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28. The Vapour Pressures of Some Heavy Transition Metal Hexafluorides.

29. Vapour Pressures of Some Fluorides and Oxyfluorides of Moylbdenum, Tungsten, Rhenium and Osmium.

by

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THE VAPOUR PRESSURES OF SOME HEAVY TRANSITION METAL HEXAFLUORIDES

The vapour pressures of the hexafluorides of tungsten, molybdenum, rhenium, osmium and iridium have been measured by a static method using a diaphragm gauge of high sensitivity. Hitherto unknown solid-solid transitions are reported for rhenium, osmium and iridium hexafluorides together with those known for tungsten and molybdenum hexafluorides. These are, respectively: -1.9°, -0.4°, +0.4°, -8.2°, and -8.7°. From the vapour pressure data more accurate physical constants, latent heats of vaporisation, and sublimation, heats of fusion and transition, and entropies of fusion, transition and vaporisation have been calculated. Nuclear magnetic resonance studies with both solid and liquid hexafluorides suggest that there is molecular rotation in the solid state above the transition point.

The hexafluorides of tungsten, rhenium, osmium and iridium form an interesting series of third row transition metal fluorides with almost the same molecular weight but differing from one another by the number of 5d electrons. Molybdenum is the only second row element which forms a volatile hexafluoride and its properties are remarkably similar to the heavier rhenium hexafluoride. Low temperature X-ray diffraction measurements on the solids show them to be isostructural and of cubic symmetry.[1]

The vapour pressures of the above hexafluorides were first measured by Ruff and co-workers[2,3,4,5] in the earlier part of the century. Apart from some recent preliminary measurements with osmium and rhenium hexafluorides[1,6] and a more detailed study of the vapour pressure of liquid tungsten hexafluoride[7], there have been no further measurements made on these compounds, although the handling of elemental fluorine and the improved techniques of preparation have led to much purer products than could have been realized in Ruff's time. With this thought in mind, the vapour pressures of the

hexafluorides of tungsten, rhenium, osmium, iridium and molybdenum have now been measured over considerably greater temperature ranges than those previously recorded. The large temperature intervals over which the previous vapour pressure measurements were made undoubtedly led the early workers to overlook unknown solid-solid transitions in all of the heavy transition metal hexafluorides.

EXPERIMENTAL.

Vapour Pressure Measurements.

The measurements were made with a pyrex diaphragm gauge used as a null instrument. Previous experience with the handling of transition metal hexafluorides in pyrex glass has shown that, providing the apparatus is dry, there is no tendency for the fluorides to attack the glass even at the boiling point.

The diaphragm gauge, which was of one piece construction, was connected on the side of the diaphragm away from the sample to a high vacuum manifold, a mercury manometer, a micro-leak-valve for slowly admitting air when desired and a mercury diffusion pump. A glass rod of 0.1 mm. diameter and 30 cm. length was sealed at one end to the center of the diaphragm. It served as a pointer to indicate when the pressures were equal on the two sides of the diaphragm. The gauge was also fitted with two break-seal side-arms. A speciman of the compound to be measured contained in a pyrex break-seal vessel was glass-blown onto the base of the gauge after placing a glass covered breaker above the seal. The gauge was then pumped under high vacuum and

the glass surfaces above the specimen were flamed over a period of several hours to remove adsorbed moisture and permanent gases. During this flaming period the volatile hexafluoride was cooled in liquid oxygen. When the gauge and side arms had been baked for a sufficient length of time, the seal connecting the hexafluoride to the diaphragm compartment was broken and pumping continued for an hour. During this time, the oxygen coolant was removed for a short time interval to allow a small portion of the hexafluoride to distill out of the gauge. This procedure was adopted so that any traces of silicon tetrafluoride trapped in the specimen would be removed. The compound was again cooled with liquid ocygen, pumping continued for half an hour and then the gauge was sealed at A. The vacuum manifold was then isolated from the mercury diffusion pump.

A five liter Dewar vessel which served as the thermostat bath was placed in a position such that the entire gauge except for the upper part of the pointer was immersed in the bath liquid. For low temperature measurements (-78.0° to 0.0°) a normal propyl alcohol - solid carbon dioxide mixture was used. For temperatures between 0.0° and 80.0° water was used as the bath liquid. The temperature was measured with a calibrated Chromel-Alumel thermocouple and a portable potentiometer. Temperatures were measured with precision of 0.05°. All temperatures were controlled and maintained within 0.1°.

The position of the pointer was viewed with a Bausch and Lomb travelling microscope, the eye piece of which contained a calibrated scale. A small bright light source placed at C

served to facilitate the viewing of the pointer. The mercury manometer was read with a high precision cathetometer and the pressures recorded with an accuracy of 0.01 mm. Gauges with sensitivities of 0.1 to 0.05 mm. were used for the measurements.

