Vapour-density Determinations of Group 5 Pentafluorides

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Vapour-density determinations on the saturated vapours of NbF_5, TaF_5, and SbF_5 at temperatures above their boiling points have been made by a modified Dumas method. The average molecular weights of the vapour-phase species near the boiling points are close to those for the respective trimers. Approaching 400 °C (or 300 °C for SbF_6), however, the major constituent of the vapour is the monomeric pentafluoride.

FOR VF_5, PF_5, and AsF_5 vibrational spectroscopic results[1-10] indicate the presence of monomeric gaseous phases containing molecules of D_{3h} symmetry, consistent with the interpretation of electron-diffraction studies on VF_5,[11] PF_5,[12] and AsF_5.[13] By contrast, NbF_5, TaF_5, and SbF_5 are known to be associated.[11,14-20]

Comparison of theoretical with experimental radial distribution curves from electron-diffraction studies of NbF_5 and TaF_5 has led to the conclusion that tetramers predominate in the gas phase,[21] as in the solids.[22] On the other hand mass-spectrometric studies on the neutral species sampled from the saturated vapours of NbF_5 [23,24] and TaF_5 [23] have been interpreted to suggest an abundant concentration of monomeric, dimeric, and trimeric ions, whereas ions with four or more metal atoms are scarce or absent. In the SbF_5 case,[23] the observation of pentameric ions has been explained by the suggestion that the vapour of this compound is not composed predominantly of tetrameric rings. Thus it is clear that, although the heavier Group 5 pentafluorides are largely polymerised in the vapour, uncertainties about the quantitative composition of the vapours complicate the interpretation of vibrational and mass-spectrometric data.

The aim of the present study was to determine the average molecular weight of molecules in the saturated vapours of niobium, tantalum, and antimony pentafluorides at a range of temperatures above their boiling points.

EXPERIMENTAL

Reagents.—Niobium pentafluoride and TaF_5 were prepared by the direct fluorination of the hydrogen-reduced metal powders at *ca.* 300 °C in dynamic systems. Purification was achieved by slow sublimation under high vacuum and purity was monitored by determination of melting points[25] and from *X*-ray powder patterns.[22] Antimony pentafluoride was prepared by direct fluorination of antimony in a sloping reactor and was purified by repeated sublimation under high vacuum until a highly viscous product was obtained with a conductivity of 6×10^{-6} S cm^{-1}.

Vapour-density Determinations.—Samples of the pentafluorides were sealed under vacuum in predried and prefluorinated, silica, modified Dumas bulbs of *ca.* 35 mm in diameter (Figure 1). The bulbs were scored with a glass knife at points close to the top and close to the bottom of the stem. Bulbs were lowered into thermostatted baths (concentrated H_2SO_4 was used at temperatures up to 200 °C and I.C.I.'s 'Cassel' TS 150 at >200 °C) at predetermined temperatures above the boiling points of the pentafluorides. The tips of the bulbs were removed when it was estimated that the pressure in the bulb had reached atmospheric. (Successful opening was signified by a smooth continuous emission of vapour. If the bulb was

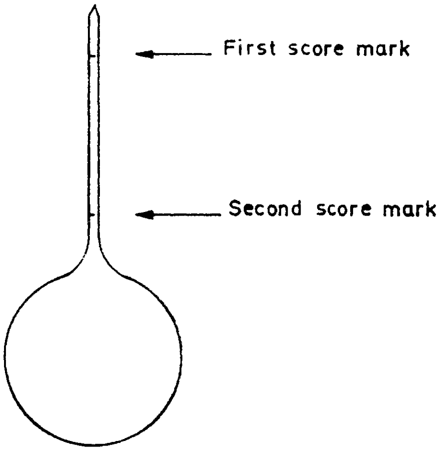

FIGURE 1 Silica Dumas bulb (⅔ scale)

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opened too early no pentafluoride vapour emerged and if too late the emission was pulsatory.) The bulb was maintained at the constant bath temperature until emission had ceased and was then sealed rapidly above the second score-mark. The bulb was cooled, washed, and allowed to equilibrate with the surroundings before it was weighed (see Table). The bulb was broken under degassed distilled water at room temperature and the bulb, water, and any residual air-lock were weighed. The bulb was filled with water from a syringe, reweighed, and then, finally, weighed empty. The measured values were tabulated and the degree of association calculated by a traditional Dumas method, making corrections for buoyancy and for incomplete filling of the bulbs with vapour as outlined in the Table.

