

PREPARATION AND CHARACTERISATION OF THE PLATINUM

GROUP METAL FLUORIDES.

A thesis presented for the degree of

DOCTOR OF PHILOSOPHY

in the

Faculty of Science

by

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University of Leicester

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STATEMENT

The experimental work described in this thesis has been carried out by the author in the Department of Chemistry of the University of Leicester between October 1985 and September 1988. The work has not been submitted, and is not currently being submitted, for any other degree at this or any other university.

date: 27-04-89 signed: G. Steger

Dedicated to my Parents.

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ABSTRACT

PREPARATION AND CHARACTERISATION OF THE PLATINUM GROUP METAL FLUORIDES

G. STANGER

An extensive review of the platinum group metal fluorides has been carried out and in the light of this, new preparative routes have been developed and characterisation has been significantly improved.

The preparation of the platinum group metal fluorides in both static and dynamic systems is discussed in chapter two. The fluorinations of ruthenium, rhodium and platinum sponges in dynamic systems proved to be of greatest interest. In these studies large amounts of ruthenium hexafluoride and platinum hexafluoride were produced and traces of rhodium hexafluoride were noted, where as previously more forcing conditions had been employed in the preparation of these compounds. It is believed that rigorous drying of the flow line and hydrogenation of the metal in situ are responsible for the success of this new preparative route.

When ruthenium is fluorinated in the dynamic system ruthenium hexafluoride and tetrameric ruthenium pentafluoride are produced in large quantities, and smaller amounts of a red glassy material is also formed. There have been no previous reports of any red material forming during this reaction. It is now believed that this material is a trimeric form of ruthenium pentafluoride.

The characterisation of these fluorides was carried out using a large variety of techniques, the most useful being mass spectrometry and matrix isolated infrared spectroscopy. Mass spectrometry proved invaluable in the characterisation of the trimeric ruthenium pentafluoride, while matrix isolation enabled good quality infrared spectra of the reactive hexafluorides to be recorded. These techniques were also utilised to give the first insight into the behaviour of the tetrameric pentafluorides in the gas phase. Iridium pentafluoride has been shown to be monomeric at elevated temperatures, under similar conditions ruthenium and osmium pentafluorides decompose to the metal and fluorine. Platinum pentafluoride is known to be unstable at room temperature and thought to decompose to the hexafluoride and tetrafluoride. Using matrix isolation, direct evidence of this has been obtained.

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Chapter 1

A Review of the Platinum Group Metal Fluorides

Chapter 1

A Review of the Platinum Group Metal Fluorides

1.1 Ruthenium

1.1.1 Ruthenium Octafluoride

The existence of ruthenium octafluoride has been reported by only one group [1,2] and thus we await further independent verification of its existence.

Preparation

Ruthenium octafluoride is reported to be produced by the fluorination of both ruthenium and ruthenium dioxide and is separated from the principle product, RuF_5 , by microsublimation at low temperatures.

Appearance and Physical Properties

Ruthenium octafluoride is a bright yellow solid. Its vapour pressure has been reported over a limited temperature range and the variation with temperature is given by $\log p = 7.67 - 1636/T$.

It is thermally unstable and decomposes to lower fluorides at temperatures above -50°C .

Spectroscopy

The infrared spectrum of the octafluoride shows bands at 1030 and 385 cm^{-1} with a combination band at 1285 cm^{-1} .

1.1.2 Ruthenium Hexafluoride

Preparation

Ruthenium hexafluoride was first prepared in 1961 by the

Table 1.1.2 Redox Reactions of RuF₆ [2]

Reagent	Product
PF ₃ /AHF	[Ru(PF ₃)F ₄] _n , PF ₅
AsF ₃	RuF ₄ ·AsF ₅
SbF ₃	RuF ₅ , SbF ₅ ^b
BiF ₃	RuF ₅ , BiF ₅ ^b
ClF ₃ ^a	ClF ₃ ·RuF ₅ , ClF ₅ ·RuF ₅
CS ₂	CF ₄ , SF ₄
H ₂ /AHF	RuF ₅ → RuF ₄ ^c
Ru/AHF	RuF ₅
Ru/KH/AHF	KRuF ₆

a: Only volatile products listed

b: Only pentafluoride reported, no attempt made to determine if an adduct formed.

c: RuF₅ was slowly reduced to RuF₄.

induction heating of ruthenium metal in a fluorine atmosphere at 300mm Hg pressure. The reaction was carried out in a quartz reactor fitted with a cold finger [3]. A 49% yield of RuF_6 was obtained. Recently, Burns and O'Donnell [4] reported a new method of preparing RuF_6 using a very simple apparatus. This consisted of a reaction vessel, furnace and cooling collar containing an acetone and solid CO_2 slush which facilitated rapid cooling of RuF_6 to a temperature at which dissociation does not occur. In this apparatus ruthenium powder is heated (350–400°C) with a slight deficiency of F_2 for 1 hour. The RuF_6 formed is used directly from the reactor as the lower fluorides and unreacted metal are involatile and so remain behind. Due to the simplicity of the equipment this is the best known preparative route for RuF_6 .

Appearance and Physical Properties

Solid RuF_6 is dark brown. Its vapour is brownish red and the vapour pressures over a selected temperature range are given below (table 1.1.1)[3];

Table 1.1.1. Vapour Pressure of RuF_6

Temp (°C)	0.0	4.6	8.6	11.1	14.4	17.6
Pressure (mmHg)	23	32	40	46	56	67

Although RuF_6 is thermally unstable, decomposing completely to RuF_5 and F_2 at 200°C, it can be stored for weeks at room temperature in a nickel can. However, it will rapidly attack Pyrex and to a slightly lesser extent, quartz [3].

Chemical Properties

The oxidation-reduction reactions of RuF_6 with a selected series of reductants have been studied [4]. The reactions follow a simple pattern, the reductant being oxidised to a higher fluoride and the hexafluoride being reduced to oxidation states V or IV. The solid

products containing ruthenium are rarely the penta- or tetrafluoride but are usually adducts or complexes (table 1.1.2).

The hydrolysis of RuF_6 in HF produces the oxonium salt $\text{H}_3\text{O}^+\text{RuF}_6^-$ [5]. RuF_6 is condensed at -196°C on to HF containing trace amounts of water. When the mixture warms to room temperature the red colour due to RuF_6 spontaneously disappears, an almost colourless solution with a tint of green is produced and oxygen is evolved. On removal of the HF a white solid remains, which is $\text{H}_3\text{O}^+\text{RuF}_6^-$. X-ray powder photography shows this to be isostructural with $\text{H}_3\text{O}^+\text{IrF}_6^-$ and $\text{H}_3\text{O}^+\text{PtF}_6^-$ both of which have a rhombohedral unit cell. The oxonium salt gradually darkens and eventually turns black.

Both NOF and NO react with RuF_6 at 25°C over a period of 21 hours to give NORuF_6 [6]. The infrared spectrum of this material has been recorded and peak positions are given in table 1.1.3.

Table 1.1.3. Infrared absorption Frequencies for NORuF_6 (cm^{-1})

RuF_6^-			NO^+
$\nu_1 (\text{A}_{1g})$	$\nu_2 (\text{E}_g)$	$\nu_5 (\text{F}_{2g})$	$\nu (\text{NO}^+)$
660.3	600	277	2330
	578	266	
		254	

The halogen exchange reactions of RuF_6 with BCl_3 and BBr_3 have been investigated. In both cases mixed halides were formed, but stoichiometric products were not produced [7]. These reactions are highly exothermic and require conditions to moderate their rate. Inert n-perfluoroalkane solvents can be conveniently used to dissipate the heat of reaction.

Structure

Ruthenium hexafluoride undergoes a solid-solid transition at 2.5°C and atmospheric pressure. The high-temperature modification is

cubic; $a=6.11\pm0.01\text{\AA}$ at 25°C , $Z=2$ with a calculated density $D=3.13\pm0.03\text{ gcm}^{-3}$. The low-temperature modification is orthorhombic; $a=9.44\pm0.02\text{\AA}$, at -30°C , $Z=4$ with a calculated density $D=3.50\pm0.03\text{ gcm}^{-3}$ [8].

Spectroscopy

The infrared spectrum of gaseous RuF_6 has been recorded between $230\text{--}4000\text{cm}^{-1}$ [73]. Bands were observed at $275(\nu_4)$, $735(\nu_3)$ and combination bands at $997(\nu_3+\nu_5)$ and $1410(\nu_1+\nu_3)\text{cm}^{-1}$, from which ν_1 and ν_5 were estimated to be at 675 and 262cm^{-1} respectively. The spectrum of RuF_6 can be interpreted in terms of it being a regular octahedron with O_h symmetry. However, less bands are observed than for any other hexafluoride, the ν_2 vibration being broadened due to the Jahn-Teller effect to an extent where some bands cannot be resolved.

1.1.3 Ruthenium Pentafluoride

Preparation

Ruthenium pentafluoride was first prepared in 1925 by Ruff and Vidic [9] by the reaction of fluorine on ruthenium sponge. This method was later developed by Holloway and Peacock [12] and remains the best known synthetic route. A mixture of fluorine and nitrogen is passed over the metal at $280\text{--}900^\circ\text{C}$ and a dark green viscous liquid containing RuF_5 is collected in a Pyrex trap. RuF_5 is separated from impurities, usually Ru metal or RuO_2 , by vacuum distillation. The fluorination of ruthenium dioxide also yields RuF_5 [10], as does the treatment of Ru sponge with BrF_3 [11]. The latter reaction is extremely vigorous at room temperature, a brownish solution being formed from which a pale cream solid is obtained after the removal of excess of solvent. This solid has a composition RuBrF_8 and when heated to 120°C in a vacuum, melts with decomposition forming emerald green droplets of RuF_5 and evolving BrF_3 . Unfortunately, small amounts of RuOF_4 are also produced and this is difficult to separate completely from the pentafluoride.

Appearance and Physical Properties

Ruthenium pentafluoride is a dark green crystalline solid which melts at 86.5°C to a green viscous liquid. Its vapour is almost colourless and the vapour pressure has been measured over the temperature range 17–157°C (table 1.1.4.) [12].

Table 1.1.4. Vapour Pressure of RuF₅

T(°C)	19	49.9	59.8	69.6	79.8	107.8
P(mmHg)	0.1	0.2	0.5	0.8	1.5	6.8
T(°C)	119.8	129.5	139.0	148.5	156.8	
P(mmHg)	12.5	21.7	26.3	45.9	64.6	

Variation with temperature is given by [12] :-

$$\log P(\text{mmHg}) = 9.54 - 3329/T$$

By extrapolation of the vapour pressure data the boiling point of RuF₅ can be estimated to be 227°C, this agrees well with the measured value of 230°C.

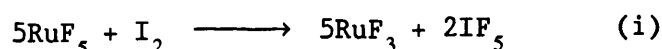
The enthalpy of vapourisation and entropy of vapourisation have been calculated to be 63.66 kJmol⁻¹ and 127.07 Jmol⁻¹deg⁻¹ respectively [12]. The enthalpy of formation of RuF₅ was measured by direct combination of the elements in a combustion bomb calorimeter. The standard enthalpy of formation was calculated to be -213.41±0.35 kcalmol⁻¹ [13].

The magnetic moment, μ_{eff} of RuF₅ is between 3.3–3.6BM. After allowance for the Curie temperature, 34°C, the magnetic moment was calculated to be 3.83BM at 27°C.

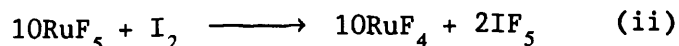
Chemical Properties

Dry RuF_5 can be stored and handled in glass at room temperature but attacks it slowly at 100°C and at 180°C reaction between RuF_5 and glass is fast, producing a black deposit and a red liquid [12]. RuF_5 is extremely sensitive to atmospheric moisture and rapidly blackens in its presence. With water, rapid hydrolysis occurs to produce a brown solution, a voluminous black precipitate of hydrated dioxide $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ and RuO_4 is evolved [11,12]. Treatment of the hydrolysis products with F_2 produces RuO_4 [14].

If RuF_5 is treated with a large excess of iodine at 150°C , iodine pentafluoride and ruthenium trifluoride are produced [15,16] (equation i).



When an excess of RuF_5 dissolved in pure IF_5 is allowed to react with I_2 , however, reduction takes place according to equation (ii):



Little heat is evolved and after IF_5 and the excess of RuF_5 are removed, a non volatile sandy yellow residue remains which is pure RuF_4 [17].

Ruthenium pentafluoride reacts with SF_4 to give a pink solid $\text{SF}_4 \cdot \text{RuF}_5$ which melts at 150°C to a red liquid [18]. By mixing solutions of RuF_5 and thallous fluoride both in SeF_4 , the thallous hexafluororuthenate (V), TlRuF_6 , is formed [11].

Xenon difluoride reacts with RuF_5 to produce three adducts (table 1.1.5). The adduct formed is dependent on the stoichiometry of the reagents [19,20].

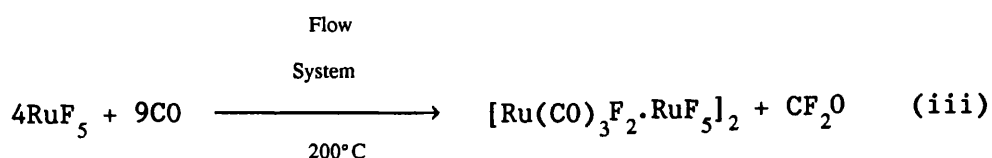
Table 1.1.5. XeF₂ Adducts of RuF₅

Adduct	Mpt. (°C)	Colour	Reference
XeF ₂ .RuF ₅	115-125	Pale yellow green	[19,20]
XeF ₂ .2RuF ₅	52-56	Bright green	[19,20]
2XeF ₂ .RuF ₅	98-99	Pale yellow green	[20]

The physical and spectroscopic properties of the XeF₂ adducts of RuF₅ show that all three have ionic structures XeF⁺RuF₆⁻, XeF⁺Ru₂F₁₁⁻, Xe₂F₃⁺RuF₆⁻ [20]. The adducts XeF⁺RuF₆⁻ and XeF⁺Ru₂F₁₁⁻ were prepared by melting stoichiometric amounts of XeF₂ and RuF₅ in a Pyrex reactor [19]. All three adducts were prepared by mixing stoichiometric amounts of XeF₂ and RuF₅ in BrF₅ [20]. Attempts to prepare and isolate XeF₄ adducts of RuF₅ have so far proven unsuccessful.

RuF₅ reacts with KrF₂ to form KrF₂.RuF₅ and KrF₂.2RuF₅ which, according to their Raman spectra, can be formulated KrF⁺RuF₆⁻ and KrF⁺Ru₂F₁₁⁻ respectively. These adducts are unstable in HF forming F₂, Kr and RuF₅, and also decompose in BrF₅ [21].

If carbon monoxide is passed over RuF₅ a yellow brown moisture-sensitive, non-volatile solid of composition [Ru(CO)₃F₂]₂ is formed [22] (equation iii);



Further reaction occurs at high pressure (100atms.) and 200°C to yield a pale involatile crystalline solid [Ru(CO)₃F₂]₄ which has a tetragonal unit cell of dimensions; *a* = 11.055Å, *c* = 9.376Å, [23]. The structure consists of tetrameric rings of Ru(CO)₃F₂ units. This compound can be compared with the compound reported in the work of Misra on IrF₅ [24].

Structure

RuF_5 was the first tetramer to be found with bent Ru-F-Ru bridges [25]. X-ray powder photographs show RuF_5 to be isostructural with OsF_5 [12], RhF_5 [74], IrF_5 [104], and PtF_5 . The structure, a distorted version of the MoF_5 structure [26], is monoclinic with dimensions $a=12.47\pm0.01$, $b=10.01\pm0.01$, $c=5.42\pm0.01\text{\AA}$, $\beta=90^\circ50'\pm30'$ belonging to the space group $P_1^2/a=C_{2h}^5$; $Z=8$ [25].

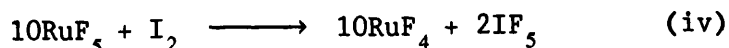
Mass Spectrometry

Using molecular beam mass spectrometry it has been shown that the vapour phase of RuF_5 is associated. Signals due to monomeric, dimeric, trimeric and tetrameric ions have been observed [27,28,60].

1.1.4 Ruthenium Tetrafluoride

Preparation

When an excess of RuF_5 , dissolved in pure iodine pentafluoride, is allowed to react with iodine, reduction takes place according to equation (iv):



Little heat is evolved and after the IF_5 and excess of RuF_5 have been removed, an involatile, sandy yellow residue remains which is pure RuF_4 [17].

Physical Properties

Magnetic properties of RuF_4 from -183 – 27°C have been studied. The observed effective magnetic moment at ordinary temperatures is higher than the spin only value for two unpaired electrons [17].

Chemical Properties

Ruthenium tetrafluoride is blackened immediately by moist air, but it can be conveniently handled in Pyrex glass apparatus under dry

conditions [17]. It reacts violently with water, depositing RuO_2 but no tetroxide is formed, as happens for RuF_5 [17]. Samples of RuF_5 heated to 280°C in Pyrex do not melt, but above 280°C they attack the glass, forming a volatile compound and a black residue which is probably RuO_2 [17].

Structure

Ruthenium tetrafluoride is poorly crystalline, but powder-diffraction photographs suggest that it has a simple structure [17].

