81. *Ruthenium Pentafluoride and Ruthenium Oxytetrafluoride.*

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The preparation of ruthenium pentafluoride and oxytetrafluoride is described. The vapour pressures have been measured by a static method, a diaphragm gauge of high sensitivity being used. The physical constants, heats of vaporisation, and entropies of vaporisation have been derived from the vapour-pressure data. The magnetic moments have been measured over the temperature range 100—300°K.

THERE is little information about the fluorides of ruthenium, and no oxyfluoride has been reported. Two methods for the preparation of ruthenium pentafluoride appear in the literature: a direct fluorination of the metal reported by Ruff and Vidic,[1] and a reaction of the metal with the fluorinating agent bromine trifluoride (Hepworth, Peacock, and Robinson [2]).

Ruthenium Pentafluoride.—Ruthenium readily reacts with elemental fluorine, carried by a slow stream of nitrogen, at temperatures between 280° and 900°, to give a dark, opaque, viscous, green liquid. Ruthenium pentafluoride can be separated by distilling this mixture under vacuum, and a black-brown non-volatile solid containing ruthenium metal and ruthenium dioxide remains behind.

Ruthenium pentafluoride is a dark green crystalline solid which melts at 86·5° to a dark green viscous liquid which does not easily recrystallise. The vapour is colourless. The dry compound is stable, and can be handled and stored in glass at room temperature,

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[1] Ruff and Vidic, *Z. anorg. Chem.*, 1925, **143**, 163.
[2] Hepworth, Peacock, and Robinson, *J.*, 1954, 1197.

but attacks it slowly at 100°. At 180° the reaction is faster and a black deposit and a red liquid are formed. The pentafluoride dissolves exothermally in water to give a brown solution and a voluminous precipitate of the hydrated dioxide. Ruthenium tetroxide is evolved. Debye *X*-ray powder photographs show ruthenium pentafluoride to be isostructural with osmium pentafluoride and a single-crystal *X*-ray diffraction investigation [3] has shown that the structure consists of discrete tetrameric units, Ru_4F_{20}, with the ruthenium atoms lying at the corners of a square. The fluorine atoms are arranged about each ruthenium atom in a distorted octahedron, and the structure resembles that of molybdenum pentafluoride,[4] but the Ru–F–Ru bridging bonds are not linear.

The vapour pressure of ruthenium pentafluoride has been measured over the temperature range 290—430°K (Table 1). Owing to the low vapour pressure of the solid pentafluoride it is not possible to obtain an accurate curve for the solid by using the diaphragm-gauge technique. However, consistent values of the melting point have been obtained directly in thin-walled glass capillaries. The boiling point, found by extrapolation of the vapour pressure data, is 227°. This is in good agreement with a value (230°) obtained by direct measurement. The vapour pressure equation for liquid ruthenium pentafluoride (90—160°) is $\log p = 9{\cdot}54 - 3329/T$. The calculated heat of vaporisation is 15,230 cal. mole^{-1}, and the entropy of vaporisation is 30·4 cal. mole^{-1} deg.$^{-1}$. The vapour-pressure data closely resemble those for osmium pentafluoride.[5] Some physical properties of the pentafluorides are compared in Table 2.

TABLE 1.

Vapour pressure of ruthenium pentafluoride.

T(°K)	292·2	322·8	333·0	342·8	353·0	381·0	393·0	402·7	412 2	421·7	430·0
p (mm.)	0·1	0·2	0·5	0·8	1·5	6·8	12·5	21·7	26·3	45·9	64·6

TABLE 2.

Physical properties of some pentafluorides.

	M. p.	B. p.	Heat of vaporisation (cal. deg.$^{-1}$)	Entropy of vaporisation (cal. mole^{-1} deg.$^{-1}$)
NbF_5 [6]	80°	235°	12,900	25·4
MoF_5 [5]	67	213·6	12,370	25·4
RuF_5	86·5	227	15,230	30·4
TaF_5 [6]	95	229	13,000	25·9
ReF_5 [5]	48	221·3	13,880	28·1
OsF_5 [5]	70	225·9	15,680	31·4

The results of magnetic measurements on the pentafluoride are given in Table 3.

TABLE 3.

Magnetic moment of ruthenium pentafluoride.

