517. *The Preparation and Properties of Vanadium Tetrafluoride.*

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Reaction of vanadium tetrachloride and anhydrous hydrogen fluoride in trichlorofluoromethane solution to give pure vanadium tetrafluoride is described. The results of density, magnetic susceptibility, and crystallographic measurements on the tetrafluoride are reported. The salt K_2VF_6 has been obtained from potassium fluoride and vanadium tetrafluoride in selenium tetrafluoride solution, but the analogous cæsium salt cannot be obtained pure. Vanadium tetrafluoride reacts with ammonia and pyridine to give the same products as does vanadium pentafluoride. Other chemical reactions of vanadium tetrafluoride are also reported.

VANADIUM TETRAFLUORIDE was first reported by Ruff and Lickfett [1] in 1911. However, despite recent interest in vanadium trifluoride,[2] vanadium pentafluoride,[3] and complex fluoro-salts of quadrivalent vanadium,[4,5] no further study of the tetrafluoride has been reported. Indeed, there are even reports that vanadium tetrafluoride does not exist.[6] To clarify the situation and to permit comparisons with the trifluoride and pentafluoride, we have examined the preparation and some properties of vanadium tetrafluoride.

Our first preparations of vanadium tetrafluoride from vanadium tetrachloride and anhydrous hydrogen fluoride followed the procedure of Ruff and Lickfett.[1] However, the product usually contained vanadium trifluoride, and possibly unchanged tetrachloride, presumably arising from a surface reaction between hydrogen fluoride and frozen vanadium tetrachloride. Addition of an inert solvent, such as trichlorofluoromethane, to the reaction mixture resulted in a solution which remained liquid at —78°. A homogeneous, pure product was thus obtained. Vanadium tetrafluoride may also be prepared from the metal and gaseous fluorine. At 200°, all three known vanadium fluorides, VF_3, VF_4, and VF_5 are formed, but their different volatilities allow complete separation during the reaction.

Pure vanadium tetrafluoride, prepared from vanadium tetrachloride and hydrogen fluoride, is a brilliant lime-green powder which, on exposure to moisture, hydrolyses to a brown powder and eventually to a blue paste. The brown product obtained by Ruff and Lickfett [1] was probably the brown surface-hydrolysed form. Fluorination of vanadium metal (and sublimation of vanadium tetrafluoride) yielded a dark green, massive solid which presumably differs only in compactness, for the powdered and the massive forms of vanadium tetrafluoride had identical *X*-ray patterns. The massive form is also hydrolysed less readily. Vanadium tetrafluoride is insoluble in a variety of organic and inorganic solvents.

Vanadium tetrafluoride is thermally unstable. At 100—120° in a vacuum, disproportionation into vanadium trifluoride and pentafluoride, first reported by Ruff and Lickfett,[1] is quite rapid. The rate of disproportionation increases with temperature, but a high temperature (*e.g.*, Ruff and Lickfett's report [1] of 325° as the disproportionation temperature) is not necessary to induce disproportionation. Samples of vanadium tetrafluoride stored for 4—6 days at room temperature, sealed in dry glass tubes, at atmospheric pressure, contained about 5% of vanadium trifluoride plus a gas, which is presumably silicon tetrafluoride arising from the reaction of vanadium pentafluoride with the glass. At —78°,

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

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

[3] (*a*) Clark and Emeléus, *J.*, 1957, 2119; (*b*) 1958, 190; (*c*) Trevorrow, *J. Amer. Chem. Soc.*, 1957, **79**, 5165.

[4] Huss and Klemm, *Z. anorg. Chem.*, 1950, **262**, 25; Hoppe, *Rec. Trav. chim.*, 1956, **75**, 569.

[5] Liebe, Weise, and Klemm, *Z. anorg. Chem.*, 1961, **311**, 281.

