305. *The Vapour Pressures of Some Heavy Transition-metal Hexafluorides.*

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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 (the third-row transition-metal fluorides) have almost the same molecular weights but differ from one another in the number of 5*d*-electrons. Molybdenum is the only second-row element which forms a volatile hexafluoride of which the properties are remarkably similar to those of 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 these hexafluorides were first measured by Ruff and his co-workers [2] some time ago. Apart from some recent preliminary measurements with osmium and rhenium hexafluoride [1,3] and a more detailed study of the vapour pressure of liquid tungsten hexafluoride,[4] there have been no further measurements 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 intrument (Fig. 1). 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, even at their b. p., to attack the glass.

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 centre 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 specimen of the compound to be measured contained in a Pyrex break-seal vessel was glass-blown on to the base of the gauge after a glass-covered breaker had been placed above the seal. The gauge was then pumped under a high vacuum and the glass surfaces above the specimen were flamed for several hours

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[1] Weinstock and Malm, *J. Amer. Chem. Soc.*, 1958, **80**, 4466.

[2] Ruff and Tschirch, *Ber.*, 1913, **46**, 929; Ruff and Ascher, *Z. anorg. Chem.*, 1931, **196**, 413; Ruff and Kwasnik, *ibid.*, 1934, **219**, 65; Ruff and Fischer, *ibid.*, 1937, **233**, 282.

[3] Malm, Selig, and Fried, *J. Amer. Chem. Soc.*, 1960, **82**, 1510.

[4] Barber and Cady, *J. Phys. Chem.*, 1956, **60**, 505.

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 adequately baked, 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 to allow a small portion of the hexafluoride to distil 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 oxygen, pumping continued for ½ hr., and the gauge sealed at A. The vacuum manifold was then isolated from the mercury diffusion pump.

A 5-l. 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 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 a precision of 0·05°, and were controlled within 0·1°.

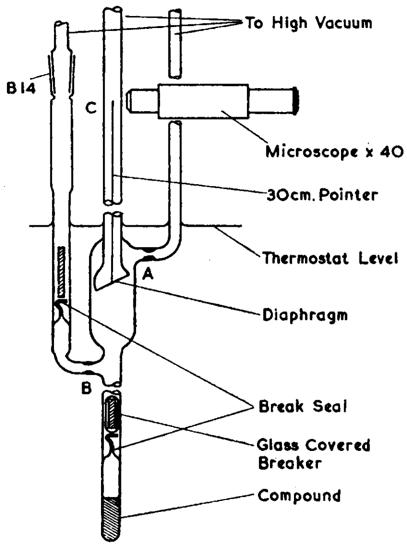

FIG. 1. *Apparatus.*

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 facilitated the viewing of the pointer. The mercury manometer was read with a high-precision cathetometer and the pressures were recorded with an accuracy of 0·01 mm. Gauges with sensitivities of 0·10—0·05 mm. were used for the measurements.

The vapour-pressure measurements were made by a null method. The zero point of 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 one of the break-seal side-arms attached to the part of the system containing the hexafluoride. With equal pressures on each side 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. The vapour-pressure measurements were then repeated. Concordant results indicated the original material to be of high purity. A third break-seal side-arm (not shown in the Figure) 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 before 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 [5] 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 b. p.s of the five hexafluorides were also determined by use of a standard boiling-point apparatus, the temperature of the vapour in equilibrium with the liquid being measured by a calibrated copper–constantan thermocouple. M. p.s were observed visually during experimental vapour-pressure runs and some transition points were observed from warming-curve data.

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

Materials.—The hexafluorides of tungsten, rhenium, osmium, iridium, and molybdenum were prepared by direct fluorination of the powdered elements in a copper vessel. 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.

TABLE 1. *Vapour-pressure equations for* WF_6, ReF_6, OsF_6, IrF_6, *and* MoF_6.

