306. *Vapour Pressures of Some Fluorides and Oxyfluorides of Molybdenum, Tungsten, Rhenium, and Osmium.*

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The vapour pressures of the pentafluorides, ReF_5, MoF_5, OsF_5, the oxytetrafluorides, $ReOF_4$, $MoOF_4$, WOF_4, and the oxyfluorides $ReOF_5$ and ReO_2F_3 have been measured by a static method using a diaphragm gauge of high sensitivity. The physical constants, heats of sublimation and vaporisation, and entropies of vaporisation have been derived from the vapour-pressure data. The oxypentafluoride, $ReOF_5$ has been studied in detail and a hitherto unknown solid–solid transition at 30·0° is reported. The thermal disproportionation of the pentafluorides is described.

WITHIN the past four years several new transition-metal fluorides have been prepared and characterised, *e.g.*, platinum hexafluoride,[1] the pentafluorides of molybdenum, rhenium, and osmium,[2,3] and platinum pentafluoride.[4] Tungsten and molybdenum oxytetrafluorides were first described by Ruff *et al.*[5,6] who determined the melting and boiling points of the compounds but not their vapour pressures. Ruff and Kwasnik[7] reported a white rhenium oxytetrafluoride, but later work by Aynsley, Peacock, and Robinson[8] showed the compound to be the oxypentafluoride, $ReOF_5$. The true rhenium oxytetrafluoride

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[1] Weinstock, Claassen, and Malm, *J. Amer. Chem. Soc.*, 1957, **79**, 5832.
[2] Hargreaves and Peacock, *J.*, 1960, 1099.
[3] Hargreaves and Peacock, *J.*, 1960, 2618.
[4] Bartlett and Lohmann, *Proc. Chem. Soc.*, 1960, 14.
[5] Ruff, Eisner, and Heller, *Z. anorg. Chem.*, 1907, **52**, 256.
[6] Ruff and Eisner, *Ber.*, 1907, **40**, 2931.
[7] Ruff and Kwasnik, *Z. anorg. Chem.*, 1934, **219**, 65.
[8] Aynsley, Peacock, and Robinson, *J.*, 1950, 1622.

has been prepared recently by Hargreaves and Peacock.[2] The present paper deals with measurement of the vapour pressures of MoF_5, ReF_5, OsF_5, $MoOF_4$, $ReOF_4$, WOF_4, $ReOF_5$, and ReO_2F_3. Physical constants obtained from the vapour pressures are also given. Boiling points for MoF_5, ReF_5, and OsF_5 have been obtained by extrapolation of vapour-pressure data. These substances disproportionate below their boiling points, so those previously reported are in error.

EXPERIMENTAL

Vapour-pressure measurements were made with a Pyrex diaphragm gauge used as a null instrument (described in the preceding paper).

A UCCO polyethylene glycol bath was used for temperatures up to 200°, and the temperatures were measured with a thermometer reading to 0·1°, the latter being calibrated against a Bureau of Standards thermometer. The mercury manometer was read with a cathetometer with a precision of $\pm 0{\cdot}05$ mm. The sensitivity of the gauge was 0·1 mm. per scale division, so the pressures could be measured with a precision of $\pm 0{\cdot}1$ mm. Hg.

Materials.—The starting materials for the preparation of MoF_5, ReF_5, $ReOF_4$, and OsF_5 were the hexafluorides of molybdenum, rhenium, and osmium, these being prepared by direct fluorination of the powdered metals in a copper vessel. The fluorine, which was diluted with oxygen-free nitrogen, was supplied by General Chemical Division, Allied Chemical and Dye Corporation. The volatile products were purified by bulb-to-bulb vacuum-distillation and stored over anhydrous sodium fluoride in Pyrex break-seal vessels. Tungsten and molybdenum hexacarbonyls were purified by sublimation in a high vacuum.