Measurements and calculation of the degree of association

Room temperature (r.t. in K) $= a$
Temperature of thermostat bath (K) $= b$
Atmospheric pressure (mmHg) $= c$
Weight of sealed bulb + vapour (g) $= d$
Weight of bulb + water + residual air (g) $= e$
Weight of bulb full of water (g) $= f$
Weight of bulb empty (g) $= g$
Bulb capacity (cm³) $= \dfrac{f - g}{\text{density of water at r.t.}} = h$
Vapour capacity (cm³) $= \dfrac{e - g}{\text{density of water at r.t.}} = i$
Apparent weight of vapour (g) $= j$
Buoyancy of sealed bulb (g) $= \dfrac{i \times 1.296^{*} \times 273 \times c}{10^{3*} \times a \times 760} = k$
$\therefore$ True weight of vapour (g) $= (d - g) + k = l$
The weight of i cm³ of hydrogen at b K and c mmHg $= \dfrac{i \times 273 \times c \times 0.09}{10^{3} \times b \times 760} = m$
$\therefore$ Vapour density $= \dfrac{\text{weight of vapour}}{\text{weight of equal volume of hydrogen}} = \dfrac{l}{m}$
$\therefore$ Molecular weight of vapour $= \dfrac{2l}{m}$ at b K
$\therefore$ Degree of association $= \dfrac{2(l/m)}{\text{molecular weight of } MF_5 \text{ monomer}}$ at b K

* Densities of air and hydrogen were taken from ' Handbook of Chemistry and Physics,' 53rd edn., ed. R. C. Weast, Chemical Rubber Company, Cleveland, 1972.

RESULTS AND DISCUSSION

The results of measurements of the degree of association against temperature are represented in Figures 2—4. For each compound measurements were made from just above the boiling point to *ca.* 300 °C for SbF_5 and 400 °C for NbF_5 and TaF_5. The results for NbF_5 and TaF_5 are very similar. The average degree of association varied from *ca.* 3, close to the boiling point, to *ca.* 1 approaching 400 °C, the average number of MF_5 units associated at a given temperature being slightly higher in the tantalum fluoride case. Values obtained by Beattie and his co-workers[16] for NbF_5 are also shown in Figure 2. The degrees of association they observed at a given temperature are generally lower than our values. This is almost certainly due to the fact that their experiments were made with unsaturated vapours. The overall pictures are closely similar and clearly establish that at temperatures close to 400 °C monomeric NbF_5 species are the most abundant, and at lower and lower temperatures there is increasing polymerisation until, at the boiling point, the average molecular weight is close to that of Nb_3F_{15}. This rather high average value suggests a virtual absence of monomer and the possibility of a significant proportion of tetramer or larger oligomer in the saturated vapour phase near the boiling point. The interpretation of the mass-spectrometric results of Gotkis *et al.*[24] is in agreement with this, but is counter to the suggestion by Falconer *et al.*[23] that species with four or more metal atoms are scarce or absent under these conditions. This underlines the difficulty in interpreting mass-spectrometric results where electron-beam fragmentation of species and ion–molecule reactions occur. For TaF_5 higher temperatures are required to produce monomers than in the NbF_5 case, but again the mean value of the degree of association at the boiling point is $\geqslant 3$ (Figure 3).

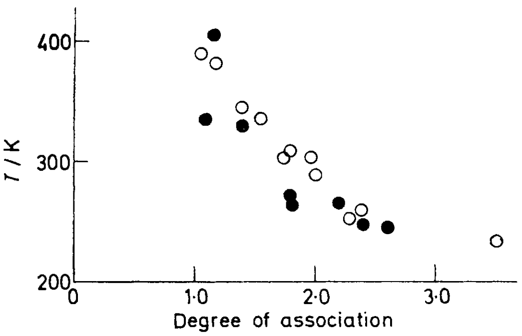

FIGURE 2 Plot of temperature against degree of association for NbF_5(○); (●), values obtained by Beattie and his co-workers[16]

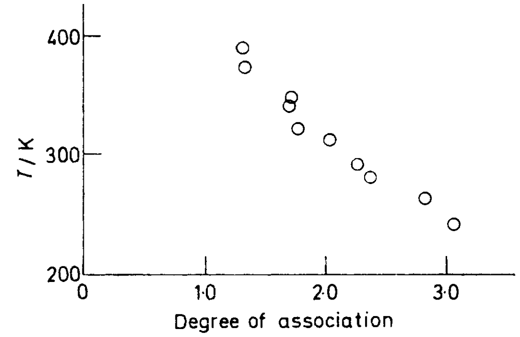

FIGURE 3 Plot of temperature against degree of association for TaF_5

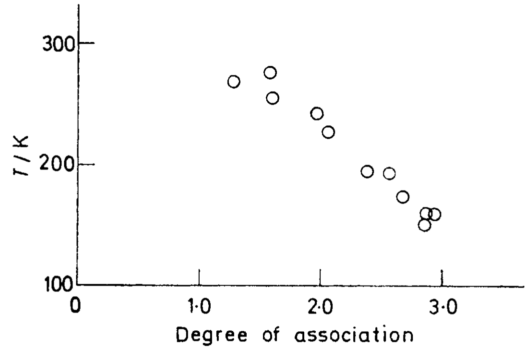

FIGURE 4 Plot of temperature against degree of association for SbF_5

The results for SbF_5 (Figure 4) are totally in accord with the earlier, but less detailed, experiments of Hub and Robinson,[26] who also used a Dumas method. Our values are closely related to those of niobium and tantalum pentafluorides; the average degree of association at the boiling point is 3 whilst, at 300 °C, the main constituent is the monomer. This close correlation suggests that the nature of the vapour of SbF_5 is not greatly different from those of the other two compounds and implies that, in all cases, a considerable proportion of tetramers (or possibly larger oligomers) occurs in the vapours at temperatures close to the boiling point.

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