Liquid WF_6 (2·0—17·1°) $\log P = 7{\cdot}635 - 1380{\cdot}5/T$	Solid WF_6 (−8·2° to 2·0°) $\log P = 8{\cdot}758 - 1689{\cdot}9/T$	Solid WF_6 (−60° to −8·2°)$_5$ $\log P = 9{\cdot}951 - 2006{\cdot}0/T$
Liquid ReF_6 (19·0—33·8°) $\log P = 7{\cdot}732 - 1489{\cdot}1/T$	Solid ReF_6 (−1·9° to 18·0°) $\log P = 8{\cdot}539 - 1724{\cdot}7/T$	Solid ReF_6 (−50° to −1·9°) $\log P = 10{\cdot}110 - 2151{\cdot}2/T$
Liquid OsF_6 (34·0—47·5°) $\log P = 7{\cdot}470 - 1472{\cdot}8/T$	Solid OsF_6 (−0·4° to 34·0°) $\log P = 8{\cdot}726 - 1857{\cdot}7/T$	Solid OsF_6 (−40° to −0·4°) $\log P = 10{\cdot}290 - 2284/T$
Liquid IrF_6 (44·0—54°) $\log P = 7{\cdot}952 - 1656{\cdot}5/T$	Solid IrF_6 (0·4—44·0°) $\log P = 8{\cdot}618 - 1867{\cdot}5/T$	Solid IrF_6 (−50·0° to 0·4°) $\log P = 10{\cdot}000 - 2245{\cdot}7/T$
Liquid MoF_6 (17·4—34°) $\log P = 7{\cdot}766 - 1499{\cdot}9/T$	Solid MoF_6 (−8·7° to 17·4°) $\log P = 8{\cdot}533 - 1722{\cdot}9/T$	Solid MoF_6 (−60° to −8·7°) $\log P = 10{\cdot}216 - 2166{\cdot}5/T$

TABLE 2. *Physical constants of* WF_6, ReF_6, OsF_6, IrF_6, *and* MoF_6.

	B. p.	Triple pt.		Transition pt.		Heat of fusion	Entropy of fusion	Heat of transition	Entropy of transition
	(°c)	(°c)	(mm.)	(°c)	(mm.)	(cal. mole^{-1})	(cal. mole^{-1} deg.$^{-1}$)	(cal. mole^{-1})	(cal. mole^{-1} deg.$^{-1}$)
WF_6	17·1	2·0	413·2	−8·2	239·9	420	1·45	1400	5·28
ReF_6	33·8	18·7	436·5	−1·9	153·1	940	3·21	2090	7·71
OsF_6	47·5	33·4	474·5	−0·4	81·3	1760	5·72	1970	7·20
IrF_6	53·6	43·8	518·8	+0·4	61·7	1190	3·74	1700	6·21
MoF_6	34·0	17·40	398·1	−8·7	104·7	920	3·15	1960	7·40

TABLE 3. *Latent heats of vaporisation and sublimation, and entropies of vaporisation.*

	Latent heat of vaporisation of liquid (cal. mole^{-1})	Latent heat of sublimation		Entropy of vaporisation of liquid (cal. mole^{-1} deg.$^{-1}$)
		(above transition pt.) (cal. mole^{-1})	(below transition pt.) (cal. mole^{-1})	
WF_6	6330	7750	9150	21·8
ReF_6	6860	7800	9890	22·3
OsF_6	6720	8480	10,450	21·0
IrF_6	7380	8570	10,270	22·6
MoF_6	6940	7850	9810	22·5

Since the high-temperature fluorination of rhenium metal resulted in the formation of some rhenium heptafluoride,[3] 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 before 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 a high vacuum and stored at liquid-oxygen temperature until ready for use.

Some difficulty was experienced in the purification of rhenium hexafluoride and in its separation from the less volatile rhenium heptafluoride. The compound was repeatedly vacuum-distilled at a low temperature, the first fraction and tailings being discarded, 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 60 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 by using the variable-temperature probe.

Results.—The vapour-pressure data for the solid and liquid hexafluorides are summarized by the equations in Table 1.

The equations were derived from the vapour-pressure data, the curve for each phase being considered to be a straight line. The number of vapour-pressure measurements used in determining the relevant equations varied according to the individual compounds. At least ten observations were recorded for all compounds from −78° to the transition points, and a similar number of observations was made for each of the other two phases. Vapour pressures were normally recorded at 3° intervals except when the phase under investigation was of short temperature range. In such circumstances, pressures were recorded at 1° intervals. The maximum deviations of the observed vapour pressures and those calculated from the equations are ±0·5 mm. in the pressure region 0—100 mm. Hg. and ±3 mm. at 760 mm.