[6] Simons and Powell, *J. Amer. Chem. Soc.*, 1945, **67**, 75.

vanadium tetrafluoride could be stored for at least two weeks without excessive decomposition into tri- and penta-fluoride. As no method of separating vanadium tetrafluoride from vanadium trifluoride is available, all work must be done with freshly prepared tetrafluoride. The disproportionation of vanadium tetrafluoride into the tri- and pentafluoride is apparently irreversible and is analogous to the disproportionation of vanadium trichloride into the di- and tetra-chloride. Vanadium tetrafluoride is one of the few simple fluorides which spontaneously disproportionate into higher and lower fluorides.

Coincident with disproportionation, vanadium tetrafluoride sublimes at 100—120° in a vacuum and is redeposited as a dark green solid which has the same *X*-ray powder pattern as powdered vanadium tetrafluoride. Vanadium tetrafluoride thus resembles titanium and chromium tetrafluorides which also sublime in a vacuum between 100° and 200°,[7,8] but differs from the tetrafluorides of zirconium and hafnium which sublime only at red heat.[7]

Vanadium tetrafluoride appears to have a crystal structure unlike any of the known tetrafluoride structures. The best agreement with the powder photograph has been obtained with a hexagonal unit cell of dimensions $a = 5{\cdot}38$, $c = 5{\cdot}16$ Å ($c/a = 0{\cdot}96$) containing two formula units. The volume of the unit cell is 129·9 Å^3 which corresponds to a volume of 16·2 Å^3 for each fluoride ion if the contribution of V^{4+} ion is neglected. Similar volumes have been observed in other fluoride structures.[9] The *X*-ray density of $3{\cdot}2_5$ g./c.c. agrees satisfactorily with the pyknometric density of $3{\cdot}1_5 \pm 0{\cdot}1_5$ g./c.c.

Lack of definite information on the atomic positions within the unit cell precludes a complete discussion of this structure. However, vanadium tetrafluoride is clearly not isostructural with the monoclinic ZrF_4 type, which includes hafnium tetrafluoride and the actinide tetrafluorides,[10] nor is it isostructural with tetrafluorides such as those of silicon and germanium,[11] which form cubic crystals of discrete tetrahedral molecular units in which the metal atom is tetraco-ordinate. The greater volatility of vanadium tetrafluoride than those of zirconium and hafnium tetrafluorides also suggests that it is not as highly associated as they are.

Recent studies on the specific heat of titanium tetrafluoride[12] support Hückel's proposal[7] that this fluoride does not condense with a molecular lattice but rather as a polymer of condensed octahedral TiF_6 groups in which the titanium atom is hexaco-ordinate. The similar volatilities of titanium and vanadium tetrafluorides, the unique crystal structure of the latter, and the tendency of vanadium to achieve its maximum co-ordination of six suggest that vanadium tetrafluoride crystallises with a lattice constructed from condensed octahedral VF_6 units sharing four fluorine atoms with other octahedral units. Vanadium trifluoride has been shown to contain condensed VF_6 units[13] with all fluorine atoms shared, thus achieving hexaco-ordinate vanadium. Also it has been suggested[14,15] that vanadium pentafluoride condenses as a polymer of hexaco-ordinate VF_6 units, each sharing two fluorines with adjacent octahedra. The regular increase in volatility from the trifluoride to the pentafluoride thus follows the probable order of decreasing molecular condensation. It is interesting that vanadium tetrafluoride is apparently not isostructural with platinum tetrafluoride, which has a distorted UCl_4 structure in which platinum is octaco-ordinate.[16]

The magnetic susceptibility of vanadium tetrafluoride obeys the Curie–Weiss law,

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[7] Hückel, " Structural Chemistry of Inorganic Compounds " (English translation), Elsevier, Amsterdam, 1951, Vol. II, pp. 470—474.

[8] Sadana and Clark, unpublished observations.

[9] D'Eye and Wait, " X-ray Powder Photography in Inorganic Chemistry," Butterworths Scientific Publns., London, 1960, p. 186.

[10] Zachariasen, *Acta Cryst.*, 1949, **2**, 388.

[11] Wyckoff, " Crystal Structures," Interscience Publ. Inc., New York, Vol. I, 1948.