Molybdenum pentafluoride. This was prepared by Peacock's method.[9] Molybdenum hexacarbonyl was fluorinated at −65° to give the green compound Mo_2F_9 which was then thermally disproportionated at 100° to give molybdenum pentafluoride and the non-volatile molybdenum tetrafluoride. The former sublimed out of the heated zone and was purified by vacuum-sublimation before being transferred to a break-seal vessel. Molybdenum pentafluoride was also prepared by direct interaction of molybdenum hexacarbonyl and molybdenum hexafluoride.[10] A mixture of the pentafluoride and tetrafluoride was obtained, and the former was readily separated from the non-volatile tetrafluoride by vacuum sublimation.

Rhenium pentafluoride and oxytetrafluoride. These were prepared as described by Hargreaves and Peacock.[2] The pentafluoride was obtained by reduction of rhenium hexafluoride with tungsten hexacarbonyl in the presence of tungsten hexafluoride as a solvent. Pure rhenium pentafluoride was readily separated from the reaction mixture by vacuum distillation at 100°. The oxytetrafluoride was prepared in a similar manner by reaction of an excess of rhenium hexafluoride with tungsten hexacarbonyl. After the vigorous reaction the green product was heated to 65° under a high vacuum, to yield blue crystals of rhenium oxytetrafluoride which sublimed out of the heated zone. The compound was purified by vacuum-sublimation and transferred to a break-seal vessel.

Osmium pentafluoride. This was prepared by Hargreaves and Peacock's method.[3] Reduction of osmium hexafluoride with tungsten hexacarbonyl gave a mixture of the pentafluoride and tetrafluoride from which the former was readily separated by vacuum distillation at 120°. The pentafluoride was further purified by vacuum-distillation.

Tungsten and molybdenum oxytetrafluorides. These compounds were prepared by direct fluorination of the powdered metals in the presence of oxygen. A 3 : 1 fluorine–oxygen mixture was used. The oxytetrafluorides were readily separated from any hexafluoride formed simultaneously by pumping under a vacuum at room temperature, the volatile hexafluoride being readily removed. The compounds were then purified by vacuum-sublimation before being transferred to break-seal vessels.

Rhenium oxypentafluoride and dioxytrifluoride. These were prepared by Aynsley, Peacock, and Robinson's method.[8] Rhenium oxypentafluoride was prepared by direct fluorination of rhenium metal in the presence of oxygen. The oxypentafluoride was separated from a small quantity of rhenium hexafluoride, also formed in the reaction, by vacuum-distillation and was purified by repeated vacuum-distillation over sodium fluoride, the fore and tail fractions being discarded. The oxypentafluoride was also prepared by direct fluorination of anhydrous rhenium

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[9] Peacock, *Proc. Chem. Soc.*, 1957, 59.

[10] Hargreaves and Peacock, unpublished work.

dioxide; this method gave rhenium dioxytrifluoride as the major product, but the oxypentafluoride was readily removed owing to its high volatility. Rhenium dioxytrifluoride was purified by vacuum-distillation at 130°.

The m. p.s of MoF_5, ReF_5, OsF_5, and ReO_2F_3 were determined directly in thin-walled Pyrex capillaries. The transition and melting points of $ReOF_5$ were determined from both warming- and cooling-curve data in addition to the values obtained from the vapour-pressure data. The b. p. of $ReOF_5$ was also determined by using a boiling-point apparatus similar to that described by Fairbrother and Frith.[11] The temperature of the vapour in equilibrium with the liquid was measured with a calibrated chromel–alumel thermocouple.

Results.—The vapour-pressure data are summarised by the equations in Table 1. The equations were derived from a minimum of ten observed pressures for each phase. Vapour pressures were normally recorded at 5° intervals except in the case of rhenium oxytetrafluoride, when pressures were recorded at 1° intervals between the transition point and the m. p. The maximum deviations of the observed vapour pressures and those calculated from the equations are ±0·5 mm. at a pressure of 100 mm., ±1 mm. at 400 mm., and ±3 mm. at 760 mm.