The vapour pressure measurements were made by a null method. The zero pointof the gauge was determined with a high vacuum on both sides of the diaphragm There was no tendency for hysteresis to take place even when the gauge was heated to 400° for several hours In determining the vapour pressures, the movable pointer was brought back to the zero position by allowing dry air to leak into the ballasted manifold through the micro-leak-valve. The pressure was read directly from the manometer. Vapour pressure measurements were made with temperatures approached from below and above the desired point.

On completion of an experimental run, a connection was made between the vacuum manifold and a break-seal side-arms attached to the part of the system containing the hexafluoride. With equal pressures on both sides of the break-seal the latter was broken and the gauge compartment was pumped while the compound was cooled with liquid oxygen. By removing the liquid oxygen, half of the sample in the gauge was pumped away. The remaining compound was cooled in liquid oxygen and the gauge re-sealed at B after a short time interval. The vapour pressure measurements were then repeated. Concordant results indicated the original material to be of high purity. A third break-seal side-arm enabled re-entrance to the gauge and allowed dry air to be leaked into the diaphragm compartment

in order to equalize the pressure across the diaphragm prior to removal of the gauge from the vacuum manifold. Several experimental runs were made with different samples of the freshly distilled hexafluoride.

The difficulties experienced by Fairbrother and Frith[8] in the sealing of closed glass systems containing reactive fluorides were not observed with the above apparatus and no residual gas pressure due to silicon tetrafluoride was found at the completion of an experimental run.

The boiling points of the five hexafluorides were also determined using a standard boiling point apparatus. The temperature of the vapour in equilibrium with the liquid being measured by a calibrated copper constantan thermocouple. Melting points were observed visually during experimental vapour pressure runs and some transition points were observed from warming curve data.

Materials.

The hexafluorides of tungsten, rhenium, osmium, iridium and molybdenum were prepared by direct fluorination of the powdered elements in a copper reactor. Fluorine supplied by the General Chemical Division of Allied Chemical and Dye Corporation was used. The gas was diluted with dry oxygen-free nitrogen before passing over the metal. The volatile products were purified by bulb to bulb vacuum distillation and stored at low temperatures over anhydrous sodium fluoride in break-seal vessels.

Since the high temperature fluorination of rhenium metal

resulted in the formation of some rhenium heptafluoride, the preparation of rhenium hexafluoride was conducted at as low a temperature as possible. Reduction of the finely powdered metal in hydrogen at red heat prior to fluorination gave a very reactive surface which burned in fluorine without the application of external heat and little rhenium heptafluoride was formed.

The hexafluorides were further purified by repeated vacuum distillations over anhydrous sodium fluoride and were finally transferred to break-seal vessels attached to the vacuum line. These were sealed off under high vacuum and stored at the liquid oxygen temperature until ready for use.

Some difficulty was experienced in the purification of rhenium hexafluoride and its separation from the less volatile rhenium heptafluoride. The compound was repeatedly vacuum distilled at a low temperature discarding the forerun and tailings until a constant vapour pressure for the product was obtained at the ice point.

Nuclear Magnetic Resonance Spectra

The nuclear magnetic resonance spectra of both solid and liquid tungsten and molybdenum hexafluorides were obtained through the use of Varian model 4311B high resolution spectrometer employing a sixty megacycle oscillator. The probe was capable of being heated to 60° or cooled to -30°. Attempts were made to observe the spectra of rhenium, osmium and iridium hexafluorides using the variable temperature probe.

RESULTS

The vapour pressure data for the solid and liquid hexafluorides

are given in Table 1. The temperatures are in degrees absolute with the ice point taken at 273.2°, and the pressures are given in mm. of mercury at 0.0°C. The data are summarized by the equations in Table 2.

The equations were derived from the vapour pressure data considering the curve for each phase to be a straight line. The vapour pressures of the five hexafluorides are compared with each other in Fig. 2 where log P is plotted against the reciprocal of the absolute temperature.

The values of the triple points in Table 3 are observed melting points and are accurate to 0.2°. The breaks in the vapour pressure curves were within ± 0.2 degrees of the observed triple points. These are tabulated together with heats of fusion and transition, and entropies of fusion and transition. The heats of fusion were derived from the differences between the calculated heat of sublimation and vaporization at the triple point, and the heat of transition from the differences between the heats of sublimation at the transition point. The transition points were obtained from the intersections of the sublimation curves and the values obtained from solution of the vapour pressure equations were in agreement within ± 0.2°.

The heats of sublimation and vaporization, and the entropies of vaporization for the five hexafluorides are given in Table 4. These were derived using the Clausius-Clapeyron equation.

Well defined nuclear magnetic resonance spectra were obtained for tungsten and molybdenum hexafluorides. The former gave a single peak and the latter a large central peak with six small satellite peaks due to molybdenum isotope effects.[9] The same spectra were obtained for the solid hexafluorides as those obtained when the

compounds were in the liquid phase. Below the transition points the spectra broadened out so much that lines were not observed.