[12] Euler and Westrum, *J. Phys. Chem.*, 1961, **65**, 132.

[13] Gutmann and Jack, *Acta Cryst.*, 1951, **4**, 246.

[14] Cavell and Clark, *J. Inorg. Nuclear Chem.*, 1961, **17**, 257.

[15] Clark, *Chem. Rev.*, 1958, **58**, 869.

[16] Bartlett and Lohmann, unpublished work; Mooney, *Acta Cryst.*, 1949, **2**, 189.

$\chi_M' = C/(T + \theta)$, with C = 0·5835 c.g.s. units, and θ = 198°. χ_M' denotes molar susceptibility, corrected for diamagnetic contributions of the ions by the values given by Selwood.[17] The magnetic moment at 295° K, calculated[18] from the expression $\mu_{eff} = 2{\cdot}84\sqrt{\chi_M'(T + \theta)}$, is 2·17 Bohr magnetons.

Vanadium tetrafluoride is readily converted into vanadium pentafluoride by bromine trifluoride and elemental fluorine. Liquid nitryl fluoride has no effect on vanadium tetrafluoride, but in the presence of iodine pentafluoride it formed vanadium pentafluoride as the nitryl salt $(NO_2)VF_6$.[3b]

Vanadium tetrafluoride is much less reactive than the pentafluoride, as shown by the lack of reaction with sulphur dioxide or trioxide, both of which are fluorinated by the pentafluoride.[3b]

Vanadium tetrafluoride forms 1 : 1 complexes with ammonia, pyridine, and selenium tetrafluoride. Pyridinetetrafluorovanadium(IV), $PyVF_4$, and amminetetrafluorovanadium(IV), NH_3VF_4, which were previously reported as the products of the reactions of pyridine and ammonia with vanadium pentafluoride,[14] have now been prepared from the components. These complexes resemble the 1 : 1 tetrafluoride–base complexes reported by Muetterties[19] and are probably fluorine bridge polymers.[14,19] Formulation of the SeF_4,VF_4 adduct as a donor–acceptor complex does not seem possible in view of the evidence that selenium tetrafluoride is not a good electron-donor.[20] Alternatively the adduct could be regarded either (*a*) as the ionic structure, $SeF_3^+VF_5^-$, or an equivalent one such as $(SeF_3^+)_2(V_2F_{10}^{2-})$ in which the vanadium atoms are hexaco-ordinate through polymerisation of the anion,[21] or (*b*) as the related fluorine bridge structure with two fluorines shared between selenium and vanadium, the latter again maintaining its hexaco-ordination. The ionic structures may be considered less likely in view of the fact that KVF_5 could not be prepared from the components; however, this in itself is not sufficient evidence to exclude ionic structures because large cations such as SeF_3^+ may exert a stabilising influence. The failure of sulphur tetrafluoride to form a complex with vanadium tetrafluoride can be explained in terms of the lower stability of SF_3^+ relative to SeF_3^+ or in terms of the lesser ability of sulphur tetrafluoride to act as a fluoride acceptor,[20] depending on the formulation chosen for the complex SeF_4,VF_4.

The magnetic susceptibility of SeF_4,VF_4 obeys the Curie–Weiss law with C = 0·665 c.g.s. units, and θ = 134°. The magnetic moment, calculated as above, is 2·32 Bohr magnetons at 295° K. The temperature-dependence of the susceptibilities of amminetetrafluorovanadium(IV) and pyridinetetrafluorovanadium(IV) was not investigated, but the moments at 292° K are 1·82 and 1·79 Bohr magnetons, respectively.