TABLE 1. *Vapour-pressure equations.*

Liquid MoF_5 (70·0—160°): $\log P = 8{\cdot}58 - 2772/T$.	
Liquid $MoOF_4$ (95—185°): $\log P = 8{\cdot}716 - 2671/T$.	Solid $MoOF_4$ (40—95°): $\log P = 9{\cdot}21 - 2854/T$.
Liquid ReF_5 (48·0—140°): $\log P = 9{\cdot}024 - 3037/T$.	
Liquid $ReOF_4$ (108—172°): $\log P = 10{\cdot}09 - 3206/T$.	Solid $ReOF_4$ (50—107°): $\log P = 11{\cdot}88 - 3888/T$.
Liquid OsF_5 (75—180°): $\log P = 9{\cdot}75 - 3429/T$.	
Liquid $ReOF_5$ (41—73°): $\log P = 7{\cdot}727 - 1678{\cdot}6/T$.	Solid $ReOF_5$ (30—41°): $\log P = 8{\cdot}620 - 1958{\cdot}9/T$.
Solid $ReOF_5$ (0—30°): $\log P = 9{\cdot}581 - 2250{\cdot}1/T$.	
Liquid ReO_2F_3 (90—170°): $\log P = 10{\cdot}36 - 3437/T$.	
Liquid WOF_4 (105—186°): $\log P = 9{\cdot}69 - 3125/T$.	Solid WOF_4 (50—104°): $\log P = 10{\cdot}96 - 3605/T$.

The values of the triple points of $MoOF_4$, $ReOF_4$, WOF_4, and $ReOF_5$ were determined by solution of the vapour-pressure equations and are in good agreement (±0·2°) with m. p.s obtained directly in thin-walled capillaries. The m. p.s of MoF_5, ReF_5, OsF_5, and ReO_2F_3 were found to be, respectively, 67·0°, 48·0°, 70·0°, and 90·0°. Owing to the very low vapour pressure of the pentafluorides below the m. p.s, it was not possible to obtain accurate sublimation pressures by using the diaphragm-gauge technique. The solid–solid transition at 30·0° and the m. p. of 40·8° for $ReOF_5$ were obtained from the two plateaux in a warming curve.

Some physical constants of the compounds are shown in Table 2. The heat of fusion was derived from the difference between the heats of sublimation and vaporisation at the triple point. The heat of transition was derived from the difference between the two heats of sublimation at the transition point. These values are probably not accurate closer than 10 cal. per mole.

TABLE 2. *Physical constants of* MoF_5, ReF_5, OsF_5, WOF_4, $MoOF_4$, $ReOF_4$, $ReOF_5$, *and* ReO_2F_3.

		Triple point		Transition point		Heat of fusion	Entropy of fusion	Heat of transition	Entropy of transition
	B. p. (°c)	(°c)	(mm.)	(°c)	(mm.)	(cal. mole^{-1})	(cal. mole^{-1} deg.$^{-1}$)	(cal. mole^{-1})	(cal. mole^{-1} deg.$^{-1}$)
MoF_5 ...	213·6	67·0	—	—	—	—	—	—	—
$MoOF_4$ ...	186·0	97·2	28·8	—	—	1020	2·768	—	—
ReF_5 ...	221·3	48·0	—	—	—	—			
$ReOF_4$ ...	171·7	107·8	45·2	—	—	3230	8·478	—	—
OsF_5 ...	225·9	70·0	—	—	—	—	—	—	—
$ReOF_5$ ...	73·0	40·8	237·1	30·0	144·6	1220	3·886	1339	3·868
ReO_2F_3	185·4	90·0	—	—	—	—	—	—	—
WOF_4 ...	185·9	104·7	25·1	—	—	2260	5·981		

The heats of sublimation and vaporisation for $MoOF_4$, $ReOF_4$, WOF_4, and $ReOF_5$, and the