T(°K) ...	292	280	263	250	242	227	212	190	170	152	132	114	100
$10^6\chi_A$ ...	5516	5826	6088	6398	6676	7067	7555	8287	9014	9921	10,961	12,428	13,653
μ_{eff}	3·60	3·63	3·59	3·59	3·61	3·59	3·59	3·56	3·52	3·49	3·42	3·38	3·32

For a $d\varepsilon_3$ ion such as Ru^{5+} in a cubic field, Kotani's theory [8] and its modification [9] predict a temperature-independent moment near the spin-only value of 3·88 B.M. For ruthenium pentafluoride μ_{eff} is 3·3—3·6 B.M.; after allowance for a Curie temperature of 34°,

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[3] Holloway, Peacock, and Small, unpublished work.
[4] Edwards, Peacock, and Small, *J.*, in the press.
[5] Cady and Hargreaves, *J.*, 1961, 1568.
[6] Fairbrother and Frith, *J.*, 1951, 3051.
[7] Peacock, *Proc. Chem. Soc.*, 1957, 59.
[8] Kotani, *J. Phys. Soc.* (*Japan*), 1949, **4**, 293.
[9] Griffith, *Trans. Faraday Soc.*, 1958, **54**, 1109.

μ_{calc} (300°K) = 3·83 B.M. Deviations from theory can be expected because the ligand field acting on the ruthenium atom in the pentafluoride is not cubic.

Ruthenium Oxytetrafluoride.—Ruthenium metal reacts violently with a mixture of bromine trifluoride and bromine at 20°, and after removal of the excess of reagents, a pale green residue remains. This is the nearly colourless oxytetrafluoride together with a small proportion of a green impurity which is probably ruthenium pentafluoride. Complete separation of the oxyfluoride from the green substance has not been possible and, consequently, our samples of the oxytetrafluoride have always contained small quantities ($<5\%$) of the impurity.

Ruthenium oxytetrafluoride forms colourless, or very pale green, crystals which melt at 115° to a mobile pale green liquid. The liquid solidifies rapidly below the melting point and the freshly prepared crystals sometimes assumes a reddish tinge. The vapour is colourless. The oxytetrafluoride is very sensitive to moisture with which it combines to form a dark red material. Prolonged heating in glass at about 120° also results in the formation of a dark red substance which does not crystallise easily (cf. the pentafluoride). Debye X-ray photographs of the oxyfluoride are complex, and probably indicate a low crystal symmetry. They do not resemble those of the pentafluoride.

The vapour pressure of ruthenium oxytetrafluoride has been measured for the temperature range 290—430°K (Table 4). The vapour-pressure equation for the solid (20—110°) is $\log p = 9{\cdot}22 - 2857/T$ and for the liquid (120—160°) is $\log p = 8{\cdot}60 - 2616/T$. The calculated triple point is 115°, which agrees with the measured value. The boiling point, found by extrapolation of the vapour-pressure data, is 184°. The calculated heat of vaporisation is 11,970 cal. mole^{-1}, and the calculated entropy of vaporisation is 26·1 cal. mole^{-1} deg.$^{-1}$. These data resemble closely those of molybdenum oxytetrafluoride.[5] Some physical properties of the oxytetrafluorides are given in Table 5. The melting point of ruthenium oxytetrafluoride is the same as that previously recorded for the pentafluoride.[1]

TABLE 4.

Vapour pressure of ruthenium oxytetrafluoride.

T(°K)	304·4	313·7	324·7	333·0	342·4	351·7	361·7	372·7	382·2	392·2	401·2	410·2	428·0
p (mm.) ...	0·8	1·5	2·4	4·8	6·8	13·7	26·5	37·8	57·6	77·4	115·8	171·3	296·4

The magnetic moment of ruthenium oxytetrafluoride (Table 6) is nearly independent of temperature ($\mu_{\text{eff}} = 2{\cdot}8$—$2{\cdot}9$ B.M.). For a $d\varepsilon_2$ ion in a cubic field, Kotani's theory predicts a magnetic moment of 1·22 B.M. at 0°K, increasing with temperature according to the equation $\mu_{\text{eff}}^2 = 3/2 + 9\,kT/\breve{\varepsilon}_{4d}$ where $\breve{\varepsilon}_{4d}$ is the spin-orbit coupling constant. The observed values are very much larger than expected, and approach the spin-only value for two unpaired electrons ($\mu = 2{\cdot}83$ B.M.). The difference cannot be accounted for by the presence of small amounts of paramagnetic impurities, such as ruthenium pentafluoride, and it is probable that the orbital contribution to the moment has been suppressed. However, if a structure be assumed with part of the ruthenium in the quinquevalent state the susceptibility would be higher than expected for a $d\varepsilon_2$ configuration, for example, if the ruthenium is in quinquevalent and octavalent states, *i.e.*, $3\,\text{Ru(VI)} \longrightarrow 2\,\text{Ru(V)} + \text{Ru(VIII)}$, then the observed susceptibility is very near that calculated on the basis $\chi\text{Ru(VI)} = 2/3\chi\text{Ru(V)}$ [$\chi\text{Ru(VIII)} = 0$]. This is of course a purely

TABLE 5.