Potassium hexafluorovanadate(IV) was prepared from potassium fluoride and vanadium tetrafluoride in selenium tetrafluoride. The trigonal form of the salt was obtained, with lattice constants a = 5·68 Å, c = 4·66 Å, corresponding to the low-temperature form obtained by Liebe *et al.*[5] by fluorination of $K_2V^{III}F_5$. The calculated density of 3·09 g./c.c. is not in good agreement with the pyknometric density of 2·56 g./c.c. under carbon tetrachloride. Attempts to prepare the cæsium salt in the same manner resulted in a mixture of hexagonal Cs_2VF_6 (the low-temperature form obtained by Liebe *et al.*[5]) and penta- and ter-valent salts such as $CsVF_6$ and Cs_3VF_6, etc. Neither the potassium salt nor the cæsium salt could be prepared free from "quinquevalent" M^IVF_6 when iodine pentafluoride was used as a solvent. Calcium and barium hexafluorovanadate(IV) salts could not be prepared, presumably because the lattice energies of calcium and barium fluorides,[22a] which are approximately three times as great as the lattice energies of alkali fluorides,[22b] are

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[17] Selwood, "Magnetochemistry," Interscience Publ. Inc., New York, 2nd edn., 1956, p. 78.

[18] Figgis and Lewis, in "Modern Co-ordination Chemistry," ed. Lewis and Wilkins, Interscience Publ. Inc., New York, 1960, Chapter 6, p. 435.

[19] Muetterties, *J. Amer. Chem. Soc.*, 1960, **82**, 1082.

[20] Bartlett and Robinson, *J.*, 1961, 3417.

[21] Peacock, *Progr. Inorg. Chem.*, 1960, **2**, 193.

[22] Waddington, *Adv. Inorg. Chem. and Radiochem.*, 1959, **1**, (*a*) 210, (*b*) 190.

sufficiently high to make the formation of these hexafluorovanadate(IV) salts thermodynamically unfavourable.

The absence of oxidation or reduction in the formation of 1 : 1, A,VF_4 complexes and in the treatment of vanadium tetrafluoride with fluorides such as iodine pentafluoride and sulphur tetrafluoride contrasts sharply with the prevalence of oxidation–reduction of vanadium during attempts to prepare hexafluorovanadate(IV) salts. There is insufficient information about the behaviour of these fluoride solvents in the presence of alkali-metal fluorides and transition-metal fluorides to provide a complete explanation of the oxidation and reduction of vanadium in the salt preparations.

The magnetic susceptibility of potassium hexafluorovanadate(IV) obeys the Curie–Weiss law with $C = 0{\cdot}515$ c.g.s units, and $\theta = 118°$. The magnetic moment, calculated as above, is 2·05 Bohr magnetons at 295° K. These results agree closely with those of Liebe *et al.*[5] except for their value of 78° for the Weiss constant (θ) of K_2VF_6.

The present and other [5] results show that the magnetic susceptibilities of the fluorine compounds of vanadium(IV) all obey the Curie–Weiss law with high values of the Weiss constant, ranging from 75° to 200°, as shown in Table 1. The high θ values may be due to antiferromagnetic interaction, as suggested by the positive sign of θ, or to spin–orbit interaction, or perhaps a combination of both.

TABLE 1.

Weiss constants of vanadium(IV) fluorides.

Compound	VF_4	SeF_4,VF_4	K_2VF_6	K_2VF_6	Rb_2VF_6	Cs_2VF_6
Weiss constant	198°	134°	118°	78°	101°	103°
Reference	Present work			Ref. 5		

High θ values, ranging from 50° to 225°, have been found [23] in the salts of quinquevalent molybdenum and rhenium, of the general formula AMF_6. However, these salts have moments fairly close to the spin-only value for one and two unpaired electrons, respectively, when θ corrections are applied. Since Kotani's theory [24] does not apply it was concluded that the source of θ is antiferromagnetic interactions.

In the case of vanadium(IV) fluorides, correction for θ yields moments greater than the spin-only value. Plots of μ_{eff} [calculated from $\mu_{\text{eff}} = 2{\cdot}84\surd\chi'_{\text{M}}(T + \theta)$] against temperature do not agree with the predictions of Kotani's theory;[24] hence the large value of θ is probably due to antiferromagnetic interactions. Hargreaves and Peacock [23] have suggested that tetragonal distortions (*i.e.*, compression or expansion along one axis of the octahedron) of the MF_6^- ions may have a large effect on the antiferromagnetism of complex salts and hence on the magnetic moments. Thus the large θ values in vanadium(IV) fluorides may arise from tetragonal distortions of the octahedral co-ordination about the vanadium.