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

TABLE 3. *Heats of vaporisation and sublimation and entropies of vaporisation.*

	Heat of vaporisation (cal. mole^{-1})	Heat of sublimation (cal. mole^{-1})	Heat of sublimation below solid–solid transition (cal. mole^{-1})	Entropy of vaporisation (cal. mole^{-1} deg.$^{-1}$)
MoF_5	12,370	—	—	25·4
$MoOF_4$........	12,090	13,110	—	26·3
ReF_5	13,880	—	—	28·1
$ReOF_4$........	14,590	17,820	—	32·7
OsF_5	15,680	—	—	31·4
$ReOF_5$........	7720	8940	10,280	22·3
ReO_2F_5	15,700	—	—	34·3
WOF_4	14,230	16,490	—	31·0
NbF_5	12,900	—	—	25·4 [11]
TaF_5	13,000	—	—	25·9 [11]
IF_5				27·2 [11]
VF_5	10,640	11,940	—	33·1 [11]

heats of vaporisation for MoF_5, ReF_5, OsF_5, and ReO_2F_3 were calculated from the slopes of the lines of the vapour-pressure equations. These values are given in Table 3, together with the entropies of vaporisation for all the liquid states. Table 3 also contains values for NbF_5, TaF_5, IF_5, and VF_5 taken from the literature. These are given to permit comparison of various pentafluorides with each other.

Discussion

Both tungsten and molybdenum oxytetrafluoride have been known for many years. The former was first prepared by Ruff, Eisner, and Heller,[5] and the latter by Ruff and Eisner.[6] The m. p.s of WOF_4 and $MoOF_4$ reported were 110° and 97°, and the b. p.s 185° and 180° respectively. These workers gave no vapour pressures. The physical constants derived from the present vapour-pressure data are in general agreement with those of Ruff *et al.* Their value for the m. p. of tungsten oxytetrafluoride is somewhat higher than the 105° reported here; however, there is excellent agreement in the values of the b. p.s. In a similar manner there is good agreement regarding the m. p. of molybdenum oxytetrafluoride, but the b. p.s do not agree well.

Ruff and Kwasnik[7] described rhenium oxytetrafluoride as a white substance with m. p. 39·7° and b. p. 62·7°. The preparation was repeated by Aynsley, Peacock, and Robinson,[8] who showed that the volatile oxyfluoride prepared by the fluorination of rhenium in the presence of oxygen was the oxypentafluoride $ReOF_5$ and not the oxytetrafluoride $ReOF_4$. The m. p. and b. p. of the oxypentafluoride reported by Aynsley, Peacock, and Robinson were 34·5° and 55·0° respectively. No vapour pressures were given. Ruff and Kwasnik measured the sublimation pressures of their compound, but did not record any data for the liquid state. Their data were published as a graph and it has not been possible to compare their results in detail with those reported here. Rhenium oxypentafluoride has now been studied extensively. In addition to the m. p. of 40·8° and the b. p. of 73·0°, a solid–solid transition has been found to occur at 30·0°. The m. p. of 40·8° reported here is thus in agreement with Ruff's value of 39·7° although the b. p.s differ substantially. Since Ruff and Kwasnik did not record any vapour-pressure measurements above the m. p. of rhenium oxypentafluoride, their extrapolated b. p. of 62·7° could have been in considerable error. The close agreement in the m. p.s suggests that their compound was pure, however, and verifies the conclusions of Aynsley, Peacock, and Robinson that the compound reported by Ruff and Kwasnik to be rhenium oxytetrafluoride was in fact rhenium oxypentafluoride. The rather low values of the physical constants of the oxypentafluoride reported by Aynsley, Peacock, and Robinson are presumably the result of the presence of the more volatile rhenium hexafluoride in their sample of the oxypentafluoride.

Rhenium oxytetrafluoride, a deep blue, readily sublimable solid, was prepared recently by Hargreaves and Peacock.[2] The physical constants reported here show that the compound has similar properties to those of tungsten and molybdenum oxytetrafluorides. The rhenium compound is considerably more reactive than the tungsten and the molybdenum compound as shown by its attack upon glass at 170° and above. Tungsten and molybdenum oxytetrafluorides had no tendency to attack glass at 186°.