DISCUSSION

The vapour pressure of tungsten hexafluoride was first reported by Ruff and Ascher[2] and there is good agreement between their results and those reported here, except in the temperature region below the transition point. Ruff and Ascher gave a melting point of 2.3° and a boiling point of 17.5°, but they completely overlooked the solid solid transition at -8.2°, although their data show evidence for a break in the curve at -8.2°. Later, Barber and Cady[7] measured the vapour pressure of liquid tungsten hexafluoride from 11.8° to 51.38° with high precision. Their boiling poing of 17.05 ± 0.5° is somewhat lower than Ruff's value, but is in excellent agreement with our figure of 17.1°. From a warming curve of solid tungsten hexafluoride, Barber and Cady observed a solid-solid transition at -8.2° as well as the melting point at 2.0 ± 0.3°. Their estimated heats of transition and fusion from the warming curve data, namely 1,600 ± 300 cal. per mole, and 500 ± 100 cal. per mole respectively, are in rather good agreement with the values shown in Table 3. Ruff and Ascher's value of 2,400 cal. per mole for the heat of fusion of tungsten hexafluoride is very high, but this is obviously a result of not recognizing the existence of a solid-solid transition at -8.2°.

The vapour pressure of rhenium hexafluoride has been repoeted previously by Ruff and Kwasnik[3] who gave a graph but no numerical data. Their boiling point of 47.5° is considerably higher than the value 33.8° found in this research. This discrepancy has been explained by Malm, Selig and Fried[6] who produced a mixture of rhenium hexafluoride with rhenium heptafluoride, the latter being the less

volatile of the two, by the high temperature fluorination of metallic rhenium. The heptafluoride readily formed solid solutions with the hexafluoride thereby causing the mixture to be less volatile than pure rhenium hexafluoride and the authors are of the same opinion as Malm, Selig and Fried that Ruff and Kwasnik measured the vapour pressure of such a mixture. The preliminary vapour pressure measurements of pure rhenium hexafluoride reported by Malm, et al. are in excellent agreement with the data of this research. The measurements of this research show that rhenium hexafluoride has a solid-solid transition at -1.9°.

The yellow volatile fluoride of osmium was first reported by Ruff and Tschirch[4] to be the octafluoride OsF_8 with a melting point of 34.4° and a boiling point of 47.5°. The identity of this compound was maintained for some forty years until recent work by Weinstock and Malm[1] disproved the octafluoride and showed the highest fluoride of osmium to be the hexafluoride, a fact further substantiated by Hargreaves and Peacock[10] from magnetic susceptibility measurements. In the present study the vapour pressure of pure osmium hexafluoride has been measured over a wide temperature range. The data indicate a melting point of 34.0° and boiling point of 47.5°, values in good agreement with those of Ruff and Tschirch and of Weinstock and Malm. Ruff and Tschirch measured the vapour pressure of osmium hexafluoride using the method of Smith and Menzies; consequently, they obtained values only for the liquid hexafluoride. It was not possible for them to observe a triple point or a solid-solid transition from vapour pressures. Our low temperature data clearly show a solid-solid transition at -0.4°.

The vapour pressure of iridium hexafluoride was first measured by Ruff and Fischer[3], and there is good agreement between their

results and those reported here. However, a direct comparison of results cannot be made because their actual data are not reported. Although Ruff and Fischer report a melting point of 44.0°, their vapour pressure curve does not show a break at the triple point. As with rhenium and osmium hexafluorides, a hitherto unreported solid-solid transition was observed in the present research, the value for IrF_6 being 0.4°.

The vapour pressure of molybdenum hexafluoride has been reported previously by Ruff and Ascher[2] and there is good agreement between their results and those reported here. The maximum temperature for which Ruff and Ascher made measurements was 21.0° and their extrapolated boiling point of 35.0° is a little higher than the value, 34.0°, found in this research. As with tungsten hexafluoride, Ruff and Ascher overlooked a solid solid transition at -8.7° although their data suggest a break in the curve at this temperature. Brady, Meyers and Clauss[11] have recently measured the heat capacity of molybdenum hexafluoride and have reported a solid-solid transition at -9.6°. Their value for the heat of transition of 1,960 cal. per mole is in excellent agreement with the value found in this study of 1,917 cal. per mole calculated from the differences in the heats of sublimation at the transition point. The erroneous heat of fusion of 2,500 cal. per mole reported by Ruff and Ascher is the result of not realizing the existence of a solid-solid transition. The thermal value, 1059 ± 10 cal./mole of Brady, Meyers and Clauss is higher than the value, 915 cal/mole, found in this study.