1.1.5 Ruthenium Trifluoride

Preparation

Ruthenium trifluoride is prepared by the reduction of RuF_5 . The best route is the treatment of RuF_5 with a large excess of I_2 at 150°C . IF_5 is produced and the involatile RuF_3 is left [15]. This residue should then be heated to 500°C and pumped on for 12 hours to remove traces of I_2 , IF_5 or RuF_5 still present and to facilitate crystal growth [16]. RuF_5 can also be reduced by sulphur at temperatures above 200°C , [15] by passing it over Ru metal at elevated temperatures [29], and by perfluorocyclobutene in perfluoro-1,2 dimethyl cyclohexane at 70°C [29].

Appearance and Physical Properties

Ruthenium trifluoride is a dark brown solid which is visibly crystalline [15].

Chemical Properties

Ruthenium trifluoride is insoluble in water and dilute acids and alkalies, but is decomposed by boiling sulphuric or nitric acids [15].

Structure

Ruthenium trifluoride must be classed with VF_3 , FeF_3 and CoF_3 since the fluorine atom arrangement is distorted from a closed-packed

hexagonal arrangement. It is indexed on a bimolecular rhombohedral unit cell, but the unit cell dimensions vary depending on the conditions of the preparation (table 1.1.6) when prepared by the reduction of RuF_5 with I_2 or S.

Table 1.1.6 Cell Dimension for RuF_3

Method of preparation	a (Å)	α (°)	V (Å)
Excess of RuF_5	5.386	54.79	97.1
Excess of RuF_5	5.392	54.78	97.4
Small excess of I_2	5.403	54.67	97.7
Large excess of I_2	5.408	54.67	98.0
Large excess of S	5.407	54.66	97.9

When excess of reducing agent is used the unit cell values are at their greatest. It is thought unlikely that this is due to iodine or sulphur replacing fluorine as the elemental analysis shows only Ru and F and the variation is constant. This is probably the "ideal" RuF_3 . When a deficiency of reducing agent is present it is probable that a small proportion of the Ru atoms are not reduced to the trivalent state but remain in the tetra- or pentavalent state.

1.2. Osmium

1.2.1 Osmium Heptafluoride

Preparation

Osmium heptafluoride is reported to be prepared by the union of fluorine and osmium metal 500–600°C under a pressure of 400atms. in a nickel bomb [160]. Very recently, the existence of OsF_7 was independently verified when it was prepared by heating (250°C) OsO_3F_2 with elemental fluorine (30atm. pressure) for 72 hours [162].

Appearance and Physical Properties

Osmium heptafluoride is only stable under a high pressure of fluorine and above -100°C it dissociates to OsF_6 and F_2 . The magnetic moment at -183°C is about 1.08 BM [160].

Spectroscopy

The infrared spectrum shows bands at 715, 550, 483, 366, and 282cm^{-1} [160]. This was initially interpreted as showing a pentagonal pyramidal structure. However, recently an identical infrared spectrum was observed using the technique of matrix isolation [162]. This result has been interpreted as showing a capped trigonal prismatic structure. However, the structure appears to fluctuate even at 14K and, thus, no definite assignment can be made [162]. The mass spectrum shows the presence of the ions OsF_6^+ , OsF_5^+ , OsF_4^+ , OsF_3^+ , OsF_2^+ , Os^+ , [160].

1.2.2 Osmium Hexafluoride

Preparation

In 1913 Ruff and Tishirch reported the formation of OsF_4 , OsF_6 and OsF_8 by the direct fluorination of osmium powder at elevated temperatures [30]. The compound that they had identified as " OsF_8 " was later shown to be OsF_6 [31]. In this and all subsequent preparations OsF_6 is prepared by direct fluorination of osmium metal [32–38].

Weinstock and Malm [31-32] carried out their fluorinations in a flow system, passing fluorine at 250mmHg pressure over osmium powder heated in a Pyrex furnace. The OsF_6 was collected in cool traps and purified by vacuum distillation. Yields of 84-100% were reported. Similar methods were reported by Cady and Hargreaves [36] and by Hargreaves and Peacock [35]. Producing OsF_6 in a flow system remains the best synthetic route.

Other groups [33,34] carried out their fluorinations in static systems, heating the metal to 350-400°C with an excess of fluorine for 3 hours. In one instance [33] the metal was heated inductively in a hydrogen atmosphere prior to fluorination in order to reduce traces of oxide.

Appearance and Physical Properties

Osmium hexafluoride is a volatile yellow solid with a colourless vapour. Its melting point has been recorded as 32.1°C [31] and 33.4°C [36] and its boiling point as 45.9°C [31] and 47.5°C [36]. The latter value in each case is probably the more accurate due to improved manipulation and purification procedures. Both values of the boiling point were obtained by extrapolation of the vapour pressure measurements. Various thermodynamic values have been calculated [36] (table 1.2.1) from these vapour pressure measurements.

The magnetic behavior of OsF_6 has been measured over the temperature range -193 to 24°C. The results vary as expected for a sexivalent osmium with two unpaired spins. The magnetic moment follows the Curie-Weiss relationship (i):

$$\chi_A \propto 1/(T+\theta) \quad (i)$$

with the Curie-Weiss constant, θ , equal to 66°C [35]. The magnetic moment, μ_{eff} , is 1.50BM at 24°C.

The force constant of OsF_6 has been calculated to be 4.91md/Å [39]. The solubility of OsF_6 in HF has been determined to be 0.97 molg⁻¹ of HF and the electrical conductivity and Raman spectrum of the solution have been recorded [159].

Table 1.2.1. Thermodynamic Data for OsF₆ [36]

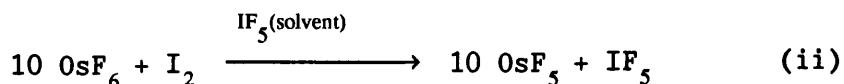
$\Delta_{\text{fus}} \text{ H}^\circ$	(306.6K)	=7.36)
$\Delta_{\text{trs}} \text{ H}^\circ$	(272.8K)	=8.23	
$\Delta_{\text{vap}} \text{ H}^\circ$	(320.7K)	=28.1) kJmol ⁻¹
$\Delta_{\text{sub}} \text{ H}^\circ$	(>272.8K, cubic → pfg)	=35.4	
$\Delta_{\text{sub}} \text{ H}^\circ$	(<272.8K, orthorhombic → pfg)	=43.7)
$\Delta_{\text{fus}} \text{ H}^\circ$	(306.6K)	=23.90)
$\Delta_{\text{trs}} \text{ H}^\circ$	(272.8K)	=30.10) Jmol ⁻¹ deg ⁻¹
$\Delta_{\text{vap}} \text{ H}^\circ$	(320.7K)	=87.8)

Chemical Properties

Oxidation-reduction reactions of OsF_6 with selected reductants have been studied [40]. The reductant, if gaseous, is condensed on to the OsF_6 at -196°C . For solid reductants the reverse occurs, the OsF_6 being condensed on to the reductant. The mixture is then allowed to warm to room temperature. The reaction products are shown in table 1.2.2 and a general trend is observed, the hexafluoride being reduced to either the penta- or tetravalent state and the reductant being oxidised to a higher fluoride. The isolated product of the reduction of OsF_6 is rarely a simple fluoride, it is usually an adduct or complex.

OsF_6 reacts with OsO_4 at 150°C to produce OsO_2F_3 [149], and undergoes oxygen-fluorine exchange with boric acid to form OsOF_4 and BF_3 [40]. The halogen exchange reactions of OsF_6 with BCl_3 , BBr_3 , BI_3 and CCl_4 have been studied [7,34]. The reaction of OsF_6 with BCl_3 produces a binary chloride, OsCl_5 , whereas the other reagents produce mixed halides. The reaction of BBr_3 and OsF_5 produce the stoichiometric mixed halide, $\text{Os}_2\text{Br}_4\text{F}_5$, but neither BI_3 or CCl_3 produce stoichiometric mixed halides. All of these reactions are very exothermic and are, therefore, carried out at low temperatures in the presence of an inert solvent. Usually an n-perfluoroalkane is used to dissipate the thermal energy. The compound, OsBrF_5 , has been isolated and characterised by infrared and u.v. spectroscopy, X-ray methods and magnetic measurements. It is known to be polymeric.

Tungsten carbonyl reacts vigorously with an excess of OsF_6 at 0°C , carbon monoxide is evolved and a green suspension is observed below a green liquid. Once the excess of OsF_6 and WF_6 (produced during the reaction) are pumped away, a grey-green mixture of OsF_5 , OsF_4 and osmium metal is produced [43]. This mixture can be separated by vacuum distillation. Osmium hexafluoride is also reduced to OsF_5 by iodine in IF_5 (equation ii):



For a clean reaction OsF_6 must be in excess because, if an excess of I_2 is present, a black compound of composition OsIF_4 is produced.

Table 1.2.2 Redox reactions of OsF₆

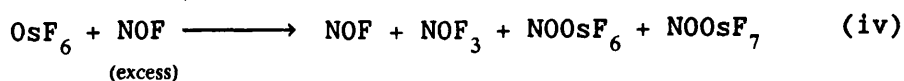
Reagent	Product	Ref.
PF ₃	Os, PF ₅ ^a [40]	
PF ₃ /AHF	Os(PF ₃) ₂ F ₄ , PF ₅ [40]	
AsF ₃	AsF ₃ ·OsF ₅ , AsF ₅ [40]	
SbF ₃	no reaction ^b [40]	
SF ₄	SF ₄ ·OsF ₅ , SF ₆ [41]	
SeF ₄	SeF ₄ ·OsF ₅ , SeF ₆ [42]	
CS ₂	CF ₄ , SF ₄ [40]	
H ₂ (100°C)	Os, HF [40]	
H ₂ /AHF	OsF ₅ [40]	
Metal/AHF	OsF ₅ [40]	
Metal/AHF/KF	KOsF ₅ [40]	

a: Other unidentified Os-containing compounds.

b: No reaction at room temperature or on heating to 100°C.

When OsF_6 is placed in an evacuated glass vessel filled with Pyrex wool and kept at 25°C for two days, very little reaction occurs, but when the temperature is raised to 80°C , OsF_6 immediately reacts with the moisture on the glass to produce a yellow solid OsOF_4 [44]. Hydrolysis of OsF_6 in HF also leads to the formation of OsOF_4 [45].

Various groups have investigated the reaction of OsF_6 with NO and NOF [6,41,46,48,50] and all are in close agreement (equations iii and iv).



The reaction of OsF_6 with NOF (equation iv) is complex. The quantities of NOF_3 formed indicate the existence of an unstable fluorine intermediate, since, NOF_3 is not produced from NOF and O_2 . The compounds NOOsF_6 and NOOsF_7 are also produced, both of which have a cubic unit cell with values of a being 10.126 and 5.14 Å respectively [46,48]. Raman spectra of NOOsF_6 (table 1.2.3) show this compound to be $\text{NO}^+\text{OsF}_6^-$ [6].

Table 1.2.3 Raman Data for NOOsF_6 (cm^{-1})

Species	OsF_6^-			NO^+
Designation	ν_1	ν_2	ν_3	ν
Symmetry Species	(A_{1g})	(E_g)	(F_{2g})	
Ref. [4]	688	623 605	261 247	2334
Ref. [47]	691	624 606	262	

Structure

X-ray diffraction studies [8,31,48] have shown OsF_6 to exhibit two crystalline forms, a cubic modification near room temperature, with $a=6.23\text{\AA}$ and $Z=2$ and a low-temperature orthorhombic modification with $a=9.59$, $b=8.75$ and $c=5.04\text{\AA}$, $Z=4$. The transition temperature has been reported to be 1.4°C at atmospheric pressure [31,48].

The ^{19}F nuclear magnetic resonance spectra and spin relaxation times of OsF_6 show tetragonal distortion of the hexafluoride octahedra at low temperatures as would be expected for an orthorhombic cell.

Spectroscopy

The infrared and Raman spectra of OsF_6 have been recorded [31,37,49,51,52,53,54]. As expected for an octahedral molecule of O_h symmetry there are two infrared active fundamentals ν_3 and ν_4 , three Raman active fundamentals ν_1 , ν_2 and ν_5 and one inactive fundamental ν_6 . In the infrared spectrum several combination bands are also observed and from these the other fundamentals have been calculated. A list of fundamentals determined by various groups is given in table 1.2.4.

A typical infrared spectrum was recorded by Weinstock, Claassen and Malm [51] who observed peaks due to fundamentals at 720 (ν_3) and 268 (ν_4) cm^{-1} and combination bands at 1453 ($\nu_1+\nu_3$) and 1352 ($\nu_2+\nu_3$) cm^{-1} . Claassen and Selig [54] observed a typical Raman spectra, with peaks being recorded at 730.7 (ν_1), 643 (ν_2) and 272 (ν_5) cm^{-1} , ν_1 being the most intense.

The infrared spectrum of OsF_6 differs from those of other P.G.M. hexafluorides; the band due to $(\nu_2+\nu_6)$ is missing, $(\nu_2+\nu_4)$ is weak and $(\nu_2+\nu_3)$, although intense, is very broad. This broadening of the $(\nu_2+\nu_3)$ mode is of particular interest because a characteristic feature of the infrared spectra of the P.G.M. hexafluorides is that $(\nu_1+\nu_3)$ and $(\nu_2+\nu_3)$ are almost identical in shape and intensity. In the Raman spectrum ν_2 was not observed under conditions where ν_1 and ν_5 were clearly visible. This behaviour of

Table 1.2.4 Fundamental Vibrational Frequencies for OsF₆

Designation	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
Symmetry Species	A_{1g}	E_g	F_{1u}	F_{1u}	F_{2g}	F_{2u}
Spectral Activity	Raman Pol	Raman de-pol	i.r.	i.r.	Raman Pol	inactive
Ref. [51]	(733)	(632)	720	268	(252)	(230)
[49]	732	640	---	---	---	---
[52]	(733)	(632)	720	---	(249)	---
[53]	(733)	(668)	720	272	(276)	(205)
[54]	730.7	643	---	---	272	---
[55]	730.7	(668)	720	268	(276)	(205)

ν_2 and its combination bands is a consequence of the Jahn-Teller effect [157].

U.v.-visible spectrum of OsF_6 has been recorded in the gas phase, [56] and when isolated in a nitrogen matrix [57], table 1.2.5 shows the values observed and their assignment.

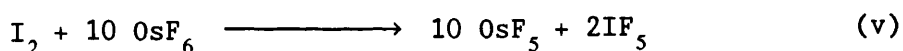
These two data sets differ significantly. The peak at $40,800\text{ cm}^{-1}$ is probably due to OsO_4 [163] which is a persistent impurity in OsF_6 , and the peak at $35,700\text{ cm}^{-1}$ is a composite of the second OsO_4 band at *ca.* $35,000\text{ cm}^{-1}$ and the genuine OsF_6 band at $36,200\text{ cm}^{-1}$.

Electron diffraction experiments show good evidence for the symmetrical octahedral structure of OsF_6 . From this study the Os-F bond length was calculated to be 1.831 \AA [58]. Further evidence for the octahedral structure of OsF_6 is produced by electron diffraction experiments [33] in that a molecular beam of OsF_6 was not defocused when an electric quadropole field was applied.

1.2.3 Osmium Pentafluoride

Preparation

The best preparative route for OsF_5 appears to be the reaction of OsF_6 with iodine pentafluoride [59,43] (equation v).

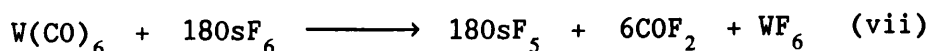
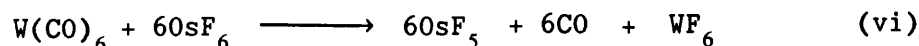


It is essential that the hexafluoride is present in excess to prevent the formation of osmium iodotetrafluoride.

Hargreaves and Peacock [43] investigated two other possible preparations : firstly, the reaction of OsF_6 with hexacarbonyl tungsten [59,43,60,61] where presumably either tungsten is oxidised to WF_6 (equation vi) or the CO is oxidised to COF_2 and the tungsten to WF_6 (equation vii). There is also the possibility that a carbonyl fluoride may form which ultimately decomposes. It is known for example that $[\text{Os}(\text{CO})_3\text{F}_2]_4$ exists [21]. Secondly, the irradiation of OsF_6 with u.v. light at 25°C also yields OsF_5 (equation viii)

Table 1.2.5 Ultra violet-visible Spectra of OsF₆

Gas Phase [56]	Matrix Isolated [57]	Assignment
	> 51,000	$\Pi(F) \longrightarrow t_{2g}(0s)$
	45,435 (630)	$\Pi(F) \longrightarrow t_{2g}(0s)$
40,800		see text
	36,230 (660)	$\Pi(F) \longrightarrow t_{2g}(0s)$
35,700		see text
17,300	17,340	${}^3T_{1g}(\Gamma_3) \longrightarrow {}^1A_{1g}$
8,500		${}^3T_{1g}(\Gamma_3) \longrightarrow {}^1T_{2g}, {}^1E_g$
4,300		${}^3T_{1g}(\Gamma_3) \longrightarrow {}^3T_{1g}(\Gamma_4, \Gamma_1)$
3,930		Hot Band ?
(E max/cm ⁻¹ and Δν/cm ⁻¹)		



Osmium pentafluoride can also be produced by the reduction of OsF_6 vapour on a hot tungsten filament [62]. The reaction temperature is controlled by immersion in an ethylenedichloride slush (-36°C) to provide a vapour pressure of OsF_6 in the 10-20 mmHg range. Small amounts of tungsten fluorides are found in the product.