Other vanadium(IV) compounds, such as the vanadyl salts [25] and vanadium tetrachloride,[26] do not exhibit such high θ values, suggesting that large θ values are not characteristic of the d^1 V(IV) electronic configuration but rather of the symmetry about the vanadium atom in the fluorides. Complete structural determinations of vanadium(IV) compounds, necessary to test this proposal, are unfortunately not available.

EXPERIMENTAL

Reactions were carried out in all-glass vacuum-systems with taps replaced by combinations of capillary constrictions and magnetic break-seals. Silica reaction vessels were used for reactive fluorides such as selenium tetrafluoride and iodine pentafluoride. The systems were

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[23] Hargreaves and Peacock, *J.*, 1958, 3776.

[24] Kotani, *J. Phys. Soc.* (*Japan*), 1949, **4**, 293.

[25] Perakins, *J. Phys. Radium*, 1927, **8**, 473.

[26] Klemm and Hoschek, *Z. anorg. Chem.*, 1936, **226**, 359.

" flamed out " under a vacuum before use, to ensure the complete removal of moisture. All hygroscopic solids were transferred in a dry-box. Magnetic susceptibilities were determined with a Gouy balance equipped with a thermostat-controlled temperature compartment, which has been described elsewhere.[27] The apparatus was calibrated with $HgCo(SCN)_4$.[28] *X*-Ray powder photographs were taken on a General Electric unit with a camera of 14·4 cm. diameter, and Cu-K_α radiation. The samples were sealed in 0·5 mm., thin-walled *X*-ray capillaries (Pantak Ltd.) to protect them from atmospheric moisture.

Vanadium was estimated as described previously,[14] except that oxidisable anions (*e.g.*, I^-, SeO_3^{2-}) were removed by adsorbing the vanadium(IV) cation on a Dowex-50W cation-exchange resin and eluting the extraneous anions. Fluorine was estimated by distillation from perchloric acid at 130—135°,[29] followed by precipitation as lead chloride fluoride. Selenium was estimated as the metal after precipitation from a strongly acidic solution with sulphur dioxide. Chlorine was determined as silver chloride.

Preparation of Vanadium Tetrachloride.—Vanadium tetrachloride was prepared by passing chlorine (Matheson Co.) over vanadium metal at 300—350° and distilling the product in an all-glass still, the fraction boiling between 152° and 154° being collected (Found: V, 26·4; Cl, 73·5. Calc. for VCl_4: V, 26·4; Cl, 73·6%).

Vanadium Tetrafluoride.—(*a*) *Preparation from vanadium tetrachloride.* Vanadium tetrachloride (~10 g.) was placed in a polyethylene reactor (~250 ml.) containing a Teflon-coated magnetic stirring bar. The reactor was connected to a polyethylene condenser, trichlorofluoromethane (Freon-11, Dupont Co.) (20 g.) was added, and the reactor chilled to −78°. A vigorous stream of nitrogen was maintained throughout the operation to flush out moisture. Stirring was begun and 25—30 ml. of anhydrous hydrogen fluoride were condensed into the reactor. The vessel was permitted to return to room temperature during 3 hr. At this point the reaction was complete and any excess of hydrogen fluoride or solvent was boiled off by warming the reactor to 30—35°, to leave pure *vanadium tetrafluoride* (Found: V, 40·0, 40·4; F, 59·0, 59·6. VF_4 requires V, 40·3; F, 59·7%). The magnetic moment at 293° K, without θ correction, was 1·65 Bohr magnetons. The temperature-dependence of the magnetic susceptibility of VF_4 is given in Table 2.

TABLE 2.

Magnetic susceptibilities of vanadium(IV) fluorides.