Rhenium dioxytrifluoride was first prepared by Aynsley, Peacock, and Robinson,[8] who reported the liquid to be very viscous, congealing, when cooled, to a glass which crystallised only after long standing. The solid melted at 90—95° and boiled at about 200°. The physical constants were re-investigated by Aynsley and Hair,[12] who reported the m. p. and b. p. to be 95° and 126°, respectively. The physical constants of rhenium dioxytrifluoride reported here and derived from vapour-pressure data are in agreement with the observations of Aynsley, Peacock, and Robinson. The very low b. p. reported by Aynsley and Hair is difficult to explain and is presumably the result of a printing error.

Attempts were made to measure the vapour-pressure of osmium oxytetrafluoride,[3] but in all cases the compound decomposed above about 70°, probably owing to its high reactivity.

The oxytetrafluorides of the third-row transition elements are remarkably similar as shown by the data in Table 2. The chemical reactivity increases with molecular weight. This is further shown by the fact that osmium oxytetrafluoride is very difficult to prepare and iridium oxytetrafluoride has not yet been successfully identified. The data in Table 3 show that there is an increase in both the latent heat and entropy of vaporisation with increase in molecular weight of the compound as one passes from molybdenum to rhenium. The high values of the Trouton constants, particularly for WOF_4 and $ReOF_4$, suggest considerable association in the liquid state.

The three pentafluorides MoF_5, ReF_5, and OsF_5 form an interesting series in that they all undergo irreversible disproportionation at higher temperatures. The diaphragm-guage technique is particularly useful for studying such compounds since the point at which disproportionation takes place can be readily observed from the increase of pressure at constant temperature. The b. p.s of the pentafluorides reported here are extrapolated values. Because of the thermal disproportionation, these values are considered more reliable than those obtained by actually boiling the substances at one atmosphere pressure.

Rhenium pentafluoride undergoes irreversible thermal disproportionation at 130° to give the hexafluoride and the non-volatile tetrafluoride. This particular property of rhenium pentafluoride was used by Hargreaves and Peacock[2] to prepare pure rhenium tetrafluoride. Molybdenum pentafluoride begins to disproportionate at 165°, and osmium pentafluoride at 180°. In each instance, the products of the disproportionation are the volatile hexafluorides and the non-volatile tetrafluorides. This disproportionation can be represented by the general equation: $2MF_5 \longrightarrow MF_6 + MF_4$.

As with the oxytetrafluorides, the heats and entropies of vaporisation of MoF_5, ReF_5, and OsF_5 increase with increase of molecular weight (Table 2). There is also a close similarity in the b. p.s of the compounds. It is pertinent to compare some of the physical properties of MoF_5, ReF_5, and OsF_5 with those of the other pentafluorides shown in Table 3. All the pentafluorides have high Trouton constants, indicative of considerable association in the liquid state. It is now well known that iodine pentafluoride undergoes self ionisation according to the reaction $2IF_5 \longrightarrow IF_4^+ + IF_6^-$. Clark and Emeléus[13] have shown from conductivity measurements that vanadium pentafluoride undergoes a similar type of self-ionisation: $2VF_5 \longrightarrow VF_4^+ + VF_6^-$. In view of the isolation of stable hexafluoromolybdates,[14] hexafluororhenates,[15] and hexafluoro-osmates[16] containing

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[12] Aynsley and Hair, *J.*, 1958, 3747.

[13] Clark and Emeléus, *J.*, 1957, 2119.

[14] Hargreaves and Peacock, *J.*, 1957, 4212.

[15] Peacock, *J.*, 1957, 467.

[16] Hepworth, Peacock, and Robinson, *J.*, 1954, 1197.

the MoF_6^-, ReF_6^-, and OsF_6^- ions, it is reasonable to assume that molybdenum, rhenium, and osmium pentafluoride also self-ionise to some extent: $2MF_5 \longrightarrow MF_4^+ + MF_6^-$.

The crystal structure of molybdenum pentafluoride is being investigated by Edwards and Peacock,[17] using single-crystal *X*-ray diffraction. They have found that MoF_5 is monoclinic with two molecules per unit cell, and there are two distinct types of fluorine atom although there is no evidence for a bimolecular species $(MoF_5)_2$. Edwards and Peacock suggest an ionic structure of the type $(MoF_4^+)(MoF_6^-)$, and if this is the case it may be assumed that rhenium and osmium pentafluoride may also have this ionic structure. An ionic structure for the pentafluorides would explain the ready thermal disproportionation of the compounds and also the magnetic properties of rhenium[2] and osmium[3] pentafluoride.