The physical constants shown in Table 3 clearly show that the volatilities of solid and liquid WF_6, ReF_6, OsF_6 and IrF_6 decrease with increase in molecular weight and that the transition and melting points increase. Table 3 shows that the close similarity

of the hexafluorides, particularly those of rhenium and molybdenum.

The similar entropies of transition for ReF_6, OsF_6, IrF_6, and MoF_6 suggest a close relationship between the entropies of rotation in the solid compounds. The latent heats of vaporization shown in Table 4 increase through the series WF_6, ReF_6, OsF_6, and IrF_6, except that osmium hexafluoride has a slightly lower heat of vaporization than rhenium hexafluoride. The Trouton Constants of the liquid hexafluorides are as one would expect for normal liquids.

Little can be said regarding the nuclear magnetic resonance spectra of the transition metal hexafluorides. Apart from the diamagnetic tungsten and molybdenum hexafluorides, the unpaired 5d electrons in rhenium, osmium and iridium hexafluorides prevented the observance of the fluorine resonances in these compounds in this research.

An interesting point which resulted from observations with the spectra of WF_6 and MoF_6 is that a sharp fluorine resonance was obtained with the solid compounds providing the temperature was above the transition point. Below the transition point the sharp peak broadens out completely, thus suggesting the cessation of molecular rotation. It is thus apparent the solid transition metal hexafluorides have properties similar to the so called "liquid crystal" state at temperatures between the transition point and the triple point. The transition metal hexafluorides also tend to form a glass clear mass which is presumably a single crystal when they are stored below the melting points for a considerable time.

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Department of Chemistry

Table 1.

Vapour Pressures

MF_6

T (°K)	Obs. Pres. (mm. Hg)
Solid	
220.2	7.0
230.4	17.9
235.4	27.1
240.4	40.4
245.6	61.7
250.7	89.3
255.8	128.3
260.5	178.6
263.0	211.0
266.2	256.2
269.0	301.7
270.6	324.2
273.2	372.8
274.2	392.0

T_o (°K)	Obs. Pres. (mm. Hg)
Liquid	
275.2	413.2
276.2	427.8
278.2	468.4
279.2	488.2
281.2	530.1
282.2	550.0
284.2	598.5
285.2	620.6
287.2	672.4
288.2	697.7
289.2	724.9
290.2	754.6

ReF_6

T (°K)	Obs. Pres. (mm. Hg)	T_o (°K)	Obs. Pres. (mm. Hg)
Solid		Liquid	
229.6	5.6	294.2	467.5
240.2	14.2	297.2	525.1
244.9	22.1	300.2	589.7
250.2	33.1	303.2	661.2
255.6	49.3	304.2	687.0
260.9	72.9	306.2	739.5
265.5	102.4		
270.6	145.2		
273.2	169.2		
276.2	196.8		
279.2	228.4		
282.2	265.8		
285.2	309.3		
288.2	358.1		
291.2	410.8		

OsF_6

T (°K)	Obs. Pres. (mm. Hg.)	T (°K)	Obs. Pres. (mm. Hg.)	T_o (°K)	Obs. Pres. (mm. Hg.)
Solid		Solid		Liquid	
231.0	4.7	278.2	111.6	309.2	510.3
241.5	7.1	283.2	147.1	311.2	542.5
246.9	10.9	288.2	190.3	313.2	586.9
251.5	16.2	293.2	245.5	315.2	629.3
256.4	24.2	298.2	311.8	317.2	675.3
261.6	36.1	303.2	395.4	319.2	719.0
266.5	51.4	305.2	431.9		
273.2	84.4	307.2	474.5		

Table 1. Continued.

IrF_6				MoF_6			
T_o (°K)	Obs. Pres. (mm. Hg.)	T_o (°K)	Obs. Pres. (mm. Hg.)	T_o (°K)	Obs. Pres. (mm. Hg.)	T_o (°K)	Obs. Pres. (mm. Hg.)
Solid		Liquid		Solid		Liquid	
231.3	2.2	317.2	536.7	215.4	1.7	291.2	412.2
242.3	5.4	319.2	580.2	228.2	4.7	292.2	428.1
252.0	12.2	321.2	623.6	233.5	8.3	294.2	464.2
257.6	18.9	322.2	649.7	238.5	13.4	295.2	484.6
262.1	26.3	323.2	671.0	243.4	20.8	297.2	521.2
267.1	38.5	325.2	720.2	248.3	30.9	298.2	546.4
273.2	60.4	326.2	745.0	254.0	47.3	300.2	585.0
275.2	68.4	327.2	744.0	259.2	71.2	301.2	612.9
278.2	80.1			265.0	97.5	303.2	657.7
280.2	90.0			266.8	116.4	304.2	685.6
283.2	105.4			273.2	169.5	305.2	708.3
285.2	118.2			278.2	218.4	306.2	735.2
288.2	137.3			284.2	295.9	307.2	763.0
290.2	153.4			286.2	325.3	308.2	779.5
293.2	177.8			288.2	357.5		
295.2	191.2			290.2	393.2		
298.2	227.2						
303.2	290.9						
308.2	364.9						
313.2	450.5						
315.2	493.6						