	VF_4			SeF_4,VF_4			K_2VF_6	
Temp. (K)	$10^4\chi'_M$	μ_{eff}	Temp. (K)	$10^4\chi'_M$	μ_{eff}	Temp. (K)	$10^4\chi'_M$	μ_{eff}
293°	11·91	2·17	294·5°	15·59	2·32	296°	12·56	2·05
252	12·97	2·17	273	16·32	2·31	266	13·42	2·04
243	13·11	2·16	245	17·65	2·32	241	14·16	2·03
204	14·49	2·17	215	18·70	2·29	226	15·01	2·04
181	15·23	2·16	193	20·18	2·31	209	15·47	2·02
132	17·71	2·17	165	21·87	2·29	189	17·03	2·05
83	21·01	2·17	138	24·30	2·31	186	16·32	2·00
			124	25·88	2·32	150	17·65	1·95
			88	30·15	2·32	128	21·22	2·05
	$\theta = 198°$			$\theta = 134°$		105	22·25	2·00
	$C = 0·5835$ c.g.s.u.			$C = 0·665$ c.g.s.u.		83	28·96	2·17
							$\theta = 118°$	
							$C = 0·515$ c.g.s.u.	

A sample of the tetrafluoride prepared in the above manner, but without a solvent and stirring, was contaminated with about 3·5% of vanadium(III) (Found: V, 41·2%; magnetic moment, 1·9 Bohr magnetons at 293° K, without θ correction).

(*b*) *Preparation from vanadium metal and fluorine.* Vanadium (~5 g.) in a nickel boat was placed in a 1″-diameter nickel reactor, and a series of glass traps was fitted to the exit. The reactor was heated to 150—200°, fluorine diluted with nitrogen was passed into it for 2 hr. A small amount of white solid sublimed into the glass traps which were cooled to −78°. The reactor was sealed off and dismantled in the dry-box. Around the exit of the reactor was a mass of dark green solid which was identified as vanadium tetrafluoride (Found: V, 40·5; F, 57·2%).

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[27] Clark and O'Brien, *Canad. J. Chem.*, 1961, **39**, 1030.

[28] Figgis and Nyholm, *J.*, 1958, 4190.

[29] Willard and Winter, *Ind. Eng. Chem., Analyt.*, 1933, **5**, 7.

This solid deliquesced in air to a blue paste, although not as quickly as the powder. The *X*-ray pattern was identical with that of the lime-green powder.

(*c*) *Properties.* Pure vanadium tetrafluoride is a bright, lime-green powder which becomes brown on exposure to small amounts of moisture in the dry-box. On exposure to air it deliquesced to a blue paste. It dissolved rapidly in water, yielding an acidic solution with the characteristic rich blue colour of vanadium(IV). It was insoluble in carbon tetrachloride, trichlorofluoromethane, ether, benzene, and nitrobenzene. In pyridine, acetonitrile, tetrahydrofuran, and ethoxymethoxyethane, vanadium tetrafluoride formed a greenish solution with a brown residue remaining. Chlorobenzene, toluene, and pentane converted it into a black solid while the solvent remained uncoloured. Two determinations of the specific gravity under carbon tetrachloride gave 3·28 g./c.c. (at 28°) and 3·02 g./c.c. (at 19·5°). The magnetic susceptibility was measured from 83° to 293° K and the results are given in Table 2.

(*d*) *Thermal disproportionation.* The tetrafluoride (~4 g.) was placed in a silica pyrolysis tube and connected, *via* a spray trap, to a glass trap-line. One trap was chilled to $-78°$, the system evacuated, and the temperature of the silica tube slowly increased. At 100° the evolution of gas was vigorous and powdered tetrafluoride was carried through the apparatus. The temperature was maintained between 100° and 120° for 20—30 hr., until gas evolution ceased. The pale yellow solid residue was vanadium trifluoride (Found: V, 47·4; F, 52·8. Calc. for VF_3: V, 47·3; F, 52·7%). The $-78°$ trap contained vanadium pentafluoride as a white solid, which melted to a pale yellow liquid at 20° (lit.,[3a] 19·5°) (Found: V, 33·5; F, 61·9%; F/V, 4·97/1. Calc. for VF_5: V, 34·9; F, 65·1%).