In another preparation of OsF_5 , O'Donnell and Peel [63] condensed OsF_6 onto a frozen sample of HF containing NaF and Hg. On melting, a rapid reaction occurred producing a colourless solution of NaOsF_6 and a precipitate of Hg_2F_2 . The NaOsF_6 was decanted into an empty tube and stoichiometric amounts of SbF_5 were added. After standing at room temperature for one hour the HF was distilled off and the tube warmed to 85°C . A blue-grey sublimate formed on the upper portion of the tube which was cooled to -80°C .

Paine and Asprey have prepared OsF_5 by simple one-electron reduction reaction of OsF_6 using either silicon powder or hydrogen [64,65,66]. The OsF_6 in anhydrous HF was condensed on to silicon powder in anhydrous HF. The mixture was then allowed to warm to room temperature and stirred. The reaction was assumed to be complete when the silicon powder disappeared. Vacuum distillation of the volatile products (HF and SiF_4) left OsF_5 . A similar one electron redox reaction occurs with hydrogen. Osmium hexafluoride and anhydrous HF are combined with H_2 , which is admitted to the solution at room temperature while the mixture is stirred slowly. The OsF_6 is reduced over one or two days. The reaction rate can be enhanced by the presence of platinum gauze and u.v. irradiation so that the reaction is complete in 3-4 hours. This reaction can also be carried out in the gas phase without HF but the rate is much slower.

Xenon difluoride dissolved in anhydrous HF is a moderately

strong oxidant which can be used to prepare fluorine-containing compounds [67]. It will react with either osmium metal or OsBr_3 to produce OsF_6 and OsF_5 . However, the reaction is complex because the OsF_5 forms an adduct with XeF_2 and this $\text{OsF}_5 \cdot \text{XeF}_2$ adduct is observed in the HF solution. On removal of volatile materials there is also evidence of OsF_6 and $\text{OsF}_5 \cdot 2\text{XeF}_2$. Thus, unlike the case of Ir, where IrF_5 is produced, this is not a valid method for the production of OsF_5 .

Physical Properties

Osmium pentafluoride is a blue-grey crystalline solid which melts at 70°C to a green viscous liquid. This does not easily recrystallize when cooled below its melting point. Liquid OsF_5 changes colour reversibly as it is heated. At its boiling point (233°C by direct measurement, 225.5°C by extrapolation of vapour pressure measurements) it is bright blue and gives a colourless vapour [43,59,64]. It has been reported that at 180°C , OsF_5 disproportionates to give OsF_6 and OsF_4 but, as yet, this has not been verified by an independent investigation [61].

The enthalpy and the entropy of vapourization of OsF_5 have been calculated to be 65.61 kJmol^{-1} and $143.9 \text{ Jmol}^{-1}\text{deg}^{-1}$ respectively [61].

The magnetic moment, μ_{eff} , of OsF_5 is 2.31BM at room temperature. This value is much smaller than that required for three unpaired electrons (3.88BM) and so is indicative that the compound is not a simple five covalent structure.

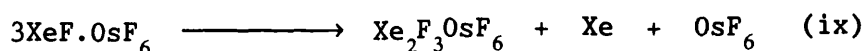
Chemical Properties

OsF_5 can be handled in glass if it is rigorously dry, but it is very sensitive to moisture and blackens rapidly, evolving OsO_4 in its presence. In water it dissolves exothermically forming a brown solution in which some of the fluorine is retained as a complex fluoro-ion; a black precipitate of hydrated OsO_2 is formed and OsO_4 is evolved [43].

Osmium pentafluoride is soluble in anhydrous HF [65,68]. It has

a higher Lewis acidity than the pentafluorides of rhenium, tantalum, molybdenum or niobium, but no $[\text{OsF}_6]^-$ ions were detected in the solution by Raman spectroscopy [68]. If OsF_5 is allowed to stand for more than one week as a powder it is difficult to dissolve it in anhydrous HF [65] this is probably due to the formation of lower fluorides, oxides or oxide fluorides on the surface.

Xenon difluoride in BrF_5 as a solvent will react with OsF_5 to produce two adducts $\text{XeF}_2 \cdot \text{OsF}_5$ and $2\text{XeF}_2 \cdot \text{OsF}_5$ [5,6]. These have been shown by Raman spectroscopy, to have ionic character associated with the ionic formulation $\text{XeF}^+ \text{OsF}_6^-$ and $\text{Xe}_2\text{F}_3^+ \text{OsF}_6^-$, the XeF^+ ion being characterized by a doublet in the $600\text{--}612\text{ cm}^{-1}$ region and Xe_2F_3^+ ion by strong bands at *ca.* 575 and 591 cm^{-1} (stretch) and 160 cm^{-1} (bend) [20]. All XeF^+ species are thermally stable except $\text{XeF}^+ \text{OsF}_6^-$ which decomposes at 20°C (equation ix).



Holloway and Knowles [19] studied the direct reaction of XeF_2 and OsF_5 . They also found the reaction to be complex. The adduct $\text{XeF}_2 \cdot \text{OsF}_5$ was isolated but was found to decompose readily at room temperature evolving OsF_6 and Xe and leaving a dark brown residue which was presumably $\text{Xe}_2\text{F}_3^+ \text{OsF}_6^-$.

Structure

From its X-ray powder diffraction pattern OsF_5 has been shown to be isostructural with RuF_5 [25]. It is now known, also to be isostructural with IrF_5 , RhF_5 and PtF_5 [70]. All these pentafluorides possess crystal structures containing tetrameric units in which the metal atoms lie at the corners of a rhombus, with nonlinear bridging fluorine atoms. The fluorine atoms are arranged about the metal atom in a distorted octahedral arrangement and are nearly hexagonal close packed. From the single crystal study [59] it is evident that OsF_5 has a monoclinic cell with $a=5.53 \pm 0.03\text{\AA}$, $b=9.91 \pm 0.10\text{\AA}$, $c=12.59 \pm 0.15\text{\AA}$, $\beta=99^\circ 30' \pm 20'$ and $Z=8$. The space group is $\text{P2}_1/\text{c}$.

Spectroscopy and Mass Spectrometry

The infrared spectra of a thin film of OsF_5 at -196°C [65] and of a nujol mull of OsF_5 at room temperature [4] have been recorded. The data is shown in table 1.2.6 but the peaks have not been assigned.

Table 1.2.6 Infrared bands of OsF_5 (cm^{-1})

Nujol Mull	710	690	655	530	Ref.[64]
Thin film	712	691	657	530	Ref.[65]

The peak at 530 cm^{-1} is probably due to the bridging F.

The mass spectrum of OsF_5 vapour has been recorded [27,28,62]. Peaks due to monomeric, dimeric and trimeric species have been observed. It has been shown [62] that when the source temperature is raised a decrease in the intensity of the dimer and trimer relative to the monomer results. The extent of the association of the neutral species is difficult to ascertain quantitatively because of fragmentation caused by electron impact ionisation.

1.2.4 Osmium Tetrafluoride

Osmium tetrafluoride is best prepared by the reduction of OsF_5 dissolved in AHF using H_2 . The solution is stirred in the presence of platinum gauze, irradiated by u.v.light and heated to 50°C . The OsF_4 precipitates from the solution [65]. The same reaction can be carried out using OsF_6 in place of OsF_5 but in this case there is a risk of producing a mixed-valent product [65].

A small amount of OsF_4 , mixed with metallic osmium is left behind when the residue from the osmium hexafluoride-tungsten carbonyl reaction is warmed to 120°C under a good vacuum to remove OsF_5 . When the temperature is raised to $280\text{--}300^\circ\text{C}$ the OsF_4 distills as a viscous yellow liquid [43].

Appearance and Physical Properties

Osmium tetrafluoride is a yellow-brown solid which melts at about 230°C [43,65].

Chemical Properties

Osmium tetrafluoride is very sensitive to moisture. It dissolves in water to give a clear yellow solution [43,65].

Spectroscopy and Mass Spectrometry

The mass spectrum of OsF_4 shows peaks due to monomeric, dimeric and trimeric species. This would appear to suggest that in the vapour phase OsF_4 is polymeric. However, since there is a peak due to MF_5^+ reported it seems probable that some OsF_5 may be present as an impurity [65], or that the OsF_4 is disproportionating to OsF_5 and OsF_3 .

The infrared spectrum of OsF_4 has been recorded, peaks are reported at 719, 702, 660 and 535 cm^{-1} but no assignment has been made [65].

1.3 Rhodium

1.3.1 Rhodium Hexafluoride

Preparation

Rhodium hexafluoride has only been prepared by burning a rhodium wire in a fluorine atmosphere in a quartz reactor cooled by liquid nitrogen [33,71]. Unfortunately, yields are low, since, the wire once ignited tends to extinguish itself and cannot be reignited once the circuit is open.

Appearance and Physical Properties

Rhodium hexafluoride is a very dark red-brown solid which appears almost black in bulk. The vapour is red-brown and its vapour pressure at various temperatures has been recorded [71] (table 1.3.1).

Table 1.3.1. Vapour Pressure of Rhodium Hexafluoride

Temperature (°C)	0	5	11	16	20
Pressure (mm)	15	19	29	40	49.5

Like all other P.G.M. hexafluorides, RhF_6 undergoes a solid-solid transition, the transition temperature being about 7°C at atmospheric pressure. The triple point of RhF_6 is 70°C at atmospheric pressure [71].

Chemical Properties

Rhodium hexafluoride is the most reactive of all the platinum group metal hexafluorides. It is also thermally unstable, decomposing to fluorine and lower fluorides at room temperature [71]. The hydrolysis of RhF_6 in HF has been studied, the RhF_6 being condensed onto HF (containing traces of water) at -196°C. As the mixture is allowed to warm to room temperature the dark red colour of the hexafluoride

disappears and a yellow-green solution results. After removal of the HF at -78°C a yellow solution remains, however, this solution darkens rapidly and has not been characterised [5].

Rhodium hexafluoride does not appear to oxidise krypton but it does oxidise xenon [72]. The reaction product has a composition close to XeRhF_6 with a combining ratio $\text{Xe}:\text{RhF}_6$ of 1:1.05. From the X-ray diffraction patterns very faint sharp lines indicate that $\text{XeF}^+\text{RhF}_6^-$ is present as a minor component. This suggests that an excess of RhF_6 , like PtF_6 interacts with Xe^+ to produce XeF^+ [48].

When RhF_6 reacts with an excess of NOF and F_2 at 25°C , NORhF_6 is formed and when it reacts with an excess of NOF, $(\text{NO})_2\text{RhF}_6$ is produced [6]. Both products have been studied using Raman spectroscopy and the results are shown in table 1.3.2.

Table 1.3.2: Raman Data for NORhF_6 and $(\text{NO})_2\text{RhF}_6$.

NORhF_6	$\nu_1(\text{A}_{1g})$	$\nu_2(\text{E}_g)$	$\nu_3(\text{f}_{2g})$	$\nu(\text{NO}^+)$
	632	554	262	2338
			248	
$(\text{NO})_2\text{RhF}_6$	$\nu_1(\text{A}_{1g})$	$\nu_2(\text{E}_{2g})$	$\nu_3(\text{f}_{2g})$	$\nu(\text{NO}^+)$
	292	500	242	2312
		480		

Structure

From X-ray diffraction studies [8,71] it is known that RhF_6 has a cubic form at room temperature with, $a=6.13\pm 0.02\text{\AA}$, $Z=2$, and a calculated density of $3.13\pm 0.03\text{gcm}^{-3}$. At lower temperatures RhF_6 has an orthorhombic modification and at -23°C , $a=9.40$, $b=8.54$, $c=4.96\pm 0.02\text{\AA}$, $Z=4$ and the density is calculated to be $3.62\pm 0.03\text{gcm}^{-3}$ [8]. The transition temperature is about 7°C but, because of the high reactivity of RhF_6 , this value is only approximate [71].

Spectroscopy

The infrared spectrum of RhF_6 can be interpreted in terms of a regular octahedral structure with point group O_h [53,71,73]. Two intense bands due to ν_3 and ν_4 are observed at 722 and 283.5 cm^{-1} respectively. Combination bands are also observed, the two strongest ($\nu_2+\nu_3$) and ($\nu_1+\nu_3$) are reported at 1314 and 1358 cm^{-1} respectively, from these the other fundamentals are calculated. The six fundamentals of RhF_6 are shown in table 1.3.3.

Table 1.3.3. Fundamental Vibrations of RhF_6

ν_1 (A_{1g})	ν_2 (E_g)	ν_3 (F_{1u})	ν_4 (F_{1u})	ν_5 (F_{2g})	ν_6 (F_{1u})	Ref.
634	595	724	283	269	192	[73]
634	592	724	283	269	189	[53]

The deflection of a molecular beam in an electric quadrupole field has been studied. No refocusing of the molecular beam was observed when an electric field was applied. This is characteristic of a nonpolar molecule and supports the assignment of octahedral structure [33].

1.3.2 Rhodium Pentafluoride

Preparation

The best known method of preparation of RhF_5 is the fluorination of rhodium sponge with gaseous fluorine (6 atms. pressure) at 400°C for 12 hours [60,74]. It is also produced from the combination of a rhodium wire in a fluorine atmosphere [75] or from RhF_3 and fluorine at high pressures [76].

Appearance and Physical Properties

Rhodium Pentafluoride is a dark red solid with a melting point of $95.5 \pm 0.5^\circ\text{C}$. It is paramagnetic and its magnetic properties are consistent with the d^4 non-bonding electron configuration expected for

Rh(V) [74,76]. The magnetic susceptibility is temperature dependent, this may be due to a distortion of the octahedra [77]. At 20°C the effective magnetic susceptibility, μ_{eff} , is 2.93BM. Theoretical calculations of the enthalpy and entropy of RhF_5 have been made but further independent verification is required.

Chemical Properties

Rhodium Pentafluoride is a powerful oxidizing and fluorinating agent. It reacts violently with water to yield an ozone like smelling gas and it fluorinates carbon tetrachloride, chlorine monofluoride being among the products [74]. Caesium fluoride and RhF_5 in a 1:1 stoichiometry react in iodine pentafluoride solution to yield caesium hexafluororhodate V [74]. This brown solid is isomorphous and almost isostructural with CsPtF_6 [72].

Structure

The crystal structure of RhF_5 has been determined by three dimensional X-ray data. The unit cell is monoclinic, $P2_1/a$, with $a=12.3376(13)$, $b=9.9173(8)$, $c=5.5173(6)\text{\AA}$, $\beta=100.42(2)^\circ$, $V=663.85\text{\AA}^3$, $Z=8$ and the calculated density $D=3.95\text{ g cm}^{-3}$. The structural unit is a fluorine-bridged tetramer similar to that reported for RuF_5 , OsF_5 , IrF_5 and PtF_5 . Each rhodium atom is coordinated by six fluorine atoms in an approximately octahedral arrangement. Each of the *cis* pairs of F-atoms in the RhF_6 group is shared with another Rh-atom the Rh-F-Rh angle being $135\pm 1^\circ$ [74,78]. The ^{19}F n.m.r. of RhF_5 has been recorded. A triplet with intensities 1:2:2 suggests that at low temperatures the compound is composed of polymers with M-F-M bridge bonds arranged *cis* to one another [79].

Mass Spectrometry

The mass spectrum of RhF_5 has been recorded [27,28,60]. Signals due to monomeric, dimeric, trimeric and tetrameric species have been observed. However, the extent of the association of the neutral species is difficult to ascertain because of fragmentation caused by electron impact ionisation.

1.3.3 Rhodium Tetrafluoride

Preparation

The fluorination of RhF_3 at 250°C for several days with a slight excess of elemental fluorine in a Teflon-gasketed Monel reactor yields a sandy-brown solid, which has been identified as RhF_4 [80]. This is the only known route to pure RhF_4 . However, it has been reported that RhF_4 can be produced by the fluorination of RhBr_3 using BrF_3 as the fluorinating agent [81] and if $\text{Rh}(\text{OH})_3$ is dissolved in hydrobromic acid and the product is then treated with BrF_3 , RhF_4 is produced [82]. However, the product of the latter two cases is a purple-red solid, due to traces of bromine which are always found as an impurity.

Appearance and Physical Properties

Pure RhF_4 is a sandy brown solid [80] although it is usually reported as being a purple-red solid due to the presence of bromine as an impurity [81,82]. The magnetic moment, μ_{eff} , of RhF_4 at 20°C is 1.1BM [83].

Kundsen cell mass spectrometry has been used to investigate ion-molecular equilibria in the gas phase of the RhF_4 system. This has led to the calculation of the electron affinity, E_a , which has been found to be $482 \pm 19 \text{ kJmol}^{-1}$ [84].

Chemical Properties

The RhF_4 used in most of the following work, will have contained small traces of bromine which may affect the chemistry. Rhodium tetrafluoride is hydrolysed in moist air liberating an ozone smelling gas [80]. It decomposes in water giving a blue solution and depositing an olive green precipitate of hydrated dioxide [82]. Hydrochloric acid is oxidised by RhF_4 to chlorine, and RhCl_4 is produced [82]. In a similar reaction, iodine is liberated from KI solution, and a black precipitate of rhodium triiodide is formed [82]. When dissolved in BrF_3 , RhF_4 reacts with sodium fluoride to form a complex of unknown composition [82].

Attempts have been made to reduce RhF_4 with SeF_4 , this led to the isolation of a pink complex, $(\text{RhF}_4)_2\text{SeF}_4$, which undergoes thermal decomposition to form a dark-coloured mixture of RhF_3 and rhodium metal [81].