TABLE 2

Vapour Pressure Equations for WF_6, ReF_6, OsF_6, IrF_6 and MoF_6

liquid WF_6 (2.0° to 17.1°)	solid WF_6 (-8.2° to 2.0°)	solid WF_6 (-60° to -8.2°)
$\log P = 7.635 - \frac{1380.5}{T}$	$\log P = 8.758 - \frac{1689.9}{T}$	$\log P = 9.951 - \frac{2006.0}{T}$
liquid ReF_6 (19.0° to 33.8°)	solid ReF_6 (-1.9° to 18.0°)	solid ReF_6 (-50° to -1.9°)
$\log P = 7.732 - \frac{1489.1}{T}$	$\log P = 8.539 - \frac{1724.7}{T}$	$\log P = 10.110 - \frac{2151.2}{T}$
liquid OsF_6 (34.0° to 47.5°)	solid OsF_6 (-0.4 to 34.0°	solid OsF_6 (-40° to -0.4°)
$\log P = 7.470 - \frac{1472.8}{T}$	$\log P = 8.726 - \frac{1857.7}{T}$	$\log P = 10.290 - \frac{2284}{T}$
liquid IrF_6 (44.0° to 54°)	solid IrF_6 (0.4° to 44.0°)	solid IrF_6 (-50.0° to 0.4°)
$\log P = 7.952 - \frac{1656.5}{T}$	$\log P = 8.618 - \frac{1867.5}{T}$	$\log P = 10.000 - \frac{2245.7}{T}$
liquid MoF_6 (17.4° to 34°)	solid MoF_6 (-8.7° to 17.4°)	solid MoF_6 (-60° to -8.7°)
$\log P = 7.766 - \frac{1499.9}{T}$	$\log P = 8.533 - \frac{1722.9}{T}$	$\log P = 10.216 - \frac{2166.5}{T}$

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TABLE 3

Physical Constants of WF_6, ReF_6, OsF_6, IrF_6 and MoF_6

	Boiling Pt. (°C)	Triple Pt. (°C)	Triple Pt. (mmHg)	Transition Pt. (°C)	Transition Pt. (mmHg)	Heat of fusion (cal $mole^{-1}$)	Entropy of fusion (cal $mole^{-1}deg^{-1}$)	Heat of transition (cal $mole^{-1}$)	Entropy of transition (cal $mole^{-1}deg^{-1}$)
WF_6	17.1	2.0	413.2	-8.2	239.9	420	1.45	1,400	5.28
ReF_6	33.8	18.7	436.5	-1.9	153.1	940	3.21	2,090	7.71
OsF_6	47.5	33.4	474.5	-0.4	81.3	1,760	5.72	1,970	7.20
IrF_6	53.6	43.8	518.8	+0.4	61.7	1,190	3.74	1,700	6.21
MoF_6	34.0	17.40	398.1	-8.7	104.7	920	3.15	1,960	7.40

TABLE 4

Latent heats of vaporisation and sublimation, and entropies of vaporisation

	Latent heat of vaporisation of liquid (cal $mole^{-1}$)	Latent heat of sublimation (above transition pt) (cal $mole^{-1}$)	Latent heat of sublimation (below transition pt) (cal $mole^{-1}$)	Entropy of vaporisation of liquid (cal $mole^{-1}$ deg^{-1})
WF_6	6,330	7,750	9,150	21.8
ReF_6	6,860	7,800	9,890	22.3
OsF_6	6,720	8,480	10,450	21.0
IrF_6	7,380	8,570	10,270	22.6
MoF_6	6,940	7,850	9,810	22.5

VAPOUR PRESSURES OF SOME FLUORIDES AND OXYFLUORIDES OF MOLYBDENUM, TUNGSTEN, RHENIUM AND OSMIUM

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. For example, platinum hexafluoride has been prepared by Weinstock, Claassen and Malm,[1] the pentafluorides of molybdenum, rhenium, and osmium by Hargreaves and Peacock[2,3] and very recently platinum pentafluoride has been reported by Bartlett and Lohmann.[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 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 vapor pressure data. These substances disproportionate below their boiling points; therefore, the boiling points previously reported in the literature are in error.

EXPERIMENTAL.

Vapour pressure measurements were made with a Pyrex diaphragm gauge used as a null instrument. A detailed description of the apparatus and the experimental technique is given elsewhere by Cady and Hargreaves.[11]

A UCCO 600 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 ± 0.05 mm. The sensitivity of the gauge was 0.1 mm. per scale division so that the pressures could be measured with a precision of ± 0.1 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. The hexafluorides were prepared by direct fluorination of the powdered metals in a copper reactor. 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 was prepared according to the method of Peacock.[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 the

direct interaction of molybdenum hexacarbonyl and molybdenum hexafluoride.[10] A mixture of the pentafluoride and tetrafluoride was obtained, and the pentafluoride was readily separated from the non-volatile tetrafluoride by vacuum sublimation.