(*e*) *Sublimation.* During one pyrolysis the exit of the silica tube became completely blocked with dark green glass, which was impure vanadium tetrafluoride (Found: V, 41·5%). This solid gave an *X*-ray powder pattern identical with that of lime-green, powdered tetrafluoride.

Analysis of a sample of vanadium tetrafluoride which had been kept for about 10 days at room temperature showed that 7·5% of the vanadium was present as vanadium(III) (Found: V, 41·6%).

Preparation of Hexafluorovanadate(IV) *Salts.*—Potassium fluoride and vanadium tetrafluoride (2 : 1 molar ratio) were mixed in a silica reaction vessel, with selenium tetrafluoride [30] (10 ml.). A dark red solution was formed above the mixed solid reactants. After 30 min. at room temperature the solvent was removed under a vacuum and the salt was heated at 150° for several hours. The residue, a pale pink powder, was potassium hexafluorovanadate(IV) (Found: V, 21·25; F, 47·3. Calc. for K_2VF_6: V, 21·0; F, 46·9%). Titration of a freshly dissolved sample, without prior treatment with sulphur dioxide, confirmed that all vanadium was present as vanadium(IV). Results of the magnetic susceptibility measurements are given in Table 2. The specific gravity of K_2VF_6 under carbon tetrachloride was 2·5 g./c.c. at 28°.

Reaction of cæsium fluoride with vanadium tetrafluoride (2 : 1 mol.) in selenium tetrafluoride as above yielded a bright pink powder which tenaciously retained solvent. After prolonged evacuation with heating, a pale pink powder, which was impure cæsium hexafluorovanadate(IV), was obtained (Found: V, 11·6. Calc. for Cs_2VF_6: V, 11·8%). Direct titration of a freshly dissolved sample indicated that not all the vanadium was present as vanadium(IV). The magnetic moment was 2·48 Bohr magnetons at 293° K. The *X*-ray powder photograph indicated hexagonal Cs_2VF_6 plus extraneous lines attributed to $CsVF_6$ and possibly Cs_3VF_6 or Cs_2VF_5.

Potassium fluoride and vanadium tetrafluoride (2 : 1 mol.) reacted in iodine pentafluoride (Matheson Co.). The pale pink product contained much free iodine and was a mixture of K_2VF_6 and KVF_6 (Found: V, 20·6. Calc. for K_2VF_6: V, 21·0. Calc. for KVF_6: V, 25·0%). Titration of a freshly dissolved sample indicated that about 20% of vanadium was present as vanadium(V) [Found: V, 15·8; Ratio V(IV)/V(total): 0·77/1]. The magnetic moment was 1·15 Bohr magnetons at 296° K. The *X*-ray powder photograph contained lines attributable to both K_2VF_6 and KVF_6.

Cæsium fluoride and vanadium tetrafluoride (2 : 1 mol.) also reacted in iodine pentafluoride. The pink product was a mixture of Cs_2VF_6 and $CsVF_6$ (Found: V, 11·4. Calc. for Cs_2VF_6: V, 11·8. Calc. for $CsVF_6$: 17·1%). Titration of a freshly dissolved sample indicated a quinquevalent vanadium content of about 35% [Found: V(IV), 7·65. Ratio V(IV)/V(total): 0·67/1]. The magnetic moment was 1·27 Bohr magnetons at 293° K.

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[30] Aynsley, Peacock, and Robinson, *J.*, 1952, 1231.

When calcium or barium fluoride had been treated with vanadium tetrafluoride (1 : 1 mol.) in iodine pentafluoride, the green solid product was found by *X*-ray powder photography to consist of the unchanged reactants.

The reaction of an equimolar mixture of potassium fluoride and vanadium tetrafluoride in iodine pentafluoride gave a non-homogeneous product in which VF_4 and possibly K_2VF_6 occurred, according to the *X*-ray powder photograph.