Structure

Rhodium tetrafluoride is isostructural with PtF_4 , IrF_4 and PdF_4 the unit cell is orthorhombic with $a=9.71(2)$, $b=9.05(2)$, $c=5.63(1)\text{\AA}$ and $Z=8$. Of the six fluorine atoms coordinated to each metal atom, four are shared 1:1 with four other octahedra. Thus, the stoichiometric requirement (MF_4) is fulfilled as each metal atom is uniquely coordinated to two fluorine atoms and has a half share in four others. The unique fluorine ligands are *cis* to one another. The M-F-M angle is, ideally, 135° [80].

1.3.4 Rhodium Trifluoride

Preparation

A detailed study of the preparation of RhF_3 by the fluorination of RhCl_3 or Rh metal using either elemental fluorine or ClF_3 as the fluorinating agent has been carried out. The results are shown in table 1.3.4 [84].

Table 1.3.4. Study of methods of Preparing RhF_3 .

Starting Material	Fluorination Agent	Temp. ($^\circ\text{C}$)	Time (hrs.)	$\frac{n(\text{Rh})}{n(\text{F})}$	X-ray Phase Analysis
Rh	F_2	320	24	2.97	RhF_3
RhCl_3	F_2	360	5	2.99	RhF_3
Rh	ClF_3	160	8	1.00	$\text{Rh}+\text{RhF}_3$
Rh	ClF_3	345	8	2.91	RhF_3
RhCl_3	ClF_3	350	6	2.94	RhF_3

It was concluded from these results that fluorination of RhCl_3 by elemental fluorine was the best synthetic route. A related method of preparation is the fluorination of RhI_3 at about 400°C using elemental

fluorine [16]. Jesse and Hoppe also prepared RhF_4 from Rh powder and fluorine. The reaction was carried out at 550°C but took 24 hours for completion [85]. The nonahydrate and the hexahydrate of RhF_3 have also been prepared [86,87] but, no details will be given here.

Physical Properties

The saturated vapour pressure and heat of sublimation of RhF_3 have been determined by high temperature mass spectrometry to be 1.87 Pa and $327.6 \pm 7.9 \text{ kJmol}^{-1}$ respectively [88].

Structure

Conflicting interpretation of the structural data on RhF_3 were published by the earliest workers in this area. Some [89,90] considered " RhF_3 " to be a rhombohedrally distorted ReO_2 structure with a unimolecular cell, and thus isostructural with FeF_3 and CoF_3 . Others [91,92] claimed that the structure was similar to that of AlF_3 , with a bimolecular unit cell. Later, quantitative X-ray investigations were carried out [16] and these showed that RhF_3 should be indexed on a bimolecular rhombohedral unit cell with $a = 5.330 \pm 0.001 \text{ \AA}$, $\alpha = 54.42 \pm 0.01^\circ$. It is not isostructural with FeF_3 or CoF_3 but has a closest packed hexagonal fluorine atom arrangement, (as do IrF_3 and PdF_3) successive close packed planes being compressed along the trigonal axis.

Mass spectrometry

The mass spectrum of RhF_3 has been recorded and the results are shown in table 1.3.5 [84].

Table 1.3.5. Relative intensities of Ions formed from RhF_3 .

Ion	RhF_3^+	RhF_2^+	RhF^+	Rh^+
Rel.Intensity	21	100	88	92

1.4. Iridium

1.4.1 Iridium Hexafluoride

Preparation

Iridium hexafluoride is always prepared by the direct fluorination of iridium sponge [33,36,58,93-96]. However, the conditions employed vary greatly. The best preparation involves the passage of a F_2/N_2 mixture over the iridium sponge held in an alumina boat and heated to 300-400°C [95]. The yellow hexafluoride is collected in a Pyrex trap at -65°C and is purified by trap to trap distillation under vacuum. It has also been prepared in a static system where iridium powder is heated (300°C) for 3 hours in an excess of fluorine at 20 atms.[33].

Appearance and Physical Properties

Iridium hexafluoride is a bright yellow volatile solid at room temperature. It has a melting point of 44°C and a boiling point of 53°C. The vapour is deep yellow and stable to red heat [95]. The magnetic moment of IrF_6 at room temperature is 3.3BM [95]. This value indicates that the fluorine atoms are octahedrally coordinated about the iridium. The variation of the magnetic susceptibility of IrF_6 with temperature has been shown to obey the Curie-Weiss law with a Weiss constant, θ , of 30° and a magnetic moment at 27°C approximately equal to 2.90BM [97]. However, due to the scattering of the data, the accuracy of this result is uncertain.

Cady and Hargreaves [36] studied the vapour pressure of IrF_6 by a static method using a diaphragm gauge of high sensitivity. They found a solid-solid phase transition at 0.4°C and 61.7mmHg pressure, and calculated the following thermodynamic data (table 1.4.1.). The triple point occurs at 43.8°C and 518.8 mmHg.

Charge transfer transitions are reported for IrF_6 with Xe [98]. Based on this spectroscopic data, estimates of the electron affinity (Ea = 7.84eV) have been made. The electron affinity has also been

Table 1.4.1 Thermodynamic Data for IrF₆ [36]

$\Delta_{\text{fus}} \text{ H}^\circ$	(317.0K)	4.97)
$\Delta_{\text{trs}} \text{ H}^\circ$	(273.6K)	7.11	
$\Delta_{\text{vap}} \text{ H}^\circ$	(326.8K)	30.85) kJmol ⁻¹
$\Delta_{\text{sub}} \text{ H}^\circ$	(>272K, cubic \longrightarrow pfg)	35.82	
$\Delta_{\text{sub}} \text{ H}^\circ$	(<272K, orthorhombic \longrightarrow pfg)	42.93)
$\Delta_{\text{fus}} \text{ S}^\circ$	(317.0K)	15.63)
$\Delta_{\text{trs}} \text{ S}^\circ$	(273.6K)	25.96) Jmol ⁻¹ deg ⁻¹
$\Delta_{\text{vap}} \text{ S}^\circ$	(326.8K)	94.47)

estimated using values for collision ionisation energy between fast alkali atoms and IrF_6 . The value using this method is $\geq 5.14\text{eV}$ [99] which is in line with the spectroscopic value. The force constant for IrF_6 has been calculated to be $4.85\text{md}/\text{\AA}$ [39].

Chemical Properties

Iridium hexafluoride is extremely reactive and behaves as a strong fluorinating agent. Most of the reactions of IrF_6 , therefore, result in its reduction to a lower valency state. Several examples of such reactions are shown in table 1.4.2. In each of these cases IrF_6 is condensed on to the reactant at -196°C and the reaction mixture is allowed to warm to room temperature [42,95,100,101]. The reaction of PF_3 and IrF_6 is extremely exothermic, causing the reduction of IrF_6 to iridium metal [100]. However, if the reaction is carried out in anhydrous hydrogen fluoride at low temperature IrF_4 and PF_5 are produced.

Other, less well documented reactions, include the reactions of IrF_6 with either $\text{SO}_3(\text{liq})$ or PCl_3 [95]. The former produces a dark blue solid which has the approximate composition $\text{IrF}_4.3\text{SO}_2$ and the latter produces a dark green solid of variable and uncertain composition.

IrF_6 is rapidly hydrolysed by water, evolving ozone, and it is also known to attack moist glass [95]. Hydrolysis of IrF_6 in HF results in the formation of the oxonium salt $[\text{H}_3\text{O}^+\text{IrF}_6^-]$ [5]. In the presence of u.v. light IrF_6 is slowly photolysed to IrF_5 [95].

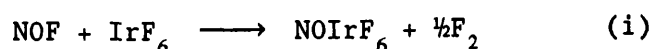
Several groups have examined the reactions of IrF_6 with NO , N_2O_4 , NOF and NO_2F [46,48,95,102]. At 20°C , IrF_6 reacts with NO to produce $(\text{NO})_2\text{IrF}_6$ and NOIrF_6 . This reaction is spontaneous and occurs if the ratio of $\text{IrF}_6:\text{NO}$ is 1:1 or if there is an excess of NO [46]. $(\text{NO})_2\text{IrF}_6$ is a pale yellow solid [95] and has a hexagonal unit cell $a=10.01\text{\AA}$, $c=3.53\text{\AA}$ [48]. With N_2O_4 the white solid, $(\text{NO}_2)_2\text{IrF}_6$, is formed [95].

IrF_6 is the only hexafluoride other than PtF_6 that has been

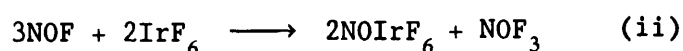
Table 1.4.2 Redox Reactions of IrF₆

Reagent	Product	Ref.
PF ₃	Ir, PF ₅	[100]
PF ₃ /HF	IrF ₄ , PF ₅	[100]
AsF ₃	IrF ₄ ·AsF ₅	[100]
SbF ₃	IrF ₄ ·SbF ₅	[100]
BiF ₃	---	[100]
SF ₄	SF ₄ ·IrF ₅ , SF ₅	[95]
SeF ₄	SeF ₃ ⁺ IrF ₆ ⁻	[42]
CS ₂	CF ₄ , SF ₄	[100]
H ₂ (100°C)	Ir, HF	[100]
H ₂ /AHF	IrF ₅	[100]
Metal/AHF	IrF ₅	[100]
Metal/AHF/KF	KrIrF ₆	[100]
CO or NH ₄	Ir	[95]
SO ₂	IrF ₅ ·SO ₂	[42]
I ₂ (R.T.)	IrF ₅ (some IF ₅)	[42]
I ₂ (120°C)	Ir ₂ F ₆ I ₃	[95]
FOCl ₂ (25°C)	(ClO ₂) ⁺ IrF ₆ ⁻	[101]

shown to liberate fluorine [46,48] during the oxidation of NOF. When NOF and IrF₆ are mixed in approximately equimolar amounts at 20°C the reaction occurs spontaneously and the overall stoichiometry is approximately that shown by equation (i).



Some NOF₃ is also formed. The yield of NOF₃ increases greatly when the ratio of NOF:IrF₆ is increased. When the ratio is 3:2 more than 60% of the theoretical yield is obtained (equation ii).



No reaction occurs between NOF₃ and IrF₆ [48]. If NO₂F and IrF₆ are allowed to react in a stoichiometric ratio the white solid NO₂IrF₆ is produced [102].

Structure

IrF₆ exhibits a cubic structure near room temperature and a phase of lower symmetry (orthorhombic) at reduced temperatures (table 1.4.3.). The phase change occurs at -1.2°C and atmospheric pressure [8].

Table 1.4.3. Crystallographic Data [8]

	<u>Cubic Phase</u>	<u>Orthorhombic Phase</u>
Temperature	25°C	-11°C
Cell dimensions	$a=6.23\pm0.02\text{\AA}$	$a=9.58\pm0.02\text{\AA}$ $b=8.73\pm0.02\text{\AA}$ $c=5.04\pm0.02\text{\AA}$
Calculated density	4.20gcm^{-3}	4.82gcm^{-3}
Z	2	4

Spectroscopy

The infrared spectrum of IrF_6 was first recorded in 1955 [94]. Two infrared active fundamentals ν_3 and ν_4 were observed at 718 and 276 cm^{-1} respectively, and from the combination bands the other fundamentals were calculated (table 1.4.4.).

Table 1.4.4. Fundamental Vibrations of IrF_6

ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	refs.
(A_{1g})	(E_g)	(F_{1u})	(F_{1u})	(F_{2g})	(F_{2u})	
(696)	(643)	718	276	(260)	(205)	[92]
(705)	(644)	720	276	-	(208)	[101]

Calculated Data ()

The spectrum is similar to the other heavy metal hexafluorides of O_h symmetry. Claassen and Weinstock [103] later examined IrF_6 for evidence of Jahn-Teller effects using i.r. spectroscopy. Since, the electronic ground state of the molecule is a Γ_8 quartet they expected to find anomalies in the spectra due to Jahn-Teller vibronic coupling. However, the combination bands ($\nu_1 + \nu_3$) and ($\nu_2 + \nu_3$) were equal in shape and intensity indicating that no Jahn-Teller effect was present. The observed and calculated fundamentals are shown in table 1.4.4.

An incomplete Raman spectra of IrF_6 was obtained by Claassen and Weinstock [103] using a 20% solution of IrF_6 in $n\text{-C}_7\text{F}_{16}$. Only ν_2 was observed; ν_1 coincided with the 5677 mercury line and ν_5 was obscured by absorption and background scattering. Later Claassen and Selig [54] observed all three Raman active fundamentals. One was intense and highly polarised the other two were weaker and depolarised (ν_1 701 cm^{-1} (intense), ν_2 645 cm^{-1} , ν_3 267 cm^{-1}). The work of Shamir and Malm agrees with these findings [49]. Here the fundamentals were observed at ν_1 704 cm^{-1} , ν_2 647 cm^{-1} and ν_5 273 cm^{-1} .

The u.v.-visible spectra of the vapour phase of IrF_6 was recorded between 4,000 and 40,000 cm^{-1} by Moffitt, Goodman, Fred and Weinstock [56]. The u.v.-visible spectra of IrF_6 in a nitrogen matrix has also been recorded and the results are compared in table 1.4.5 [57].

Electron diffraction [33,58] also indicates that the binary hexafluorides have electrically centrosymmetric structures with O_h symmetry. The Ir-F distance has been found to be 1.830Å.

1.4.2 Iridium Pentafluoride

Prior to 1965 iridium pentafluoride was confused with iridium tetrafluoride. It is now known [104] that the " IrF_4 " of Ruff and Fischer [93] and Robinson and Westland [95] is, in fact, the pentafluoride. Thus, the earlier work will be discussed below as pertaining to IrF_5 .

Preparation

IrF_5 has been prepared in many ways but the best preparative route is by the direct fluorination of iridium metal, the elements being in stoichiometric amounts and the mixture heated to 350-380°C [104]. All the other preparative routes, except, one involve reductions of IrF_6 . Ruff and Fischer [93] first prepared IrF_5 by the reduction of IrF_6 using Ir metal in a sealed quartz tube heated to 150°C. A similar method was used by Misra [24] but here the reaction was carried out in a flow line the IrF_6/N_2 mixture being passed over Ir sponge at 280°C. At just over 200°C, IrF_6 readily attacks Pyrex to produce IrF_5 [95]. This method was also tested by Bartlett and Rao [104] who heated IrF_6 with powdered glass to 350°C to produce IrF_5 . Paine and Asprey [65,66,105] have prepared IrF_5 by the one electron reduction of IrF_6 using either H_2 or Si powder. When IrF_6 is in solution in anhydrous HF both reagents react rapidly, reaction rates being enhanced by the presence of platinum gauze or u.v. irradiation. Hydrogen can also be used when IrF_6 is in the gaseous state but here the reaction is much slower. IrF_5 can also be

Table 1.4.5 u.v.-Visible Data for IrF₆

Gas Phase [56]	Matrix Isolated [57]	Assignment
42,000	43,000	$\Pi(F) \longrightarrow t_{2g}(\text{Ir})$
35,500	35,700	$\Pi(F) \longrightarrow t_{2g}(\text{Ir})$
28,200	30,400	$\Pi(F) \longrightarrow t_{2g}(\text{Ir})$
16,000	16,400	${}^4A_{2g}(\Gamma_8) \longrightarrow {}^2T_{2g}(\Gamma_8)$
13,000	13,000	${}^4A_{2g}(\Gamma_8) \longrightarrow {}^2T_{2g}(\Gamma_7)$
9,000		${}^4A_{2g}(\Gamma_8) \longrightarrow {}^2T_{2g}(\Gamma_6, \Gamma_8)$
6,400		${}^4A_{2g}(\Gamma_8) \longrightarrow {}^2T_{2g}(\Gamma_8)$

(E max/cm⁻¹ and Δν/cm⁻¹)

obtained by the reaction of a solution of XeF_2 in anhydrous HF with metallic Ir [66].

Photolysis of IrF_6 using u.v. light can also be used to prepare IrF_5 [95] but yields are low.

Apperance and Physical Properties

IrF_5 is a yellow crystalline solid which melts at 104.5°C [104] to a dark yellow liquid, and boils at just above 300°C [95]. The magnetic suseptibility has been measured from -196 – 23°C [104]. The values obtained vary little with temperature as expected of a d^4 electronic configuration in an octahedral or near octahedral 3rd row transition series metal fluoride. The magnetic moment calculated from these suseptability data is 1.32 BM at 296K [106].

Some thermodynamic data have been calculated for IrF_5 [141] but further independent verification is required.

Chemical Properties

IrF_5 is rapidly hydrolysed in moist air to produce hydrated iridium dioxide and hydrofluoric acid. With excess of water a violet colloid of IrO_2 is formed [95]. Misra [24] has studied the reaction of IrF_5 with CO at 260 – 280°C in a flow system. The stoichiometry claimed for the product is $\text{Ir}(\text{CO})_{2.5}\text{F}_2$. On further reaction with CO in a steel bomb at 100atm pressure and 200°C , a fluffy fibrous brown product with the stoicheiometry $\text{Ir}(\text{CO})_3\text{F}_2$ and a black lustrous solid of stoicheiometry $\text{Ir}(\text{CO})_2\text{F}_2$ is formed. These products have been analysed by chemical methods, and using i.r. and mass spectral data.