Rhenium pentafluoride and oxytetrafluoride were prepared by the method of Hargreaves and Peacock.[2] The pentafluoride was obtained by the 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 reacting an excess of rhenium hexafluoride with tungsten hexacarbonyl. After the vigorous reaction the green product was heated to 65° under 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 was prepared by the method of Hargreaves and Peacock.[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 the 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 vacuum at room temperature when the volatile hexafluoride was readily removed. The compounds were then purified by vacuum sublimation prior to transferring to break-seal vessels.

Rhenium oxypentafluoride and dioxytrifluoride were prepared according to the method of Aynsley, Peacock and Robinson.[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 careful 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 the direct fluorination of anhydrous rhenium dioxide. This method gave rhenium dioxytrifluoride as the major product. The two oxyfluorides were readily separated on account of the high volatility of the oxypentafluoride. Rhenium dioxytrifluoride was purified by vacuum distillation at 130°.

The melting points 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 boiling point of $ReOF_5$ was also determined using a boiling point apparatus similar to that described by Fairbrother and Frith.[12] The temperature of the vapour in equilibrium with the liquid was measured with a calibrated chromel-alumel thermocouple.

Results.

The vapour pressure data are given in Table 1. The temperatures are given in degrees absolute with the ice point taken at 273.2°. The pressures are given in mm. Hg at 0.0°C. The vapour pressure data are summarised by the equations in Table 2.

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 melting points obtained directly in thin walled capillaries. The melting points 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 melting points, it was not possible to obtain accurate sublimation pressures using the diaphragm gauge technique. The solid-solid transition at 30.0° and the melting point of 40.8° of $ReOF_5$ were obtained from the two plateaus in a warming curve.

Some physical constants of the compounds are shown in Table 3. 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 calories per mole.

The heats of sublimation and vaporisation for $MoOF_4$, $ReOF_4$, WOF_4 and $ReOF_5$, and the 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 4 together with the entropies of vaporisation for all the liquid states. Table 4 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 oxytetrafluorides have been known for many years. The former compound was first prepared by Ruff, Eisner and Heller,[5] and the latter by Ruff and Eisner.[6] The melting points of WOF_4 and $MoOF_4$ reported were 110° and 97°, and the boiling points 185° and 180° respectively. The above workers gave no vapour pressures. The physical constants derived

from the present vapour pressure data are in general agreement with the values of Ruff et al. Their value for the melting point of tungsten oxytetrafluoride is somewhat higher than the 105° reported here; however, there is excellent agreement in the values of the boiling points. In a similar manner there is good agreement regarding the melting point of molybdenum oxytetrafluoride, but the boiling points do not agree well.

Ruff and Kwasnik[7] described rhenium oxytetrafluoride as a white substance with a melting point of 39.7° and a boiling point of 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 melting and boiling points 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 melting point of 40.8° and the boiling point of 73.0°, a solid-solid transition has been found to occur at 30.0°. The melting point of 40.8° reported here is thus in agreement with Ruff's value of 39.7° although the boiling points differ substantially. Since Ruff and Kwasnik did not record any vapour pressure measurements above the melting point of rhenium oxypentafluoride, their extrapolated boiling point of 62.7° could have been in considerable error. The close agreement in the melting points suggests 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 tungsten and molybdenum oxytetrafluorides. The rhenium compound is considerably more reactive than the tungsten and molybdenum compounds 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 and upon cooling to congeal 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[13] who reported the melting and boiling points 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 boiling point 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 given in Table 3. The chemical reactivity increases as the molecular weight increases. This is further evidenced by the fact that osmium oxytetrafluoride is very difficult to prepare and iridium oxytetrafluoride has not yet been successfully identified. The data in Table 4 shows 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 of compounds in that they all undergo irreversible disproportionation at higher temperatures. The diaphragm gauge 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 boiling points 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 rhenium hexafluoride and the non-volatile rhenium 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:

$$2\ MF_5 \longrightarrow MF_6 + MF_4$$

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 3.) There is also a close similarity in the boiling points of the compounds. It is pertinent at this point to compare some of the physical properties of MoF_5, ReF_5 and OsF_5 with the other pentafluorides shown in Table 4. All of 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 equation:

$$2IF_5 \longrightarrow IF_4^+ + IF_6^-$$

Clark and Emeleus 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,[15] hexafluororhenates [16] and hexafluoroosmates[17] containing the MoF_6^-, ReF_6^-, and OsF_6^- ions, it is reasonable to assume that molybdenum, rhenium and osmium pentafluorides also self ionise to some extent according to the general equation:

$$2MF_5 \longrightarrow MF_4^+ + MF_6^-$$

The crystal structure of molybdenum pentafluoride is at present being investigated by Edwards and Peacock[18] 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 atoms 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 then it may be assumed that rhenium and osmium pentafluorides may also have this suggested ionic structure. An ionic type of structure for the pentafluorides would explain the ready thermal disproportionation of the compounds and also the yet unexplained magnetic properties of rhenium[2] and Osmium[3] pentafluorides.