Some physical properties of the fluorides and oxyfluorides of rhenium are compared in Table 4. It is noteworthy that the volatilities depend much more upon the number of atoms of fluorine and oxygen per rhenium atom in the molecule than upon whether the atoms are oxygen or whether they are fluorine. The greater the ratio (F + O)/Re, the more volatile the compound. The most volatile substances are ReF_6 and $ReOF_5$. These are followed by the group, ReF_5, $ReOF_4$, and ReO_2F_3, and these by ReO_3F, ReF_4, and $ReOF_3$. In the case of $ReOF_4$ and ReO_2F_3 there is a striking difference in viscosities, the latter compound as a liquid being much more viscous than the former. The decrease in volatility is passing from ReF_6 to ReF_4 suggests appreciable ionic character for the tetrafluoride, as seems to be the case with other transition-metal tetrafluorides.

TABLE 4. *Physical constants of some fluorides and oxyfluorides of rhenium.*

	B. p. (°c)	M. p. (°c)	Heat of sublimation (cal. deg.$^{-1}$)	Heat of vaporisation (cal. deg.$^{-1}$)	Entropy of vaporisation (cal. mole^{-1} deg.$^{-1}$)
ReF_6	33·8	18·7	7796	6857	22·3[a]
$ReOF_5$	73·0	40·8	8940	7720	22·3
$ReOF_4$	171·7	107·8	17,820	14,590	32·7
ReF_5	221·3	48·0	—	13,880	28·1
ReO_2F_3	185·4	90·0	—	15,700	34·3
ReO_3F	—	147·0	—	—	—[12]
ReF_4	Sublimes >300°	—	—	—	—[2]
$ReOF_3$	Non-volatile	—	—	—	—

[a] Preceding paper.

TABLE 5. *Physical constants of known pentafluorides and tetrafluorides of the second- and third-row transition elements.*

	NbF_5[11]	MoF_5[9]		RuF_5[18]			
M. p.	80°	67°		107°			
B. p.	235°	213·6°		313°			
	TaF_5[12]		ReF_5	OsF_5		PtF_5[4]	
M. p.	95°		48°	70°		75—76°	
B. p.	229°		221·3°	225·9°		300—305°	
		MoF_4	ReF_4	OsF_4	IrF_4[19]	PtF_4[a]	WF_4[10]
M. p.		—	—	—	106—107°	—	
B. p. ...		—	—	—	300°	—	
Volatility		Non-vol.	Sublimes *in vac.* >300°	Distils *in vac.* >350°		Non-vol.	Non-vol.

[a] Sharpe, *J.*, 1950, 3444.

A comparison of the properties of the known transition-metal pentafluorides and tetrafluorides (Table 5) indicates that iridium tetrafluoride lies in a somewhat anomalous position. This fluoride was first reported by Robinson and Westland;[18] it has m. p. 106—107° and b. p. 300°. Table 5 leads to the conclusion that iridium tetrafluoride has properties which are similar to the third-row pentafluorides rather than the tetrafluorides.

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[17] Edwards and Peacock, personal communication.

[18] Robinson and Westland, *J.*, 1956, 4481.

The transition-metal tetrafluorides so far reported are mostly non-volatile solids, and a more detailed investigation of the above iridium fluoride may show this compound to be iridium pentafluoride. The reduction of iridium hexafluoride[10] with tungsten carbonyl in the presence of tungsten hexafluoride gave a yellow volatile solid with similar properties to those of the compound reported by Robinson and Westland. However, no further studies were made with the product. It may be pointed out that similar reactions involving molybdenum, rhenium, and osmium hexafluorides gave the corresponding transition-metal pentafluorides as the principal products.

This work was done under contract with the Office of Naval Research, U.S.A. Navy Department.

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[*Received, August 4th*, 1960.]