The reactions of IrF_5 in solution in BrF_5 with xenon fluorides have been well documented [20,69]. With XeF_6 , two adducts, $\text{Xe}_2\text{F}_{11}^+[\text{IrF}_6]^-$ (mp. 135°C) and $\text{XeF}_5^+[\text{IrF}_6]^-$ (mp. 116°C), have been reported. The latter is isomorphous and almost isodimensional with $\text{XeF}_5^+[\text{PtF}_6]^-$. The salt produced is dependent on the stoicheiometry of the reactants. The same is true of the products of the reaction

of IrF_5 and XeF_2 . Here three possible salts are produced, $\text{Xe}_2\text{F}_3^+[\text{IrF}_6]^-$ (m.p. 92°C), $\text{XeF}^+[\text{IrF}_6]^-$ (m.p. 152°C) and $\text{XeF}^+[\text{Ir}_2\text{F}_{11}]^-$ (m.p. 69°C). No evidence has been obtained for adduct formation between XeF_4 and IrF_5 .

Robinson and Westland [95] have reported that, if SF_4 is passed over IrF_5 at 100°C , the IrF_5 becomes brown; while, at $350\text{--}400^\circ\text{C}$, a rapid reaction produces the brownish-black IrF_3 .

It has been shown that IrF_5 is soluble to at least 1M concentration in anhydrous HF. There is some trouble, however, in dissolving the IrF_5 if it has stood as a powder for more than a week [65]. This may be due to dissociation of IrF_5 and formation of IrF_4 .

Structure

X-ray powder diffraction has shown that IrF_5 is isomorphous and nearly isodimensional with RuF_5 , having a tetrameric molecular structure with nonlinear fluorine bridges [104]. IrF_5 adopts a monoclinic lattice; $a=12.5$, $b=10.0$, $c=5.4\text{\AA}$ and $\beta=99.8^\circ$, with Ir atoms almost octahedrally coordinated.

The fractional magnetic field shift of the nuclear magnetic resonance of ^{19}F in IrF_5 has been observed [79]. The three line absorption spectra, with intensity ratio 1:2:2 suggests that, at low temperature, this compound is composed of polymers with metal-fluorine-metal bridge bonds arranged *cis* to one another. This is in agreement with Bartlett's [104] earlier solid-state work.

Spectroscopy and Mass Spectrometry

The infrared (-196°C , thin film), Raman (melt) and visible (solution in HF) spectra of IrF_5 have been recorded and the results are tabulated below (table 1.4.6) [65].

Table 1.4.6 Spectroscopic Data for IrF₅

I.R. (cm ⁻¹)	Raman (cm ⁻¹)	visible (nm)
715 s,sh	718 s (p)	840
699 s,sh	705 w	683
678 vs	701 w	
642 s	687 w	
533 m,br	673 w	
	646 m	
	258 m	
	237 w	
	224 w	

Using molecular beam mass spectrometry Vasile, Jones and Falconer[27,28] detected signals due to monomeric, dimeric, trimeric and tetrameric ions, however, the extent of association of the neutral species is difficult to ascertain quantitatively because of fragmentation caused by electron impact ionization.

1.4.3 Iridium Tetrafluoride

Preparation

The best preparation of IrF₄ involves the interaction of Ir metal with an excess of IrF₅ [80], however, the procedure is quite long. An excess of IrF₅ and Ir metal are placed in a reaction vessel which is heated to 350°C at the bottom and 400°C at the top. These temperatures are maintained for 12 hours then the reaction vessel is allowed to cool slowly to 180°C, and the reactor is maintained at this temperature for 10 hours to facilitate crystallization of the IrF₄ from liquid IrF₅. The reaction vessel is then placed, open in a larger container which is heated under vacuum to 260°C in order to separate the IrF₅ and IrF₄.

There are several other methods of preparation. When H_2 is admitted to a solution of IrF_5 dissolved in anhydrous HF and the resultant solution is stirred in the presence of platinum gauze and u.v. radiation for 1 to 12 hours, IrF_4 precipitates as a red-brown solution [65]. The same reaction can also be carried out using IrF_6 in place of IrF_5 but a mixed valence product results.

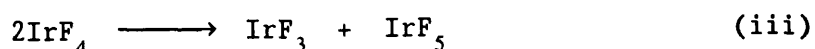
Reduction of IrF_6 on a hot filament of iridium or tungsten, using a technique similar to that described by Schröder and Grewe [107,108] to synthesis WF_5 , can also be used to produce IrF_4 [109]. This method is useful because IrF_4 is made directly from IrF_6 without the need to first produce IrF_5 . Recently, IrF_6 has been reduced by PF_3 in anhydrous HF to produce IrF_4 [100].

Appearance and Physical Properties

IrF_4 is a light brown solid [80] which sublimes at approximately $180^\circ C$ [109]. It is paramagnetic and its magnetic susceptibility obeys the Curie-Weiss Law over the temperature range $-173 - 27^\circ C$ [80]. The magnetic moment, μ_{eff} , is 1.89BM. Below $-173^\circ C$ the deviation from the Curie-Weiss Law is consistent with antiferromagnetic coupling between adjacent Ir atoms.

Chemical Properties

Very little is known of the chemistry of IrF_4 . However, IrF_4 hydrolyzes slowly in moist air to give a violet product [80]. Up to $400^\circ C$ it is stable under dynamic vacuum but above this temperature disproportionation occurs [80](equation iii),



Structure

X-ray powder photography has shown IrF_4 to be isostructural with PtF_4 . The unit cell is orthorhombic $Z=8$, $a=9.64(2)$, $b=9.25(2)$, $c=5.67(2)\text{\AA}$, and $V=505.8\text{\AA}^3$ [80]. Six fluorine atoms octahedrally coordinate each Ir atom, four being shared (1:1) with four other

octahedra. Thus, the stoichiometric requirements (MF_4) are fulfilled, in that each metal atom is coordinated uniquely to two fluorine atoms and has a half share in four others. The unique fluorines are in the *cis* relationship to one another.

Spectroscopy and Mass Spectrometry

The infrared spectrum of a powdered sample of IrF_4 has been recorded at 23°C. This shows three peaks at 691 cm^{-1} (m,sh), 688 cm^{-1} (s) and 545 cm^{-1} (s) respectively.

A sample of IrF_4 was examined using molecular beam mass spectroscopy [111]. Between 100–200°C the spectrum of IrF_5 , a possible contaminant of the synthesis, was observed but on further heating this disappeared. At 300–500°C the spectrum contained no IrF_5^+ component and no evidence of association in the saturated vapour was observed at this temperature. However, it seems unlikely that polymeric species would be stable enough to be detected.

The mass spectrum recorded by Paine and Asprey [65] of the vapour above solid IrF_4 at (100–200°C) suggested that neutral oligomers are present. However, since IrF_5^+ peaks were observed, it is probable that some IrF_5 is also present in their IrF_4 sample.

1.4.4 Iridium Trifluoride

Preparation

The best preparation of IrF_3 is via the thermal decomposition of IrF_5 (initially reported as " IrF_4 ") [16,95]. The IrF_3 produced is pure, but poorly crystalline and yields are low. It is possible to produce more crystalline IrF_3 by passing a mixture of IrF_6/N_2 over Ir powder heated to 500°C. The IrF_3 is very crystalline but unreacted metal remains as an impurity [16].

If IrF_4 is heated (400°C) under two atmospheres of argon in a Monel bomb with no cooled section for four hours, a black powder is produced. This is reported to be IrF_3 but no information on its purity has been given [109]. Reactions of SF_4 and IrF_5 also produce

IrF_3 , as does the reaction of IrF_5 with I_2 , S or H_2 . In the latter three cases the product is reported to be impure [95].

Recently, Misra prepared IrF_3 by reacting IrF_6 with an excess of CO at 200 atmospheres pressure and 200°C [24].

Appearance and Physical Properties

IrF_3 is a brownish black or black solid. Thermally it is not very stable. Above 250°C it begins to lose fluorine and eventually decomposes to iridium metal [95].

Chemical Properties

IrF_3 is unaffected by water and attacked only very slowly by concentrated acids or alkalis [95].

Structure

IrF_3 is isostructural with PdF_3 and RhF_3 . The rhomboheral unit cell contains two molecules and has dimensions $a=5.42\text{\AA}$ and $\alpha=54.3^\circ$ [95]. The fluorine atoms are in a closer-packed hexagonal arrangement, successive close-packed layers being slightly compressed along the trigonal axis so that the axial ratios are less than the ideal value of 1.633. Each fluorine has six equidistant fluorines as neighbours in its own plane and six others at shorter distances in adjacent planes. The metal atoms occupy one third of the octahedral sites in an ordered manner [16].

1.5 Palladium

1.5.1 Palladium Tetrafluoride

Preparation

Palladium tetrafluoride can be prepared via the direct fluorination of $\text{Pd}^{2+}[\text{PdF}_6]^{2-}$ using BrF_3 [80,112]. In an account giving precise details of the reaction conditions necessary to obtain a relatively pure product [112] it was noted that, during the preparation of $\text{Pd}^{2+}[\text{PdF}_6]^{2-}$, the $\text{BrF}_3 \cdot \text{PdF}_3$ complex should be decomposed at as low a temperature as possible (210°C) under vacuum in a quartz bulb. The resulting $\text{Pd}^{2+}[\text{PdF}_6]^{2-}$ is poorly crystalline and suitable for the moderate pressure (7 atmospheres) fluorination at 300°C to yield PdF_4 . It was also suggested that the bomb should be recharged with fluorine during the reaction and that the reaction should be allowed to proceed for several days. If recommendations are followed it is possible to prepare reasonably pure PdF_4 without serious contamination with unreacted $\text{Pd}^{2+}[\text{PdF}_6]^{2-}$ as found previously [112].

Appearance and Physical Properties

PdF_4 is a brick red, diamagnetic solid [112].

Chemical Properties

Raman data suggests that the adducts formed from PdF_4 with XeF_6 are $[\text{XeF}_5^+]_2[\text{PdF}_6^{2-}]$ and $[\text{Xe}_2\text{F}_{11}^+]_2[\text{PdF}_6^{2-}]$. The X-ray crystal structure of $[\text{XeF}_5^+]_2[\text{PdF}_6^{2-}]$ shows these yellow crystals to have an orthorhombic unit cell with $a=9.346(6)$, $b=12.786(7)$, $c=9.397(6)$ Å, $z=4$ and the density D has been calculated to be 3.91 gcm^{-3} [150].

Structural Data

X-ray powder diffraction studies [80,112] and neutron powder diffraction studies [113] have been undertaken in order to elucidate

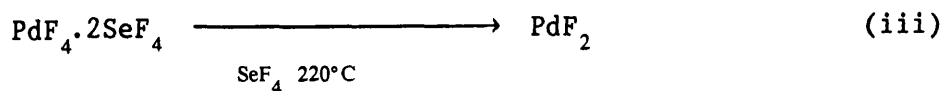
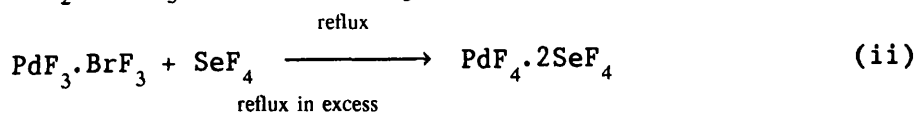
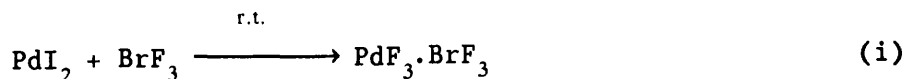
definitively the structure of PdF_4 .

In their early work Bartlett and Rao [112] suggested that PdF_4 has a tetragonal unit cell and is structurally similar to PtF_4 [114]. Platinum tetrafluoride in turn, was thought to be structurally related to UCl_4 [115] in which each uranium atom is coordinated by eight chlorine atoms arranged in two flattened tetrahedral sets. This implies that all the fluorine atoms in PdF_4 are equivalent. Later, Rao, Tressaud and Bartlett suggested that a different structure was probable [80], in which octahedral coordination of the metal was possible. In this case the fluorine atoms would no longer be equivalent. Of the six fluorine atoms octahedrally coordinating each metal atom, four are shared (1:1) with four other octahedra and two are uniquely coordinated to the metal. The two terminal fluorines are arranged in the *cis* configuration. This latter structure has been confirmed by neutron powder diffraction studies [113] and the Pd-F-Pd bridging angle was found to be $134 \pm 2.4^\circ$. This angle agrees well with that expected (135°) for ideal hexagonal close packing of octahedra.

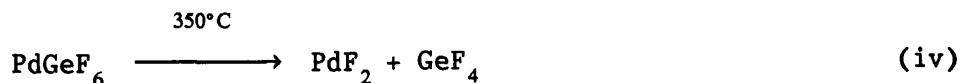
1.5.2 Palladium Difluoride

Preparation

There have been many methods reported for the synthesis of PdF_2 [116,117,118]. However, in all the preparations carried out by Ruff and Ascher [116] the PdF_2 was contaminated with palladium metal. In the early work of Bartlett and Hepworth the same problem occurred [117]. Eventually, Bartlett and Hepworth [117] developed the following reaction sequence in order to prepare pure violet PdF_2 (equations i-iii);



Another convenient preparative route is the thermal decomposition of PdGeF_6 in vacuo at 350°C [112](equation iv).



The most useful method for preparing PdF_2 , however, is the reduction of palladium II hexafluoropalladate IV with SeF_4 [118] since the intermediate fluoroselenium hexafluoropalladate decomposes directly to the difluoride at 155°C .

Appearance and Physical Properties

PdF_2 is a pale violet powder [117]. It is the only paramagnetic compound of divalent Pd II. The effective magnetic moment at R.T. is 1.84BM [119]. This low value is probably due to antiferromagnetic effects.

Chemical Properties

Palladium difluoride is hydrolysed rapidly in moist air to give the brown colour characteristic of the oxide [117]. With water, heat is evolved and a gelatinous precipitate of palladium hydroxide is formed. In hydrochloric acid, PdF_2 dissolves completely to give an orange-brown solution. PdF_2 reacts with CaF_2 and CdF_2 , at 820°C over 20-30 days in sealed platinum tubes [120], to form CaPdF_4 (purple) and CdPdF_4 (dark blue) respectively. Both compounds are crystalline, CaPdF_4 giving tetragonal crystals (KBrF_4 -type) and CdPdF_4 giving cubic crystals (CaF_2 -variant). HgPdF_4 has also been formed, this is isostructural with HgPtF_4 and both are black. CdPdF_4 is diamagnetic whereas PdPdF_4 is antiferromagnetic.

Structural Data

Several X-ray powder diffraction studies have been carried out [91,116,117,118]. Ruff and Ascher [116] first characterised PdF_2 by X-ray powder diffraction. Their results indicated that PdF_2 forms tetragonal crystals with the rutile structure. Ebert [91] confirmed this and obtained unit cell dimensions, but could not complete the structural determination. Similar values of the unit-cell dimensions

were also found by Bartlett and Hepworth [117].

More recent studies by Bartlett and Maitland [119] have produced further structural information (table 1.5.5). PdF_2 is isostructural with MnF_2 , FeF_2 , CoF_2 , NiF_2 and ZnF_2 . Each palladium atom has six fluorine atoms forming an almost regular octahedron around it. The PdF_6 coordination octahedra are joined by sharing corners.

Table 1.5.1. Interatomic Distances

4 Pd-F	2.155Å
2 Pd-F	2.171Å
8 F-F	3.060Å
2 F-F	2.664Å
2 F-F	3.389Å

A second, high-pressure form of PdF_2 is also known and this has been the subject of close structural investigation [120-125]. PdF_2 exhibits the fluorite structure at pressures exceeding 15 kbar at room temperature. This high pressure form, when quenched to atmospheric pressure, retains its fluorite structure as a metastable phase [120,122,123]. This transformation has been followed *in situ* by resistivity measurements [121,124]. X-ray diffraction methods have been used to check these results. X-ray and neutron diffraction methods have been used to study the structure of the high pressure phase. However, these measurements were carried out at atmospheric pressure [124]. The high pressure form of PdF_2 crystallises in the cubic system with $a=5.329 \pm 0.002 \text{Å}$.

1.5.3 Palladium II Hexafluoropalladate IV

Preparation

Early workers reported the preparation of " PdF_3 " [16,32,116,117] but this was later shown to be palladium II hexafluoropalladate IV $[\text{Pd}^{2+}(\text{PdF}_6)^{2-}]$ [112]. There are several reports of the preparation of $\text{Pd}[\text{PdF}_6]$ [16,82,112,116,117] but there are basically only two methods:

i) Fluorination of palladium dihalide using elemental fluorine [16,116,117].

ii) Fluorination of palladium dihalide using bromine trifluoride [82,112,117].

In the work carried out using elemental fluorine as the fluorinating agent a large variety of conditions are employed. Temperatures vary from room temperature [117] to 400°C [16] and no indication of fluorine pressure is given. The best route for the preparation of $\text{Pd}[\text{PdF}_6]$ is the fluorination of PdX_2 ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) with BrF_3 . The initial product is $\text{PdF}_3 \cdot \text{BrF}_3$. This is decomposed at 180°C to give $\text{Pd}[\text{PdF}_6]$. In this reaction an addition compound is formed in solution between PdX_2 and the solvent, thereby ensuring a rapid and quantitative reaction. The whole reaction can be carried out in a quartz flask without significant damage to the vessel [82] thus, avoiding the need for expensive equipment.