Some physical properties of the fluorides and oxyfluorides of rhenium are compared in Table 5. It is of interest 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 in 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.

A comparison of the properties of the known transition metal pentafluorides and tetrafluorides (Table 6) indicates that iridium tetrafluoride lies in a somewhat anomalous position. Iridium tetrafluoride was first reported by Robinson and Westland.[19] The compound has a melting point of 106-107° and a boiling point of 300°. A glance at the compounds listed in Table 6 leads to the conclusion that iridium tetrafluoride has properties which are similar to the third row pentafluorides rather than the tetrafluorides.

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 here, that similar reactions involving molybdenum, rhenium and osmium hexafluorides, gave the corresponding transition metal pentafluorides as the principal products.

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Table 1.

Vapour Pressure of MoF_5, $MoOF_4$, ReF_5, $ReOF_4$, OsF_5, WOF_4, ReO_2F_3, and $ReOF_5$.

MoF_5, Liquid

T, °K	P, mm
313.2	0.8
323.2	1.4
333.2	2.1
343.2	3.8
353.2.	6.0
363.2	9.7
373.2	15.3
383.2	22.9
393.2	35.8
403.2	53.6
413.2	80.8
423.2	116.3
433.2	157.7

ReF_5, Liquid

T, °K	P, mm
333.2	1.2
343.2	1.5
353.2	2.8
363.2	4.6
373.2	7.7
383.2	13.0
393.2	20.0
403.2	29.3

OsF_5, Liquid

T, °K	P, mm
303.2	0.1
313.2	0.2
323.2	0.4
333.2	0.5
343.2	0.7
353.2	1.1
363.2	1.8
373.2	3.4
383.2	6.4
393.2	11.0
403.2	17.6
413.2	28.6
423.2	44.5
433.2	68.4
443.2	104.2
453.2	149.6

$MoOF_4$

Solid		Liquid	
T, °K	P, mm	T, °K	P, mm
313.2	1.2	373.2	36.0
323.2	2.4	378.2	44.7
333.2	4.4	383.2	53.6
343.2	7.9	393.2	79.0
353.2	12.9	403.2	118.8
363.2	22.6	413.2	173.9
368.2	28.8	423.2	250.2
		433.2	344.0
		443.2	457.1
		453.2	631.0

ReO_2F_3, Liquid

Solid		Liquid	
T, °K	P, mm	T, °K	P, mm
323.2	0.4	383.2	26.0
333.2	1.4	388.2	43.5
338.2	2.0	393.2	54.8
343.2	2.7	398.2	69.0
348.2	3.8	403.2	86.5
358.2	5.8	408.2	107.7
363.2	7.8	413.2	133.5
368.2	11.4	418.2	164.8
373.2	14.5	423.2	200.3
378.2	20.3	428.2	240.8
		433.2	297.2
		438.2	367.3
		443.2	431.5
		453.2	602.6

Table 1. (Continued)

$ReOF_4$

Solid		Liquid	
T, °K	P, mm	T, °K	P, mm
333.2	1.6	383.2	51.1
343.2	3.5	388.2	66.9
353.2	7.2	393.2	86.8
363.2	14.8	398.2	109.2
373.2	28.6	403.2	138.1
378.2	37.4	408.2	172.5
		413.2	211.7
		418.2	260.1
		423.2	313.6
		428.2	355.2
		433.2	478.6
		438.2	582.1

ReO_2F_2, Liquid

T, °K	P, mm	T, °K	P, mm
333.2	1.1	393.2	43.9
343.2	2.5	403.2	75.0
353.2	4.4	413.2	116.5
358.2	6.6	423.2	183.3
363.2	8.3	433.2	286.4
373.2	14.6	443.2	421.7
383.2	25.2		

$ReOF_5$

Solid				Liquid	
T, °K	P, mm	T, °K	P, mm	T, °K	P, mm
273.2	22.1	305.2	159.6	314.2	240.8
275.2	31.1	306.2	167.0	315.2	251.2
283.2	42.4	307.2	175.0	317.2	272.3
288.2	59.1	308.2	183.1	319.2	295.0
293.2	81.7	309.2	192.0	321.2	319.4
298.2	109.4	310.2	201.4	323.2	344.5
300.2	122.1	311.2	210.4	328.2	409.0
303.2	144.6	312.2	219.8	333.2	488.8
304.2	151.8	313.2	229.5	338.2	581.8
				341.2	643.8
				343.2	690.8

