

406. Some Physical and Chemical Properties of Vanadium Pentafluoride.

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New values for the melting point, vapour pressure, boiling point, and the specific conductivity of vanadium pentafluoride are given. The strength of the pentafluoride as a fluorinating agent has been investigated by a study of its reactions with carbon tetrachloride, tetrabromide, and tetraiodide.

SINCE the first reported preparation of vanadium pentafluoride¹ it has only once been further studied, when Emeléus and Gutmann² prepared it by direct fluorination of the metal at 300° and showed that with metal fluorides it forms hexafluorovanadates of the type MVF₆. The physical properties and simple reactions of vanadium pentafluoride are thus unknown or only known approximately; this is probably due to the difficulty of handling the compound in glass apparatus.

Recent work here³ has shown that a reactive fluoride such as molybdenum hexafluoride can be prepared and purified and its properties investigated in glass systems from which moisture and vacuum grease have been rigidly excluded. This technique has now been successfully applied to the study of vanadium pentafluoride, allowing the determination of the melting point, vapour pressure, boiling point, and specific conductivity. In view of its great reactivity, vanadium pentafluoride should be an effective fluorinating agent and this property has been investigated by studying the reactions of the pentafluoride with carbon tetrachloride, tetrabromide, and tetraiodide.

EXPERIMENTAL

Vanadium pentafluoride was prepared by direct fluorination² of vanadium powder in a nickel boat at 300°. The pale yellow distillate was collected at -183° in glass traps containing sodium fluoride which had been previously heated to 750° to remove all traces of hydrogen fluoride. The traps were connected by capillaries and were fitted with glass break-seals, thus forming systems from which all traces of moisture, hydrogen fluoride, vacuum grease, and other impurities could be rigidly excluded. The impure distillate was purified by trap-to-trap distillation over sodium fluoride in similar all-glass systems, the final product being a white solid which melted slowly at room temperature to a pale yellow viscous liquid.

The molecular weight of vanadium pentafluoride was determined in the apparatus described by O'Donnell³ in which conventional glass taps were replaced by metal Hoke valves. The mean molecular weight from several determinations was 148.0 (Calc. for VF₅: *M*, 146.0).

Samples of the pentafluoride were analysed by dissolving known weights of the compound in dilute alkali. The vanadium was then determined by reduction with sulphur dioxide and titration with standard potassium permanganate. Fluorine was determined by precipitation as calcium fluoride from samples from which the vanadium had been previously precipitated as the oxine complex;⁴ this also confirmed the first vanadium analysis. Thus, the sample used in the determination of the m. p. gave V, 35.15, 34.8; F, 65.3 (Calc. for VF₅: V, 34.9; F, 65.1%).

The melting point, found to be 19.5° ± 0.5°, was determined by Stock's method.⁵ Its sharpness, as indicated by the rapid movement of the glass style through the melting material, was a further indication of the purity of the sample.

The vapour pressure of vanadium pentafluoride was determined over the temperature range -20° to +45.5° by means of a sensitive Pyrex spiral gauge which had been thoroughly dried by flaming *in vacuo* and flushing several times with dry air. The pentafluoride was purified by distillation over sodium fluoride and was finally distilled through a capillary into

¹ Ruff and Lickfett, *Ber.*, 1911, **44**, 2539.

² Emeléus and Gutmann, *J.*, 1949, 2979.

³ O'Donnell, *J.*, 1956, 4681.

⁴ Montequi and Gallego, *Anales Fis. Quím.*, 1934, **32**, 134.

⁵ Stock, *Ber.*, 1917, **50**, 156.

a small bulb attached to the spiral gauge. The capillary was then sealed to provide an all-glass system. The gauge was arranged with as large a distance as possible between the spiral and the reflecting mirror so that for measurements above room temperature all significant parts were adequately immersed in the bath liquid. The difficulties encountered by Fairbrother and Frith⁶ in the measurement of the vapour pressures of niobium and tantalum pentafluorides owing to slow hydrolysis are considerably greater in the case of vanadium pentafluoride, which is much more sensitive to oxygen and moisture, so the values tabulated below will be somewhat less reliable. These values were determined with rising temperature, but several were re-determined as the temperature fell, the agreement between the values showing that any reaction with the glass had been negligible.