Appearance and Physical Properties

Palladium II Hexafluoropalladate IV is a black crystalline solid. The magnetic moment of $\text{Pd}[\text{PdF}_6]$ at 20°C is 2.05BM [83]. Since $\text{Pd}[\text{PdF}_6]$ had been reported initially as being " PdF_3 " this result was misinterpreted in terms of a low spin electron configuration, $d(t_{2g})^6, d(e_g)^1$, for the octahedrally coordinated Pd_3^+ ion. This was in direct conflict with ligand-field theory which predicts a distorted environment for an ion with such a configuration. The problem was later resolved when it was demonstrated that " PdF_3 " is in fact $\text{Pd}_2^+[\text{PdF}_6]^{2-}$ [112]. Thus the Pd^{2+} ion is assigned the high spin electron configuration and Pd^{4+} is given the low spin electron configuration $d(t_{2g})^6, (e_g)^0$ associated with the $[\text{PdF}_6]^{2-}$ ion, as in the hexafluoropalladates which are diamagnetic.

Chemical Properties

$\text{Pd}[\text{PdF}_6]$ is rapidly hydrolysed by water.

Structural Data

Conflicting interpretations of the structural data on PdF_3 were published by the earliest workers in the area. Some [89,90] considered " PdF_3 " to have a rhombohedrally distorted ReO_2 structure

with a unimolecular cell being isostructural with FeF_3 and CoF_3 . Others [91,92] claimed that the structure was similar to that of AlF_3 , with a bimolecular cell. Later, quantitative X-ray investigations were carried out [16] and it is now known that " PdF_3 " should be indexed on a bimolecular rhombohedral unit cell. It is not isostructural with FeF_3 or CoF_3 , but has a closest packed hexagonal fluorine atom arrangement, successive close packed planes being compressed along the trigonal axis. $\text{Pd}[\text{PdF}_6]$ is isostructural with a series of compounds of general formula $\text{Pd}^{2+}[\text{MF}_6]^{2-}$ in which M= Ge, Pt, Sn [112].

1.6 Platinum

1.6.1 Platinum Hexafluoride

Preparation

There are five reported methods of preparation for platinum hexafluoride [75,102,126-129]. By far the best is that of Weinstock, Malm and Weaver [127], who heated a platinum wire electrically in a fluorine atmosphere, adjacent to a surface cooled by liquid nitrogen, the reaction being carried out in a brass container. Yields of PtF_6 were typically of the order of 70%. This was a great improvement on the group's initial reactions in Pyrex [126] where yields of PtF_6 were only about 10%.

Platinum hexafluoride has also been prepared from platinum and elemental fluorine at 500°C [128] but the yield varied from 10-90% [129]. Later, the reaction was repeated more successfully at 200°C [129] after Weinstock *et al* [127] reported that the rate of thermal decomposition of PtF_6 in the presence of fluorine at high pressure is only significant above 200°C. Under these conditions the yield of PtF_6 was 40-50%, the remainder being lower fluorides (PtF_5 and PtF_4).

PtF_6 can also be prepared, together with PtF_5 [102], by heating Pt metal and F_2 (210 atm. at R.T.) for 12 hours in a 70 cc Monel bomb. It can also be prepared in small quantities in quartz apparatus by passing F_2/N_2 mixture over platinum metal in a shallow nickel boat [75]. The boat is heated to a few hundred degrees in an electrical furnace and is placed as close as possible to a liquid oxygen trap in order to prevent decomposition of the PtF_6 .

The powerful oxidative fluorinating ability of KrF_2 has also been used to obtain platinum hexafluoride in solution in anhydrous HF or BrF_5 [21]. A solution of the metal oxide or lower fluoride in

KrF₂ gives the complexes KrF₂.PtF₅ and KrF₂.2PtF₅ which, when heated slightly, decompose vigorously with the quantitative formation of PtF₆.

Another reported method for the formation of PtF₆ involves the use of atomic fluorine [130]. The reaction, at temperatures above 100°C, is reported to be rapid. Further independent verification is needed in the cases of these last two preparations.

Appearance and Physical Properties

Platinum hexafluoride is intensely coloured, appearing bright red when viewed under a microscope and black in massive amounts. It has a melting point of 61.3°C [8] and, in the liquid phase, it is dark red in colour. The vapour of PtF₆ is brownish red, being much more intensely coloured than bromine vapour. The approximate solid vapour pressures at 0°C and 21°C are 29 and 96 mmHg respectively [32,126]. Platinum hexafluoride is less stable than OsF₆ and IrF₆ but more stable than RuF₆ and RhF₆. When stored in Pyrex or quartz it decomposes slowly leaving a red residue. However, it may be stored for weeks at room temperature in a nickel can [126]. There is virtually no thermal decomposition until 200°C but at 280°C decomposition is rapid and complete.

The enthalpy of formation of PtF₆ has recently been reported [131]. Knudsen-cell mass spectrometry was used to investigate the gas-phase equilibrium: PtF₄ + F₂ → PtF₆. The following values at 298.15 K were calculated:

$$\Delta_f H^\circ_m = -(152 \pm 12) \text{ kJmol}^{-1}$$

$$\Delta_f H^\circ_m (\text{PtF}_6 \text{ gas}) = -(676 \pm 28) \text{ kJmol}^{-1}$$

$$\Delta_f H^\circ_m (\text{PtF}_6 \text{ s.l.}) = -(714 \pm 28) \text{ kJmol}^{-1}$$

$$\Delta_f H^\circ_m (\text{PtF}_6 \text{ s.ii.}) = -(722 \pm 28) \text{ kJmol}^{-1}$$

All other thermodynamic data is summarised in table 1.6.1.

Table 1.6.1 Summary of Thermodynamic Data and Physical
Constants for PtF₆

M pt	61.3°C		
B pt	69.14°C		
Transition temp.	3°C		
Liquid Density	3.826 gcm ⁻³		
$\Delta_{\text{sub}} H^\circ$	(276.1K, orthorhombic \longrightarrow pfg)	47.82	} kJmol ⁻¹
$\Delta_{\text{sub}} H^\circ$	(276.15K, cubic \longrightarrow pfg)	38.87	
$\Delta_{\text{sub}} H^\circ$	(334.45K, cubic \longrightarrow pfg)	35.91	
$\Delta_{\text{vap}} H^\circ$	(334.45K)	7.51	
$\Delta_{\text{fus}} H^\circ$	(334.45K)	4.51	
$\Delta_{\text{trs}} H^\circ$	(276.15K)	8.95	
$\Delta_{\text{sub}} S^\circ$	(276.15K, orthorhombic \longrightarrow pfg)	173.1	} Jmol ⁻¹ deg ⁻¹
$\Delta_{\text{sub}} S^\circ$	q(276.15K, cubic \longrightarrow pfg)	140.9	
$\Delta_{\text{sub}} S^\circ$	(334.45K, cubic \longrightarrow pfg)	107.4	
$\Delta_{\text{vap}} S^\circ$	(334.45K)	94.1	
$\Delta_{\text{fus}} S^\circ$	(334.45K)	13.4	
$\Delta_{\text{trs}} S^\circ$	(276.15K)	32.6	

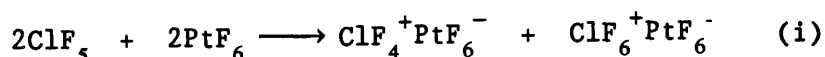
Chemical Properties

Platinum hexafluoride has extraordinary oxidising properties. This was demonstrated in 1962 when Bartlett and Lohmann [50] showed that PtF_6 would oxidise oxygen gas at 21°C to give $\text{O}_2^+[\text{PtF}_6]^-$. They had earlier prepared $\text{O}_2^+[\text{PtF}_6]^-$ when fluorinating PtCl_2 at 350°C in silica apparatus but had thought that they had prepared PtF_5 and PtOF_4 [132]. It was only later that they discovered that their 'oxyfluoride' was in fact $\text{O}_2^+[\text{PtF}_6]^-$ [133]. The salt can also be prepared by fluorinating platinum sponge or platinum salts in the presence of oxygen [50,151]. The dioxygenyl salt is a red, dimorphic, paramagnetic solid which sublimes without decomposing in vacuum above 90°C .

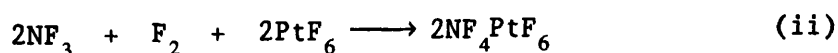
Bartlett recognised that, since, xenon has a first ionisation potential just less than that of oxygen it should also be oxidised by platinum hexafluoride. He showed that PtF_6 oxidises gaseous xenon spontaneously to give a yellow-orange solid [158]; initially thought to be $\text{Xe}^+[\text{PtF}_6]^-$. The product, however, was not as simple as first formulated [72]. The reaction has been repeated many times and followed tensimetrically and gravimetrically [41]. The combining ratio $\text{Xe}:\text{PtF}_6$ always lies between 1:1 and 1:2, with the former favoured when xenon is in excess and the concentration of reactants is low [48]. Mahieux [135,136] may have produced similar products by exploding a platinum wire in Xe/F_2 gas. Products of composition PtXeF_6 and $(\text{PtF}_6)_2\text{Xe}$ have been suggested. Unfortunately, since "XePtF₆" is amorphous it has been impossible to compare powder photographs with those of $[\text{XeF}]^+[\text{PtF}_6]^-$ [20]. Consequently, it is still not certain whether the compounds designated $[\text{Xe}]^+[\text{PtF}_6]^-$ and $\text{Xe}[\text{PtF}_6]_2$ contain $[\text{Xe}]^+$, $[\text{Xe}]^{2+}$ or $[\text{Xe}_2\text{F}]^+$ or whether "XePtF₆" is in fact XePtF_7 and "XePtF₆" and $\text{Xe}[\text{PtF}_6]_2$ are the compounds $[\text{XeF}]^+[\text{PtF}_6]^-$ and $[\text{XeF}]^+[\text{Pt}_2\text{F}_{11}]^-$ [134].

Platinum hexafluoride can be used as an oxidative fluorinator for the synthesis of coordinatively saturated complex fluoro-cations ClF_6^+ and NF_4^+ [101,153-156]. The ClF_6^+ cation can be prepared in the form of its PtF_6^- salt from the reaction of PtF_6 with either

FClo_2 [101] or ClF_5 [101,156]. If PtF_6 and ClF_5 are left to react in their gaseous state then irradiation with u.v. light is required to initiate the reaction, however, when dissolved in HF they react readily at 25°C [156] (equation i).



Attempts to prepare $\text{BrF}_6^+\text{PtF}_6^-$ in an analogous manner from BrF_5 and PtF_6 were unsuccessful [156]. The best method of preparation for $\text{NF}_4^+\text{PtF}_6^-$ is the reaction of PtF_6 with a large excess of F_2 and NF_3 at 125°C under a pressure of about 140 atms.(equation ii).



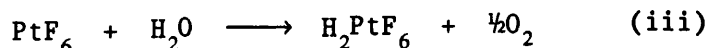
Platinum hexafluoride reacts with bromine trifluoride, plutonium tetrafluoride and neptunium fluorides to yield the highest fluoride of each [127]. It also reacts violently with uranium metal to form UF_6 [32] and with finely divided plutonium when the solid is brought to red heat and a platinum mirror is deposited on the quartz reactor [127], but no PuF_6 is found. This is probably due to the absence of a cold surface onto which the thermally unstable PtF_6 can be quenched.

In the gas phase, sulphur tetrafluoride reacts with platinum hexafluoride forming a product containing platinum in both oxidation states IV and V [41].

In contrast to the hexafluorides of osmium and iridium, which are reduced by selenium tetrafluoride to the pentavalent state, platinum hexafluoride is reduced to the tetravalent state [42].

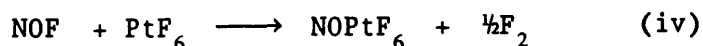
Platinum hexafluoride reacts with chlorine trifluoride [137] to form the adduct $\text{ClF}_3.\text{PtF}_5$ with evolution of fluorine. Reaction with bromine pentafluoride yields elemental fluorine and leaves a black viscous liquid of uncertain composition which contains platinum, bromine and fluorine [137].

Weinstock, Malm and Weaver attempted to investigate the hydrolysis chemistry of PtF_6 [127]. The results are summarised by the stoichiometric reaction (iii)

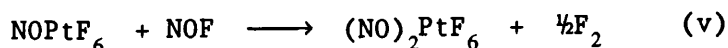


When larger samples of PtF_6 are used, however, some of the platinum is reduced further than the tetravalent state. This is probably due to the heat produced in the decomposition causing more vigorous reaction. Hydrolysis of PtF_6 in hydrogen fluoride, however, yields the oxonium salt $\text{H}_3\text{O}^+\text{PtF}_6^-$ [41]. If excess of water is present $(\text{H}_3\text{O}^+)_2\text{PtF}_6^{2-}$ can also be isolated.

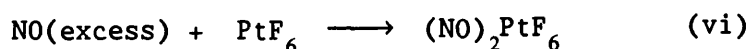
Reactions of platinum hexafluoride with NO and NOF carried out in the 1960's by Bartlett and Beaton [46,47] and independently by Gortsema and Toeniskoetter [138] appear to give inconsistent results. Bartlett and Beaton [46,47] report that the overall reaction is close to that represented by equation (iv):



Minor amounts of NOF_3 are also produced. It is further stated [48] that there is no evidence that a salt-like adduct is formed. The ability of PtF_6 to liberate fluorine on reaction with NOF was observed independently by Gortsama and Toeniskoetter [138]. However, they made no mention of NOF_3 . They also noted that further interaction of NOF with NOPtF_6 takes place with further liberation of fluorine, (equation v):



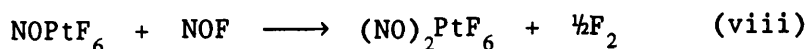
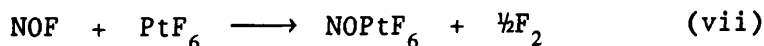
Bartlett did not report the formation of $(\text{NO})_2\text{PtF}_6$ via this method but found that it was formed from NO and PtF_6 , (equation vi):



This is not reported by Gortsama and Toeniskoetter.

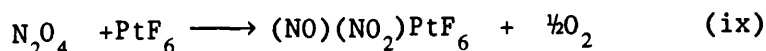
Work carried out by Griffiths and Sunder [102] on the reaction

of excess of nitrosyl fluorine with platinum hexafluoride suggests that the reaction proceeds via two distinct steps (equations vii and viii):

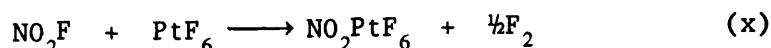


in agreement with the work of Gortsema and Toeniskoetter.

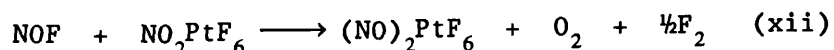
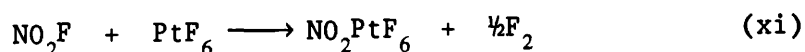
Griffiths and Sunder [102] also found the reactions of NO_2 and NO_2F with PtF_6 were more complex than previously reported [138]. Gortsema and Toeniskoetter [138] reported that the following reaction (equation ix) occurs;



whereas Griffiths and Sunder found that NOPtF_6 and $(\text{NO})_2\text{PtF}_6$ were formed. If NO_2F is reacted with PtF_6 the reaction shown in equation (x) occurs;



However, if the ratio $\text{NO}_2\text{F} : \text{PtF}_6$ is increased to 2.2:1 then at room temperature the reaction can be explained by the following sequence;



The overall stoichiometry was not exactly predicted by equations (xi) and (xii) as a small amount NOPtF_6 could also be detected.

Structural Data

X-ray powder diffraction studies have shown that PtF_6 is isostructural with OsF_6 and IrF_6 [126], and more recent work indicates that x-ray powder patterns of PtF_6 can be indexed on the basis of a body centered cubic cell [8]. At reduced temperature

(3°C) a phase transition to lower symmetry occurs. The powder pattern of the low temperature phase appears to be similar to that of UF_6 which is reported to be orthorhombic.

The ^{19}F nuclear magnetic resonance spectrum and the spin-lattice relaxation times of polycrystalline PtF_6 have been studied as a function of temperature and magnetic field. The chemical shift is large, exceeding the dipole-dipole broadening in the solid, thus, allowing determination of the extent of tetragonal distortion of the hexafluoride octahedra in the low-temperature phase. The solid-solid transition to the cubic phase of PtF_6 is found to be accompanied by a very sharp increase in spin lattice relaxation time and a lowering of the activation energy for molecular motion.

Spectroscopy

The infrared spectrum of the gaseous platinum hexafluoride has been measured between $4000\text{--}200\text{ cm}^{-1}$ [51]. Observation of bands at 273 cm^{-1} (ν_4) and 705 cm^{-1} (ν_3) and combination bands at 1306 cm^{-1} ($\nu_2 + \nu_3$) and 1360 cm^{-1} ($\nu_1 + \nu_3$) indicate that in the gas phase the PtF_6 molecule is octahedral. The derived fundamentals are shown in table 1.6.2.

Table 1.6.2. Fundamental Frequencies of PtF_6 (cm^{-1})

ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
(A_{1g})	(E_g)	(F_{1u})	(F_{1u})	(F_{2g})	(F_{1u})
655	601	705	273	242	211

Claassen and Selig [54] attempted to record the gas-phase Raman spectrum of platinum hexafluoride but, because of its relatively low vapour pressure and high reactivity at room temperature, they observed only the intense ν_1 fundamental. Their value of $\nu_1 = 656.4\text{ cm}^{-1}$ agrees well with that calculated from the infrared spectrum.

Claassen [39] used the fundamental frequencies to determine the force constants for PtF_6 , to be $+0.141\text{ md/\AA}$. The u.v.-visible spectra for gaseous platinum hexafluoride ($2,500\text{--}40,000\text{ cm}^{-1}$) [56]

and the matrix isolated hexafluoride have also been recorded [57]. The results of each are shown in table 1.6.3.