TABLE 2

Vapour Pressure Equations

Liquid MoF_5 (70.0° to 160°) $\log P = 8.58 - \frac{2772}{T}$

Liquid $MoOF_4$ (95° to 185°) $\log P = 8.716 - \frac{2671}{T}$ Solid $MoOF_4$ (40° to 95°) $\log P = 9.21 - \frac{2854}{T}$

Liquid ReF_5 (48.0° to 140°) $\log P = 9.024 - \frac{3037}{T}$

Liquid $ReOF_4$ (108° to 172°) $\log P = 10.09 - \frac{3206}{T}$ Solid $ReOF_4$ (50° to 107°) $\log P = 11.88 - \frac{3888}{T}$

Liquid OsF_5 (75° to 180°) $\log P = 9.75 - \frac{3429}{T}$

Liquid $ReOF_3$ (41° to 73°) $\log P = 7.727 - \frac{1678.6}{T}$ Solid $ReOF_3$ (30° to 41°) $\log P = 8.620 - \frac{1858.9}{T}$

solid $ReOF_3$ (0° to 30°) $\log P = 9.581 - \frac{2250.1}{T}$

Liquid ReO_2F_2 (90° to 170°) $\log P = 10.36 - \frac{3437}{T}$

Liquid WOF_4 (105° to 186°) $\log P = 9.69 - \frac{3125}{T}$ Solid WOF_4 (50° to 104°) $\log P = 10.96 - \frac{3605}{T}$

TABLE 3

Physical Constants of MoF_5, ReF_5, OsF_5, WOF_4, $MoOF_4$, $ReOF_4$, $ReOF_5$ and ReO_2F_3

	Boiling point (°C)	Triple Point (°C)	(mm Hg)	Transition Point (°C)	(mm Hg)	Heat of fusion (cal mole^{-1})	Entropy of fusion (cal mole^{-1}deg^{-1})	Heat of transition (cal mole^{-1})	Entropy of Transition (cal mole^{-1}deg
MoF_5	213.6	67.0	-	-	-	-	-	-	-
$MoOF_4$	186.0	97.2	28.8	-	-	1,020	2.768	-	-
ReF_5	221.3	48.0	-	-	-	-			
$ReOF_4$	171.7	107.8	45.2	-	-	3,230	8.478	-	-
OsF_5	225.9	70.0	-	-	-	-	-	-	-
$ReOF_5$	73.0	40.8	237.1	30.0	144.6	1,220	3.886	1,339	3.868
ReO_2F_3	185.4	90.0	-	-	-	-	-	-	-
WOF_4	185.9	104.7	25.1	-	-	2,260	5.981		

TABLE 4

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
$ReOF_5$	7,720	8,940	10,280	22.3
ReO_2F_3	15,700	-	-	34.3
WOF_4	14,230	16,490	-	31.0
NbF_5	12,900	-	-	25.4 (12)
TaF_5	13,000	-	-	25.9 (12)
IF_5				27.2 (21)
VF_5	10,640	11,940	-	33.1 (14)

TABLE 5

Physical Constants of Some Fluorides and Oxyfluorides of Rhenium

	Boiling Point (°C)	Melting Point (°C)	Heat of Sublimation (cal deg^{-1})	Heat of Vaporisation (cal deg^{-1})	Entropy of Vaporisation (cal mole^{-1}deg^{-1})	
ReF_6	53.8	18.7	7,796	6,857	22.3	(11)
$ReOF_5$	73.0	40.8	8,940	7,720	22.3	
$ReOF_4$	171.7	107.3	17,820	14,590	32.7	
ReF_5	221.3	48.0	-	13,830	28.1	
ReO_2F_3	186.4	90.0	-	15,700	34.3	
ReO_3F	-	147.0	-	-	-	(13)
ReF_4	sublimes >300°C	-	-	-	-	(2)
$ReOF_3$	non-volatile	-	-	-	-	

TABLE 6

Physical Constants of Known Pentafluorides and Tetrafluorides of the 2nd and 3rd Row Transition Elements.

	NbF_5 (12)	MoF_5 (9)	RuF_5 (19)
M. Pt.	80°	67°	107°
B. Pt.	235°	213.6°	313°

	TaF_5 (12)	ReF_5	OsF_5	PtF_5 (4)
M. Pt.	95°	48°	70°	75-76°
B.Pt.	229°	221.3°	225.9°	300-305°

	MoF_4	ReF_4	OsF_4	IrF_4 (19)	PtF_4 (20)	WF_4 (10)
M. Pt.	-	-	-	106-107°	-	
B. Pt.	-	-	-	300°	-	
Volatility	non-vol	sublimes in vac > 300°	distills in vac >350°		non-vol	non-vol