, niobium, and tantalum pentafluorides.

	VF_5	NbF_5	TaF_5
M. p. (°c)	19·5 ± 0·5 *	80·0 ± 0·02	95·1 ± 0·02
B. p. (°c)	47·9,† 48·3 *	234·9	229·2
V_m (c.c. mole^{-1})	58·33	69·71	71·10
d_4^t	2·502 (ref. 13)	2·6955	3·8800
η (cp.)	124 (25°) (ref. 13)	91·41	70·31
E_η (kcal. mole^{-1})	(13 ± 4) (ref. 13)	6·58	6·13
$10^5\kappa$ (ohm^{-1} cm.$^{-1}$)	24 *	1·63	1·56
E_κ (kcal. mole^{-1})	8·78 *	7·52	6·77
$\mu\eta$ (cm.^{2} cp. ohm^{-1} mole^{-1})	(1·8) (*, ref. 13)	0·104	0·078
ΔH_{vap} (kcal. mole^{-1})	10·64 *	12·9	13·0
ΔH_f (kcal. mole^{-1})	11·94 *	—	—
Trouton constant	33·1 *	25·4	25·9

* Clark and Emeléus, *J.*, 1957, 2119. † Trevorrow, Fischer, and Steunenberg, *J. Amer. Chem. Soc.*, 1957, **79**, 5167.

The values of ΔH_{vap} also reflect the similarity in physical properties of niobium pentafluoride to tantalum pentafluoride, and their divergence from those of vanadium pentafluoride. This is further illustrated by the values of the Trouton constants for these fluorides, which are 33·1, 25·4, and 25·9, respectively, and by the trends in viscosity.

A comparison of the several physical quantities of niobium and tantalum pentafluorides under discussion, with the corresponding values for vanadium pentafluoride is given in Table 3. Values of V_m, d_4^t, η, κ, and $\mu\eta$ are at the melting points unless otherwise stated. It may be seen from these figures that vanadium pentafluoride is more highly associated in the liquid state than niobium pentafluoride or tantalum pentafluoride and undergoes a greater degree of self-ionisation as shown by its higher conductivity and by the higher value of $\mu\eta$ (1·8).

The present results also show a striking difference between the conductivities and

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[11] Edwards, *J.*, 1964, 3714.

[12] Sands and Zalkin, *Acta Cryst.*, 1958, **11**, 615; 1959, **12**, 723.

[13] Clark, *J.*, 1963, 4261.

[14] Woolf and Greenwood, *J.*, 1950, 2200.

[15] Hoffmann, Holder, and Jolly, *J. Phys. Chem.*, 1958, **62**, 364.

[16] Kincaid, Eyring, and Stern, *Chem. Rev.*, 1941, **28**, 301.

viscosities of the molten pentafluorides of niobium and tantalum and those of their pentachlorides. Biltz and Voigt [17] reported that the specific conductivity of molten niobium pentachloride, between 220 and 235° was about $0{\cdot}22 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$ and that of tantalum pentachloride $0{\cdot}30 \times 10^{-6}$ between 230 and 240°, whilst recent measurements [18] give the viscosities (η) of these pentachlorides at their respective melting points (204·2 and 216·2°) as 0·921 and 1·003 cp. That is, the specific conductivity of niobium pentafluoride is about 70 times that of niobium pentachloride, and the specific conductivity of tantalum pentafluoride is about 50 times that of tantalum pentachloride; the viscosity of molten niobium pentafluoride is about 100 times that of niobium pentachloride, and that of tantalum pentafluoride about 70 times the viscosity of tantalum pentachloride.

We are indebted to Imperial Chemical Industries Limited for the provision of the fluorine cell, and to Messrs. Joseph Crossfield Limited for a maintenance grant to K. H. G.

THE UNIVERSITY OF MANCHESTER, MANCHESTER 13. [*Received, June* 1*st*, **1964.**]

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[17] Biltz and Voigt, *Z. anorg. Chem.*, 1922, **120**, 71.

[18] Nisel'son and Pustil'nik, *Izvest. Akad. Nauk S.S.S.R., Otdel. Tekhn. Nauk Met. i Gorn*, 1963, No. 3, 110.