The deflection of a molecular beam of PtF_6 in an electric quadrupole field has been studied. No refocusing of the molecular beam was observed when an electric field was applied [33]. The results were characteristic of a non polar molecule and support the assignment of centrosymmetric structure for PtF_6 .

1.6.2 Platinum Pentafluoride

Preparation

Platinum pentafluoride is prepared by the fluorination of either platinum sponge or platinum dichloride [60,114,132]. The fluorination of platinum difluoride is the most commonly used route, the fluorine and nitrogen (3:1) being passed over PtCl_2 , in a platinum boat, in a quartz tube. At 350°C a vigorous reaction yields PtF_5 [114]. Unfortunately, dioxygenyl hexafluoroplatinate V (originally thought to be PtOF_4 [132]) is also formed due to the presence of oxygen which originates from the attack of fluorine on the silica. This can be removed by vacuum sublimation at 100°C . However, since PtF_5 dissociates to PtF_6 and PtF_4 very easily, it is likely that some dissociation of PtF_5 occurs. It should be possible, however, to avoid the formation of dioxygenyl hexafluoroplatinate V by carrying out the reaction in an all metal apparatus. This method would then undoubtedly be the best method of preparing PtF_5 .

Falconer, Jones, Sunder and Vasile reported a preparation of platinum pentafluoride via the fluorination of platinum sponge with an excess of elemental fluorine at 6.5–7.5 atms. pressure for 12 hrs at 350°C [60]. They reported that the small amounts of PtF_6 formed were removed at room temperature to leave PtF_5 . If this is correct then this route could be the most useful preparation for PtF_5 . However, the purity of the product was only measured using mass spectrometry, and this would give no evidence of unreacted metal which would be difficult to separate from the PtF_5 .

Table 1.6.3 u.v.-Visible Data for PtF₆

Gas Phase [56]	Matrix Isolated [57]	Assignment
45,000	46,500	$\sigma(F) \longrightarrow t_{2g}(Pt)$
32,000	32,895	$\Pi(F) \longrightarrow t_{2g}(Pt)$
	26,250	$\Pi(F) \longrightarrow t_{2g}(Pt)$
25,000	23,500	$\Pi(F) \longrightarrow t_{2g}(Pt)$
16,000	16,000	${}^3T_{1g}(\Gamma_1) \longrightarrow {}^1A_{1g}$
12,000	12,000	${}^3T_{1g}(\Gamma_1) \longrightarrow {}^1T_{1g}, {}^1E_g$
5,400		${}^3T_{1g}(\Gamma_1) \longrightarrow {}^3T_{1g}(\Gamma_3)$
5,200		${}^3T_{1g}(\Gamma_1) \longrightarrow {}^3T_{1g}(\Gamma_5)$
3,300		${}^3T_{1g}(\Gamma_1) \longrightarrow {}^3T_{1g}(\Gamma_4)$

(E max/cm⁻¹ and Δν/cm⁻¹)

Appearance and Physical Properties

Platinum pentafluoride is a dark red solid, which melts at 80°C to a dark red liquid with a high viscosity and a high surface tension [114,132]. The boiling point has not been determined due to its rapid dissociation into PtF_6 and PtF_4 . The pentafluoride is paramagnetic with a magnetic moment of 2.05BM [140]. The entropy and reduced free energy of PtF_5 have been calculated in the ideal gas state ($p = 1 \text{ atm.}$) in the range 298–3200K [141]. Until experimental evidence to support these results is produced they should be viewed with some scepticism.

Chemical Properties

Platinum Pentafluoride is a very powerful oxidising agent. It reacts exothermically with water and a gas is evolved which is probably oxygen [114,132]. Approximately 25% of the platinum is precipitated as the dioxide whilst the remaining 75% goes into solution as the hexafluoroplatinate IV ion.

Xenon reacts with PtF_5 (in ratio 1:1) in the presence of excess of F_2 (80 psi) at 180–220°C [140]. Yellow needle, shaped crystals are produced with a melting point of approximately 100°C and an empirical formula F_{11}PtXe . X-ray diffraction studies on a single crystal show the formula to be $\text{XeF}_5^+ \text{PtF}_6^-$. The infrared spectrum also suggests the same structure, the band at 640–650 cm^{-1} being indicative of the ν_3 vibrational mode of PtF_6^- . The crystals are orthorhombic $a=8.16\text{\AA}$, $b=16.81\text{\AA}$, $c=5.73\text{\AA}$ and $V=785.4\text{\AA}^3$. When the $\text{Xe}:\text{PtF}_5$ molar ratio exceeds one a second compound is formed which is thought to have the composition $\text{F}_{17}\text{PtXe}_2$.

PtF_5 dissolves in BrF_3 to give a deep red solution. When an excess of solvent is removed under vacuum the residue is the 2:1 bromine trifluoride-platinum tetrafluoride adduct $[(\text{BrF}_3)_2 \cdot \text{PtF}_4]$, which can be identified by X-ray photography [114].

IF_5 dissolves PtF_5 under reflux to produce a deep red solution.

When the solvent is removed under vacuum at 23°C a pale orange solid is isolated. Analysis and X-ray photography show this compound to be the 1:1 iodine pentafluoride-platinum pentafluoride adduct $[\text{PtF}_5 \cdot \text{IF}_5]$ [114]. This adduct has a melting point of 140°C, it begins to decompose at 180°C and at 300°C decomposition is complete, the residue being PtF_4 . The compound is paramagnetic ($\mu = 0.65\text{BM}$). Water reacts vigorously with it to give a solution containing the hexafluoroplatinate IV ion. The same complex has been prepared by dissolving dioxygenyl hexafluoroplatinate V in iodine pentafluoride [50].

PtF_5 reacts with ClF_3 to give the 1:1 chlorine trifluoride-platinum pentafluoride adduct $[\text{PtF}_5 \cdot \text{ClF}_3]$. This is a pale orange solid with a melting point of around 170°C and can be sublimed under vacuum at 100°C [114]. It is paramagnetic and X-ray studies show that it has low symmetry. It reacts vigorously with water to give a pale yellow solution which can be seen from the infrared spectrum to contain hexafluoroplatinate IV ions.

SeF_4 reduces PtF_5 to the quadripositive state. The adduct produced is $(\text{SeF}_4)_2 \cdot \text{PtF}_4$ [114]. Nitrosyl fluoride reacts with PtF_5 to produce NOPtF_6 , the reaction occurring rapidly at 35°C .

Structural Data

Platinum pentafluoride is thought to be isostructural with RuF_5 and RhF_5 but, so far, no single crystal data has been obtained [140].

Spectroscopy and Mass Spectrometry

PtF_5 has been examined by molecular-beam mass spectrometry [27,28,60]. It is known that PtF_5 rapidly decomposes to form PtF_6 and PtF_4 . However, using this technique evidence of monomeric, dimeric and trimeric species in the vapour phase of PtF_5 is produced. Since, evidence of PtF_6 is also found these results provide no quantitative information about the vapour phase

composition of PtF_5 . However, the data does suggest that a series of polymers are present.

1.6.3 Platinum Tetrafluoride

Preparation

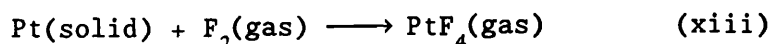
The best preparative route for platinum tetrafluoride is the fluorination of PtCl_4 or PtBr_4 using BrF_3 [82]. Vigorous reaction occurs on the addition of BrF_3 and a clear red solution forms. Evaporation of this solution under vacuum at room temperature yields a red product of empirical formula $\text{PtBr}_2\text{F}_{10}$. This is the adduct $(\text{BrF}_3)_2\text{PtF}_4$. At 180–200°C this adduct undergoes rapid decomposition to liberate BrF_3 and leave a yellow brown residue of PtF_4 . Small traces of bromine remain and these can be removed by low temperature (250°C) fluorination (F_2/N_2 mixture) of the residue. The bromine being evolved as BrF_5 [114].

PtF_4 can also be prepared by the fluorination of platinum dichloride at temperatures higher than 200°C [132], the interaction of platinum metal and ClF_3 in a bomb [142] and the action of SF_4 at 5–50 atm pressure on platinum sulphide at 150–350°C. If a stream of hydrogen fluoride diluted with N_2 is passed over PtCl_2 in a platinum boat in a nickel reactor, PtF_4 and platinum are produced [114]. Pure PtF_4 can also be obtained by heating a $\text{PtF}_6/\text{PtF}_x$ ($4 < x < 5$) mixture at about 200°C for several hours and removing excess of fluorine under vacuum [71].

Appearance and Physical Properties

Platinum tetrafluoride is a yellow-brown crystalline solid [114], and is known to be diamagnetic [114]. Previous reports that it was paramagnetic with a magnetic moment of 1.1BM are possibly due to the presence of a small amount of a bromine trifluoride-platinum trifluoride adduct, in the impure material. This would be expected to show similar properties to the analogous palladium compound [81].

A thermodynamic study of gaseous PtF_4 , formed by introducing fluorine into the effusion cell compartment of a mass spectrometer at 518-960K is reported to show that for the reaction shown in equation (xiii) the change in the Gibbs free energy is -158 kJmol^{-1} ,



and the enthalpy of formation of gaseous PtF_4 at 793K is -214 kJmol^{-1} [144]. However, when platinum is fluorinated using elemental fluorine at elevated temperatures (250-700°C) some PtF_5 and PtF_6 are also formed which will decompose to PtF_4 due to the high temperature. Therefore, until further independent measurements are made we cannot be fully confident of the interpretation of these results.

The enthalpy of formation of gaseous PtF_4 was reported using a similar method in the temperature range 860-980K involving exchange reactions in the MnF_2 - MnF_3 -Pt system. At 298K the enthalpy of formation of $\text{PtF}_4(\text{gas})$ is $-410 \pm 40 \text{ kJmol}^{-1}$ and the dissociation energy is $330 \pm 40 \text{ kJmol}^{-1}$ [145]. Again further independent confirmation of these results is required.

Chemical properties

Platinum tetrafluoride is hydrolysed slowly by water [114], some platinum being precipitated as hexafluoroplatinate (IV) ion. Hydrogen reduces PtF_4 to platinum metal at 100°C [114], but no reaction appears to occur below this temperature.

Platinum tetrafluoride dissolves in selenium tetrafluoride to give a pale yellow solution. After refluxing for 15mins at 100°C the PtF_4 is converted to a yellow solid which is recovered by removing any excess of solvent. The yellow solid is the adduct $\text{PtF}_4 \cdot 2\text{SeF}_4$ [114], which is diamagnetic and rapidly hydrolysed by water. It decomposes without melting at 350°C to give platinum metal and selenium hexafluoride. The X-ray powder pattern of $\text{PtF}_4 \cdot 2\text{SeF}_4$ has been indexed on the basis of an hexagonal unit cell, $a=15.74 \pm 0.03 \text{ \AA}$,

$a=4.93\pm0.01\text{\AA}$, $Z=4$, and density being calculated as 3.66 gcm^{-3} .

Platinum tetrafluoride also dissolves in bromine trifluoride under reflux, to give a deep red solution. After excess of BrF_3 is removed by vacuum distillation a red-brown solid remains which is the 2:1 bromine trifluoride-platinum trifluoride adduct $[\text{PtF}_4\cdot 2\text{BrF}_3]$ [114]. This compound was initially prepared by Sharpe by the reaction of bromine trifluoride on platinum tetrachloride [82], or tetrabromide. The diamagnetic solid melts at 136°C and decomposes between $180\text{--}200^\circ\text{C}$ to give PtF_4 .

PtF_4 was initially thought to react with CO under pressure to form $\text{Pt}(\text{CO})_2\text{F}_8$ [146], but this was later shown to be $\text{Pt}(\text{CO})_2\text{Br}_2$ [176]. PtF_4 in acetone reacts at 0°C with a small quantity of water, forming $\text{H}_2\text{Pt}(\text{OH})_4\text{F}_2$ and with CH_3OH in acetone it forms $\text{PtF}_2(\text{OCH}_3)_2$ which is explosive at 90°C [147]. Liquid XeF_2 at $137\text{--}147^\circ\text{C}$ oxidises PtF_4 , forming $\text{Xe}_2\text{F}_3\text{PtF}_6$ [148].

Structural Data

X-ray powder diffraction patterns indicate that PtF_4 adopts a monoclinic unit cell with $a=6.68$, $b=6.68$, $c=5.71\text{\AA}$ and $\gamma=92.02^\circ$ [114]. There are 4 molecular units in the cell and the structure is similar to that of UCl_4 in which each uranium atom is coordinated by eight chlorine atoms arranged in 2 flattened tetrahedral sets [115].

Spectroscopy

An infrared spectrum of the tetrafluoride in a nujol mull shows peaks at 675cm^{-1} (sharp) and 576cm^{-1} (broad).

Chapter 2

Fluorination of Platinum Group Metals

Chapter 2

Fluorination of Platinum Group Metals

2.1 Introduction

The previous chapter details all known preparative routes for the platinum group metal, P.G.M., fluorides. Ruthenium pentafluoride [9,12], osmium hexafluoride [31-38], rhodium pentafluoride [60,74] iridium hexafluoride [33,36,58,93-96] and pentafluoride [104] and platinum pentafluoride [60] can easily be made by direct fluorination. Ruthenium hexafluoride [3,4], rhodium hexafluoride [60,74,75] and platinum hexafluoride [75, 102, 126-129] can also be prepared by combination of the elements but more extreme conditions are required.

2.2 Present Work

The metals were each fluorinated in both static and dynamic systems, and the products were carefully analysed. Since, the aim of the work was to test the feasibility of separating the P.G.M.'s via their volatile fluorides, the hexafluorides and pentafluorides were of most interest. Careful note was made of the ratio of these compounds to the involatile lower fluorides and unreacted metal remaining after each fluorination.

2.3 Static System

2.3.1 General Procedure

All reactions were carried out in 3/4" metal reactors (chapter 6). In each case the reactor was connected to the manifold via a needle valve, [AE-30 series, Autoclave Engineers], evacuated and baked at about 300°C for 2-3 hours under dynamic vacuum. Fluorine at 400-500 mmHg pressure was admitted to the reactor and it was again baked to 300°C for 2-3 hours. It was then evacuated and taken into a

dry box where it was loaded with a carefully weighed amount of metal powder. The reactor was returned to the manifold and the nitrogen admitted while in the dry box was pumped out. When the vacuum reached 10^{-4} mmHg the reactor was left under dynamic vacuum for a further 1-2 hours.

The metal powder was then hydrogenated *in situ* by heating to 300°C in the presence of 400-500 mmHg of hydrogen for 2-3 hours. The reactor was then re-evacuated and held under dynamic vacuum for at least 12 hours to remove all traces of hydrogen. A known pressure of fluorine was condensed from the line on to the metal at -196°C. The reactor was warmed to room temperature and then heated in an electric furnace to the reaction temperature. This temperature differed for each metal (table 2.1). The reaction was allowed to continue for 3-8 hours, again depending on the metal. The reactor was then cooled to the room temperature and the products were studied (table 2.1).

2.3.2 Results and Discussion

The present results are similar to those previously reported. However, additional quantitative information has been obtained and full characterization of all the products has been achieved.

Osmium and iridium were the first metals to be studied and as expected [31-38,58,93-96] the major products were the hexafluorides. In the iridium case a small amount of iridium pentafluoride was formed, but this accounted for less than 5% of the metal. In both cases all the metal was fluorinated but, as the yields of hexafluorides (table 2.1) were lower than expected, it appears that some of the hexafluoride decomposed during transfer from the reactor to the weighing can.

Ruthenium and rhodium reacted as expected [9,12,60,74] the pentafluoride of each being the only product. Unfortunately, not all the metal was fluorinated and in each case the pentafluoride formed in the reactor was contaminated with unreacted metal.

Only 1-3% of the platinum was fluorinated to the hexafluoride, the residue being a mixture of PtF_5 , PtF_4 and unreacted metal. More

Table 2.1 Reaction Conditions Employed During Fluorinations in Static System

Reaction Conditions	Ru	Os	Rh	Ir	Pt
Initial Pressure of Fluorine at 25°C (atm).	5-6	3-4	5-6	3-4	6
Temperature of Reaction (°C).	250	300	200	300	180-190*
Time of Reaction (hours)	5-6	3-4	7-8	4-6	6-7
% Hexafluoride	—	85-95	—	75-85	1-3
Residue	RuF ₅ , Ru(m)	none	RhF ₅ , Rh(m)	IrF ₅ ~5%	PtF ₄ , PtF ₅ Pt(m)

(m)=metal

* During the fluorination of platinum the temperature is kept below 200°C as above this temperature rapid decomposition occurs [127].

fluorine was condensed on to the residue and the reaction repeated several times, but each time only 1-2% of the residue was fluorinated to the hexafluoride. After fluorinating the residue 4 or 5 times unreacted metal still remained. Thus, it seems likely that an equilibrium between the metal and its fluorides exists in the static system. This is probably due to the decomposition of PtF_6 and PtF_5 , which are both very unstable at elevated temperatures; PtF_6 decomposes to PtF_4 and fluorine while PtF_5 decomposes to PtF_6 and PtF_4 .

It appears improbable that the P.G.M.'s can be separated by fluorination of the ore in a static system, since, Ru, Rh, and Pt are not totally fluorinated but leave unreacted metal in the reactor.