Temp. (°K)	252	256	263	268	272	275.5	284	286	293	296
Pressure (mm. Hg) ...	5.0	7.5	13.0	20.5	28.5	37.5	71.5	85.0	133.5	178.5
Temp. (°K)	296.5	300	300.5	305	307	308.5	310.5	312	314.5	318.5
Pressure (mm. Hg) ...	182.0	227.0	235.0	311.0	336.0	391.0	440.0	471.0	535.0	659.0

Conductivity was measured by using the apparatus described by Haszeldine and Woolf⁷ with a Pyrex cell with circular platinum electrodes approximately 1 mm. apart. For convenience in cleaning, the cell was fitted with a ground-glass joint which was made vacuum tight with a tapered Teflon sleeve. Measurements made at 25—45° gave the following values of the specific conductivity κ :

Temp.	25°	30°	34°	36°	39°	42°	45°
10 ⁴ κ (ohm ⁻¹ cm. ⁻¹)	2.43	3.09	3.86	4.17	4.77	5.44	6.20

These values give a straight-line plot of $\log_{10}(\kappa \times 10^4)$ against $1/T$. Further measurements were made of the conductivity of a sample to which potassium fluoride had been added. However, the solubility of potassium fluoride was much lower than expected, but sufficient to increase the specific conductivity to 8.1×10^{-4} at 25°.

The reactions of vanadium pentafluoride with carbon tetrachloride, tetrabromide, and tetraiodide were also carried out in systems in which conventional taps and joints were replaced by capillaries and break-seals. The volatile products of each reaction were fractionated through such systems and the various fractions identified by the determination of vapour pressures and molecular weights in the apparatus previously described.⁸ Involatile residues were analysed for vanadium and fluorine as described above, and for other elements by standard methods.

Excess of vanadium pentafluoride reacted with carbon tetrachloride (1.50 g.) at room temperature to produce 1.18 g. of trichlorofluoromethane (Found: M , 137.7. Calc. for CCl_2F : M , 137.6). Secondary products were a yellow gaseous mixture (0.065 g.) of chlorine and dichlorodifluoromethane (Found: M , 100.1. Calc. for Cl_2 : M , 71. Calc. for CCl_2F_2 : M , 121) and a mixture (0.055 g.) of chlorotrifluoromethane and carbon tetrafluoride (Found: M , 98.5. Calc. for CClF_3 : M , 104.5. Calc. for CF_4 : M , 88). The reaction was quantitative, 97% of the carbon tetrachloride being accounted for in these volatile products. A much less volatile fraction consisting of a dark red liquid and a white solid had a molecular weight of 169 and contained vanadium, fluorine, and chlorine. Quantitative analyses confirmed the composition of the mixture as excess of pentafluoride (M , 146) and vanadium tetrachloride (M , 193). A very small amount of involatile yellow-green residue was shown to be vanadium trifluoride.

From 1.67 g. of carbon tetrabromide, after reaction at room temperature with excess of vanadium pentafluoride, 0.450 g. was recovered unchanged owing, presumably, to the formation of a protective coating of involatile vanadium salts. The remaining portion of the involatile residue dissolved readily in dilute alkali to give a green solution suggesting the presence of tervalent vanadium. Quantitative analyses showed the material to be a mixture of vanadium tribromide and tetrafluoride. The volatile products were carbon tetrafluoride (0.253 g.; Found: M , 92.5), bromotrifluoromethane (0.026 g.; Found: M , 158. Calc. for CF_3Br : M , 149), and an inseparable, dark red mixture of free bromine and excess of vanadium pentafluoride.

Carbon tetraiodide (1.74 g.), prepared by Walker's method,⁸ was allowed to react for

⁶ Fairbrother and Frith, *J.*, 1951, 3051.

⁷ Haszeldine and Woolf, *Chem. and Ind.*, 1950, 544.

⁸ Walker, *J.*, 1904, 85, 1090.

48 hr. at room temperature with excess of vanadium pentafluoride. On fractionation, the volatile products were found to be carbon tetrafluoride (0.21 g.; Found: M , 92.5), trifluoroiodomethane (0.046 g.; Found: M , 198. Calc. for CF_3I : M , 195.9), and a mixture of iodine pentafluoride and excess of vanadium pentafluoride. This mixture was identified by molecular-weight measurements (Found: M , 164. Calc. for IF_5 : M , 221.9. Calc. for VF_5 : M , 146), and by both qualitative and quantitative analyses. Of the involatile black residue, only a small portion dissolved in water to give a blue solution, leaving a considerable amount of free iodine (approx. 1.0 g.). The aqueous solution contained iodide, fluoride, and vanadium in proportions corresponding to a mixture of vanadium iodide, VI_2 , and vanadium tetra- and tri-fluorides.