Reactions of Vanadium Tetrafluoride.—(*a*) *With selenium tetrafluoride.* Selenium tetrafluoride was distilled on to vanadium tetrafluoride in a silica vessel, and refluxed for 15 min. An orange-brown solid was formed which was partly soluble in selenium tetrafluoride. Removal of unchanged selenium halide in a vacuum left a light brown solid, which was identified by the weight gain and analysis as the 1 : 1 *adduct* SeF_4,VF_4 (Found: Se, 28·5; V, 18·2; F, 50·6. $SeVF_8$ requires Se, 28·0; V, 18·1; F, 53·9%). The results of the magnetic susceptibility measurements from 88° to 296° K are shown in Table 2.

(*b*) *With sulphur tetrafluoride and iodine pentafluoride.* When vanadium tetrafluoride was treated with sulphur tetrafluoride, or refluxed with iodine pentafluoride, removal of the volatile fluoride left unchanged vanadium tetrafluoride.

(*c*) *With nitryl fluoride.* Vanadium tetrafluoride did not react with nitryl fluoride [31] during a period of 47 days at −78°; however, a vigorous reaction occurred when vanadium tetrafluoride and nitryl fluoride were mixed in iodine pentafluoride. The cream solid which remained after removal of the excess of liquid was largely NO_2VF_6 (Found: V, 23·8. Calc. for NO_2VF_6: V, 24·2%) but the observed magnetic moment of 0·4 B.M. at 293° K showed it to contain impurities such as vanadium tetra- or tri-fluoride.

(*d*) *With sulphur trioxide and sulphur dioxide.* Vanadium tetrafluoride was recovered unchanged from its mixtures with either sulphur dioxide or sulphur trioxide. Similarly, an attempted reaction of vanadium tetrafluoride with potassium fluoride in sulphur dioxide led only to the recovery of unchanged starting materials.

(*e*) *With pyridine.* An excess of dry pyridine was condensed on to 0·628 g. (4·94 millimoles) of vanadium tetrafluoride, which formed a brown mixture when the pyridine melted. Removal of excess of pyridine under a vacuum left 1·036 g. (Calc. for $C_5H_5NVF_4$: 1·02 g.) of a grey-pink powder which was identified as VF_4,Py (Found: V, 24·7. Calc. for $C_5H_5F_4NV$: V, 24·7%). Pyridine tetrafluorovanadium(IV) [14] dissolved readily in water to form a green solution. The magnetic moment of pyridine tetrafluorovanadium(IV) was 1·79 Bohr magnetons at 293° K.

(*f*) *With ammonia.* A large excess of anhydrous ammonia (Matheson Co.) was condensed on to vanadium tetrafluoride, to produce an orange-brown slurry in liquid ammonia. Removal of excess of ammonia and heating the remaining solid to 100° in a vacuum yielded a buff solid, amminetetrafluorovanadium(IV) [14] (Found: V, 35·5. Calc. for NH_3VF_4: V, 35·4%). The compound readily gave a brown aqueous solution. The magnetic moment of amminetetrafluorovanadium(IV) was 1·83 Bohr magnetons at 293° K.

(*g*) *With bromine trifluoride.* An excess of bromine trifluoride (Matheson Co.) was condensed on to 0·55 g. (4·3 mmoles) of vanadium tetrafluoride. Vanadium tetrafluoride dissolved immediately in molten bromine trifluoride, and bromine was liberated. The contents of the reaction vessel, which were completely volatile, were distilled on to 0·324 g. (4·3 millimoles) of potassium chloride. Removal of volatile material under vacuum left 0·83 g. of potassium hexafluorovanadate(V) (Found: V, 25·6; F, 54·0. Calc. for KVF_6: V, 25·0; F, 55·9%. 4·3 millimoles of VF_4 require 0·88 g. of KVF_6).

(*h*) *With fluorine.* A mixture of fluorine and nitrogen was passed over vanadium tetrafluoride at 100° in a nickel reactor. A white solid, identified as vanadium pentafluoride, was condensed in a −78° trap connected to the reactor exit.

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[31] Aynsley, Hetherington, and Robinson, *J.*, 1954, 1119.