The values of the triple points in Table 2 are observed m. p.s and are accurate to 0·2°. The breaks in the vapour-pressure curves were within ±0·2° 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 heats 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 3. These were derived by 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.[6] The same spectra were obtained for the solid hexafluorides as for 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 m. p. 2·3° and b. p. 17·5°, but they overlooked the solid–solid transition at −8·2° although their data show evidence for a break in the curve at −8·2°. Barber and Cady [4] later measured the vapour pressure of liquid tungsten hexafluoride from 11·8° to 51·38° with high precision. Their b. p. of 17·05° ± 0·5° is somewhat lower than Ruff and Ascher's value, but is in excellent agreement with ours 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 m. p. at 2·0° ± 0·3°. Their estimated heats of transition and fusion from the warming-curve data, namely, 1600 ± 300 cal. per mole and 500 ± 100 cal. per mole, respectively, are in rather good agreement with the values shown in Table 2. Ruff and Ascher's value of 2400 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 reported by Ruff and Kwasnik [2] who gave a graph but no numerical data. Their b. p. of 47·5° is considerably higher than the value 33·8° now found. This discrepancy has been explained by Malm, Selig, and Fried,[3] 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 we are of the same opinion as Malm, Selig, and Fried, *viz.*, 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 our data. Our measurements 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 [2] to be

[6] Muetterties and Phillips, *J. Amer. Chem. Soc.*, 1959, **81**, 1084.

the octafluoride OsF_8 with m. p. 34·4° and b. p. 47·5°. The identity of this compound was unchallenged for some 40 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 [7] 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 m. p. of 33·4° and a b. p. 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°.

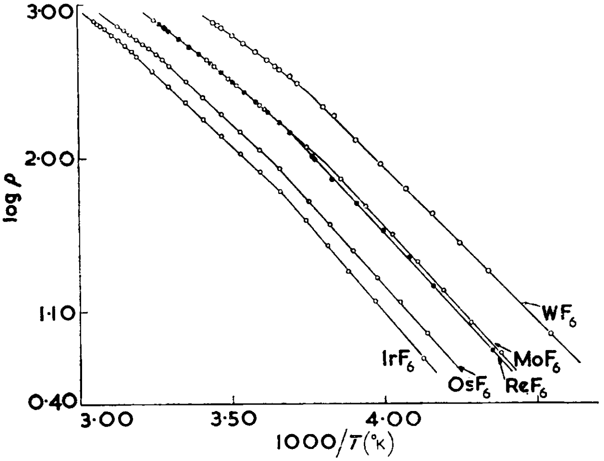

FIG. 2. *Vapour-pressure curves of fluorides.*

The vapour pressure of iridium hexafluoride was first measured by Ruff and Fischer,[2] 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 m. p. 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 by Ruff and Ascher,[2] and again their results agree with ours. The maximum temperature for which Ruff and Ascher made measurements was 21·0° and their extrapolated b. p. of 35·0° is a little higher than our value, 34·0°. 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 [8] recently measured the heat capacity of molybdenum hexafluoride and reported a solid–solid transition at —9·6°. Their value for the heat of transition of 1960 cal. per mole is in excellent agreement with the value now found, *viz.*, 1957 cal. per mole calculated from the differences in the heats of sublimation at the transition point. The erroneous heat of fusion of 2500 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, reported by Brady, Meyers, and Clauss is higher than the value, 915 cal./mole, now found.

The physical constants (Table 2) show that the volatilities of solid and liquid WF_6,

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[7] Hargreaves and Peacock, *Proc. Chem. Soc.*, 1959, 85.

[8] Brady, Meyers, and Clauss, *J. Phys. Chem.*, 1960, **64**, 588.

ReF_6, OsF_6, and IrF_6 decrease with increase in molecular weight and that the transition and melting points increase. Table 2 and Fig. 2 show 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 relation between the entropies of rotation in the solid compounds. The latent heats of vaporization shown in Table 3 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 5*d*-electrons in rhenium, osmium, and iridium hexafluorides prevented observation of the fluorine resonances in these compounds in this research.

It was interesting that for WF_6 and MoF_6 a sharp fluorine resonance was obtained with the solid compounds above the transition point. Below this point the sharp peak broadens out completely, suggesting the cessation of molecular rotation. It seems that the solid transition-metal hexafluorides have properties similar to the " 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 m. p. for a considerable time.

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