DISCUSSION

The melting point, $19.5^\circ \pm 0.5^\circ$, is in considerable disagreement with the results of Ruff and Lickfett¹ who reported that it does not melt in sealed glass tubes, even above 200° . However, they also reported its boiling point as 111.2° , and it seems highly probable that their samples of pentafluoride were badly contaminated with vanadium oxytrifluoride. The other pentafluorides of this sub-group of the Periodic Table, niobium and tantalum pentafluorides, have been shown to have m. p. of 80.0° and 91.5° respectively,⁶ while a later value⁹ for niobium pentafluoride is 78.9° . In a series of compounds such as the above three pentafluorides, higher m. p.s are to be expected with increasing molecular radii, so that this new value for vanadium pentafluoride is consistent and of the expected order.

The vapour-pressure measurements quoted above indicate that in the solid state, the vapour pressure obeys the relation $\log_{10} p(\text{mm.}) = 11.049 - 2608/T$, while for liquid vanadium pentafluoride the corresponding equation is $\log_{10} p(\text{mm.}) = 10.430 - 2423/T$. Hence the b. p. (extrapolated) is $48.3^\circ \pm 1^\circ \text{C}$, the latent heat of fusion 11,940 cal./mole, the latent heat of vaporisation 10,640 cal./mole, and the Trouton constant 33.1. Physically, the compound is thus very similar to molybdenum hexafluoride which melts at 17.5° and boils at 35° . The high value of the Trouton constant is of great interest, since it suggests considerable association in the liquid state. Iodine pentafluoride, for which the Trouton constant is 27.2, is said to associate and ionise as shown (eqn. 1), and in view of the isolation of stable hexafluorovanadates² containing the VF_6^- ion, it is reasonable to postulate that a similar process occurs in liquid vanadium pentafluoride (eqn. 2).



It is noteworthy that molybdenum hexafluoride with a normal value for the Trouton constant, 20.6, shows no signs of association, probably owing to the much greater instability of ions for which the central atom has co-ordination numbers of five and seven.

That the process (2) occurs in liquid vanadium pentafluoride is strongly supported by the conductivity measurements. The following values of the specific conductivities ($\text{ohm}^{-1} \text{cm.}^{-1}$; temperature shown in parentheses) also indicate that this ionisation occurs to a much greater extent than for iodine pentafluoride, or niobium and tantalum pentafluorides: TaF_5 , 1.56×10^{-5} (95.1°)¹⁰; NbF_5 , 1.63×10^{-5} (80.0°)¹⁰; IF_5 , $2-3 \times 10^{-5}$ (25°)¹¹; VF_5 , 2.4×10^{-4} (25°)¹²; BrF_3 , 8.0×10^{-3} (25°)¹¹. If eqn. 2 is accepted, then the increase in conductivity on the addition of potassium fluoride is to be expected.

The fluorination with vanadium pentafluoride of the three carbon tetrahalides was undertaken to provide a means of determining the strength of the pentafluoride as a fluorinating agent, since similar reactions with bromine trifluoride and iodine pentafluoride had already been performed.¹³ It was shown that, under conditions similar to

⁹ Junkins, Farrar, Barber, and Bernhardt, *J. Amer. Chem. Soc.*, 1952, **74**, 3464.

¹⁰ Fairbrother, Frith, and Woolf, *J.*, 1954, 1031.

¹¹ Banks, Emel us, and Woolf, *J.*, 1949, 2861.

¹² Present work.

¹³ Banks, Emel us, Haszeldine, and Kerrigan, *J.*, 1948, 2188.

those used here, the main products of the reactions of bromine trifluoride with carbon tetrachloride and with carbon tetrabromide were trichlorofluoromethane and bromotrifluoromethane respectively, while with carbon tetraiodide, dibromodifluoromethane and carbon tetrafluoride were produced. When it is remembered that the bromine in the reactant bromine trifluoride will considerably influence the products of the reactions, it is clear that vanadium pentafluoride appears to be just as effective as a fluorinating agent.

On the other hand, it was necessary to heat iodine pentafluoride and carbon tetrabromide to 90° to obtain an 83% yield of dibromodifluoromethane, while with carbon tetraiodide the main product was trifluoroiodomethane. Vanadium pentafluoride is therefore considerably more effective than iodine pentafluoride as a fluorinating agent, since not only does it react with carbon tetrabromide and tetraiodide at room temperatures to produce mainly carbon tetrafluoride, but in the latter case it also produces a certain amount of iodine pentafluoride.

Further work on vanadium pentafluoride is now in progress.

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