Physical properties of some oxytetrafluorides.

	M. p.	B. p.	Heat of vaporisation (cal. deg.$^{-1}$)	Entropy of vaporisation (cal. mole^{-1} deg.$^{-1}$)
$MoOF_4$ [5]	97·2°	186°	12,090	26·3
WOF_4 [5]	104·7	185·9	14,230	31·0
$ReOF_4$ [5]	107·8	171·7	14,590	32·7
$RuOF_4$.....................	115	184	11,970	26·1

TABLE 6.

Magnetic moment of ruthenium oxytetrafluoride.

T(°K)	287	277	268	248	244	229	211	188	168	150	132	102
$10^6\chi_A$	3655	3715	3846	4113	4244	4552	4869	5439	6074	6831	7738	9508
μ_{eff}	2·91	2·87	2·88	2·87	2·89	2·90	2·88	2·87	2·87	2·88	2·86	2·80

empirical, and perhaps accidental, relationship, and its explanation must await determination of structure.

EXPERIMENTAL

Reagents.—Bromine trifluoride was prepared from the elements. Ruthenium metal, in the form of a fine powder, was treated with hydrogen at a dull-red heat before use.

Ruthenium and Fluorine.—Ruthenium metal was heated in a nickel or alumina tube through which was passed hydrogen fluoride—free fluorine diluted with nitrogen. Several runs were carried out at temperatures between 280° and about 900°, and ruthenium pentafluoride was obtained easily in every case. The most convenient temperature was about 300° in a nickel tube. The black to green product of the reaction was collected and sealed under vacuum. The dark green pentafluoride, obtained by distillation of the crude *product* under vacuum, solidified after about 36 hr. (Found: Ru, 52·0; F, 48·8. RuF_5 requires Ru, 51·7; F, 48·2%).

Ruthenium and Bromine Trifluoride : *Bromine* (1 : 1).—The reaction began at about 20° with the liberation of bromine, and sufficient heat was evolved to raise the metal rapidly to incandescence. The reaction was controlled by judicious cooling with liquid oxygen, but for safety the amount of ruthenium metal was limited to <1 g. per run. The removal of bromine trifluoride in a vacuum at about 120° left a pale green liquid which quickly set to a pale green or a pale pink mass. The separation of the almost colourless oxytetrafluoride from this proved very lengthy. When the pale green material was heated at about 40° in an evacuated tube for 3—5 weeks a small quantity of a grass-green material sublimed out from the heated zone and left behind it a very pale green crystalline material, which was *ruthenium oxytetrafluoride* (Found: Ru, 52·0; F, 40·1. $RuOF_4$ requires; Ru, 52·5; F, 39·2%). Microscopic examination of the oxytetrafluoride showed that the pure compound is colourless.

Magnetic Moment.—The magnetic moments were determined by the Gouy method; the apparatus was similar to that described by Figgis and Nyholm.[10] The powdered solid was introduced into the sample tube under vacuum and the tube was sealed. The sample was then liquefied. The pentafluoride remained in a supercooled liquid form for the whole determination, but the oxyfluoride solidified immediately on cooling.

Debye X-Ray Photographs.—Specimens were mounted in evacuated Pyrex capillaries and photographed in Cu–K_α nickel-filtered radiation on a 19-cm. camera.

Vapour Pressures.—The vapour pressures measurements were made with a Pyrex diaphragm gauge used as a null instrument.[5,11]

Analyses.—Compounds were decomposed in sodium hydroxide containing hydrogen peroxide. Ruthenium was precipitated as the dioxide and estimated as metal after hydrogen reduction. Fluorine was determined as lead chlorofluoride.

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[10] Figgis and Nyholm, *J.*, 1959, 331.

[11] Cady and Hargreaves, *J.*, 1961, 1563.