2.4 Dynamic System

2.4.1 General Procedure

A flow line was designed and constructed (chapter 6). Each metal was loaded into a nickel boat which was placed in the reactor and the glassware was assembled. The design of the glassware differed depending on the metal being studied. The whole line was evacuated and checked for leaks. Once leak tight the line was heated (100°C) under dynamic vacuum for 10-15 minutes, and then under a nitrogen stream for about an hour to drive off moisture on the surfaces of the line. The metal was hydrogenated *in situ* by passing a stream of hydrogen through the line and heating the reactor to about 400°C for 1 hour. The metal was allowed to cool under hydrogen and then the line was flushed with nitrogen for at least 12 hours to remove all traces of hydrogen. In all earlier work hydrogenation had been carried out in a crucible and then the sample transferred to the reactor through the atmosphere, allowing the metal to be exposed to atmospheric oxygen and moisture.

A F_2/N_2 mixture was passed through the line for about 1 hour, and the glass traps were warmed to passivate their surfaces. Cooling baths were placed around each trap and the reactor was heated to $\sim 400^\circ\text{C}$. Once the reaction was completed the fluorine flow was stopped and the line flushed with nitrogen for 2-3 hours before the

glass traps were sealed off under about 600mmHg N₂.

2.4.2. Osmium

Only the volatile OsF₆ was expected to be produced by the fluorination of osmium [31-38]. Accordingly the apparatus was assembled as shown in figure 2.1 and dry ice cold traps were used to collect the products. Almost immediately after heating the reaction began, dense pale yellow fumes were produced and these collected in the cold traps, as a bright yellow solid. Reaction was very rapid and approximately 1g of osmium was fluorinated in 1 hour.

The yellow solid was found to be OsF₆ and, when the reactor was opened, the nickel boat was completely empty, thus, all the osmium had been transferred from the boat as volatile material.

During the initial experiments the osmium was not hydrogenated and the glass traps were not warmed in the presence of a F₂/N₂ stream. Thus, much lower yields (70-80%) of OsF₆ were produced than had been expected. Three observations help to explain this low yield. Firstly, a small amount of white material was deposited prior to the deposition of OsF₆, this material may have been OsO₄. Secondly, a small amount of greenish material was observed at the neck of the reactor, this was probably OsF₅ formed by the reduction of OsF₆ on the hot glass, and finally about 50mmHg SiF₄ was released from the traps when they were opened to the line. This was produced by the attack of the OsF₆ on the unpassivated glass.

A modified procedure involving hydrogenation of the metal and seasoning of glass, resulted in approximately 90% yields of OsF₆.

2.4.3. Iridium

Iridium was expected to behave similarly to osmium, the hexafluoride being the only product. Therefore, the same preparative conditions were employed. Immediately on heating dense yellow vapours appeared which solidified in the cold trap. A 90% yield of IrF₆ was obtained, a small amount being lost when some IrF₆ decomposes on the hot glass at the exit of the reactor.

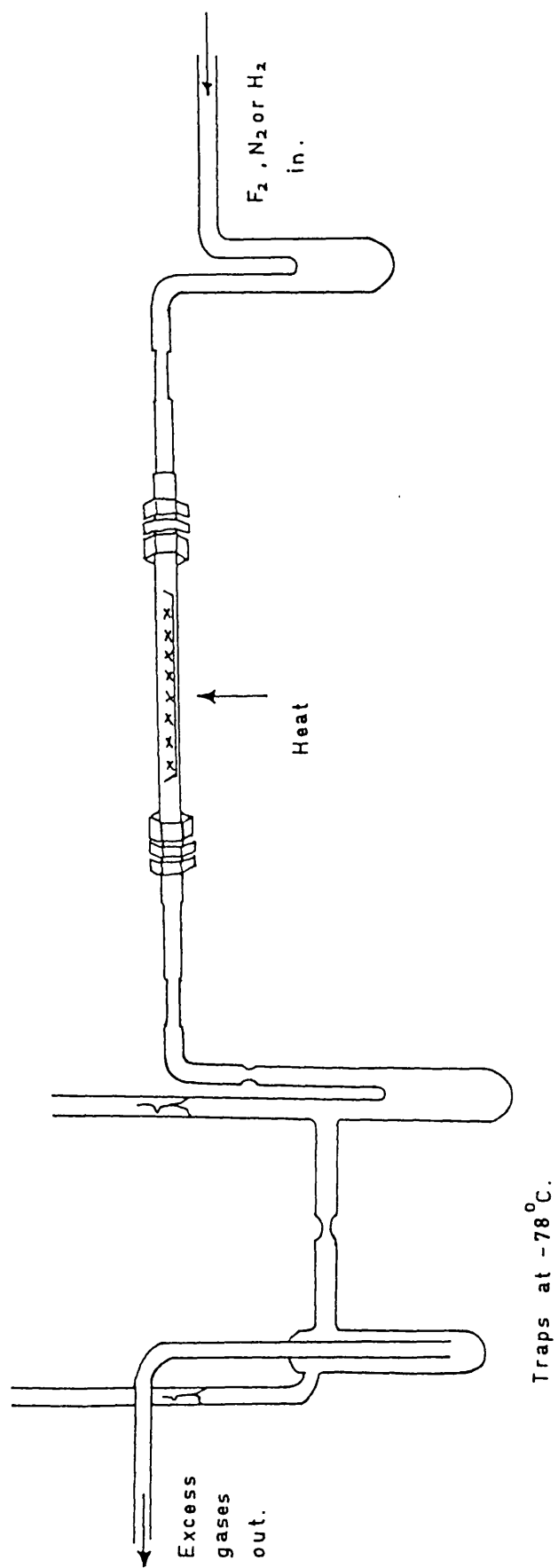


Figure 2.1 Apparatus for the Preparation of Volatile Fluorides

2.4.4. Platinum

There has been only one previous report of the fluorination of platinum in a flow system [75]. Small quantities of PtF_6 were reported to be formed but few other details were given.

It was expected that PtF_5 and PtF_4 would form as well as PtF_6 so the glassware was adapted (figure 2.2) to allow any liquid lower fluoride to flow from the copper reactor. On heating, dense yellow brown fumes appeared. These passed through the first trap, which was cooled to -24°C (ice/salt) and condensed in the trap cooled by dry ice as a deep red (almost black) crystalline solid (PtF_6). Thus, in all subsequent reactions two dry ice baths were used to prevent the loss of any PtF_6 . A red glassy material (PtF_5) and a fine yellow powder (PtF_4) were also found to collect slowly on the sidearm of the first trap. The reaction was completed in 1-2 hours, 60-70% of the platinum being converted to PtF_6 . More importantly all the metal was transferred from the boat as volatile fluoride.

Platinum tetrafluoride is not volatile thus it is possible that the PtF_4 formed results from the decomposition of PtF_5 , or was carried by the stream of F_2/N_2 through the reactor as soon as it formed.

2.4.5. Ruthenium

It has been reported that when a F_2/N_2 mixture is passed over ruthenium metal a dark green viscous liquid containing RuF_5 is produced [12]. It was also expected that tiny traces of RuF_6 would be formed. With this in mind the apparatus was assembled as shown in figure 2.2 and an ice bath and a dry ice bath were placed round traps 1 and 2 respectively. On heating, greenish brown fumes were immediately evolved and a glassy green material (RuF_5) began to form and trickle down into the first trap. Further down the side arm of the first trap a bright orange-red glassy material (chapter 5) began to form and in the second trap a buff brown solid (RuF_6) collected. The brown RuF_6 was extremely difficult to manipulate and could not be stored in a nickel can at room temperature. The percentage yield of RuF_6 produced could not, therefore, be accurately determined,

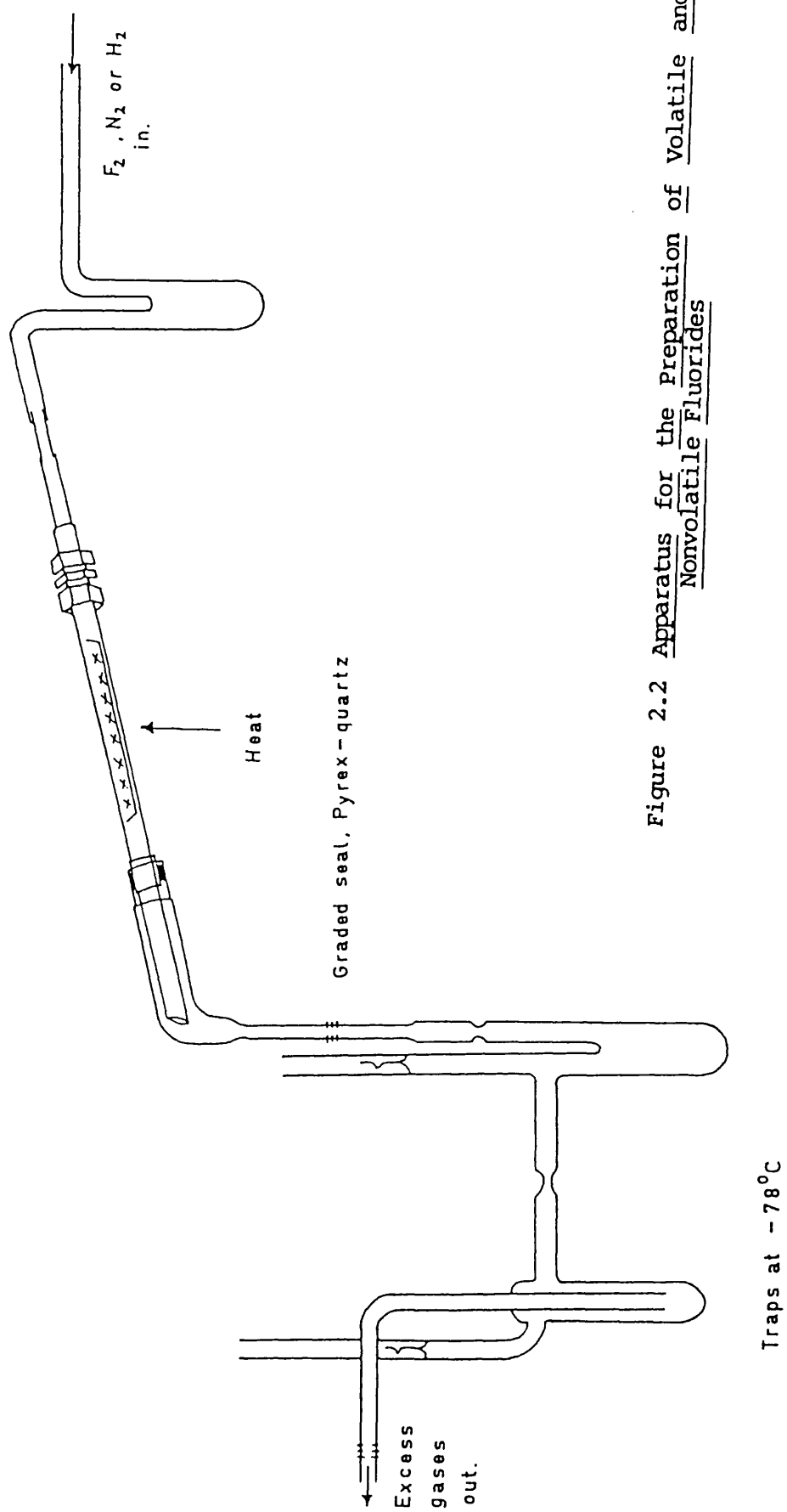


Figure 2.2 Apparatus for the Preparation of volatile and nonvolatile fluorides

although it was observed to be 40-60% of the product. The reaction was complete in 2-3 hours and on opening the reactor it was found that no metal was left in the boat, indicating that all the ruthenium had been fluorinated to volatile fluorides.

The first fluorination of ruthenium was conducted using Pyrex traps. However, large amounts of RuF_6 were produced which attacked the Pyrex and hence, all further preparations were carried out using quartz collection vessels and the design of the collection apparatus was adapted in order to aid the collection of the red glassy material (figure 2.3).

2.4.6. Rhodium

Having observed that RuF_6 and RuF_5 were formed when Ru metal was fluorinated it was expected that RhF_6 and RhF_5 would be similarly produced when Rh metal was fluorinated. Like RuF_6 , RhF_6 is an extremely powerful fluorinating agent which rapidly attacks Pyrex. Thus, the collection apparatus were constructed of quartz and assembled as shown in figure 2.2. A red glassy material (RhF_5) began to form on the side arm of the first trap about 10-15 minutes after fluorination began and then a red brown powder collected in the second trap (RhF_6). The fluorination was stopped after 4-5 hours, but it was found that 80% of the metal was still in the boat. The second reaction was allowed to continue for over 12 hours. This time only 30% of the metal remained in the boat. Thus, if the reaction was allowed to continue for a sufficient period it would be expected that all of the rhodium would be volatilised as a fluoride.

2.4.7. Palladium

After fluorinating palladium for several hours, without producing a volatile product, reaction was stopped and the reactor was taken into the dry box where it was opened. It was found to contain a black solid ($\text{Pd}[\text{PdF}_6]$) and unreacted metal. It should be noted that palladium metal is not hydrogenated before fluorination because at 400°C palladium reacts with hydrogen to form a hydride.

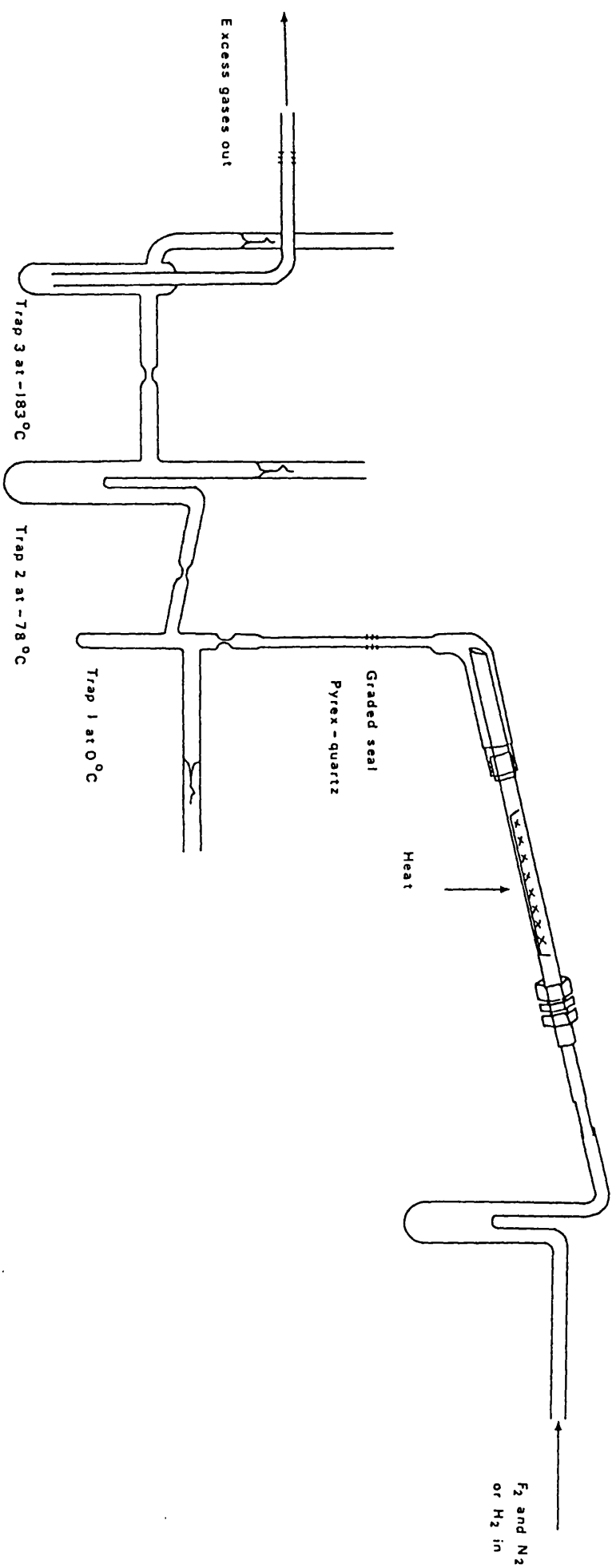


Figure 2.3 Apparatus for the Preparation of Volatile and Nonvolatile Fluorides

2.4.8. Discussion

Previous preparative procedures for the fluorination of P.G.M.'s have involved the prefluorination of a glass and metal apparatus, the hydrogenation of powdered metal at red heat in a (usually) porcelain crucible and the introduction of reduced metal into the fluorination apparatus by transfer through the atmosphere. These procedures have resulted, inevitably, in both the interior of the apparatus and the reduced metal being exposed to atmospheric moisture and oxygen.

The procedures developed in the present work have resulted in total elimination of water and oxygen and, in a number of cases, this has resulted in the products of the reaction being significantly different from those reported in earlier work. In particular, it appears that the higher oxidation state fluorides are produced in higher yields. The current work has also yielded quantitative data on the various products obtained.

In the osmium and iridium cases the fluorinations proceeded essentially as previously reported [31-38,93-96]. Hexafluorides are produced in high yields and the yields have been recorded. Platinum gave the hexafluoride, pentafluoride and the tetrafluoride but the hexafluoride was produced in 69-70% yield. This is in sharp contrast to earlier work [75] where only very low yields of PtF_6 were obtained.

Previous work on the dynamic fluorination of ruthenium metal powder has always yielded black tars which contain significant quantities of $\text{RuO}_2 \cdot 2\text{H}_2\text{O}$, but from which RuF_5 could be distilled. The early stages of this reaction produced a pale yellow volatile material, which was recently shown to be RuO_4 [163]. Using the new preparative technique the main product is RuF_6 , which is produced as a volatile brown solid, and there are smaller quantities of RuF_5 , which appears as a clear grass green liquid and glass, and a previously unknown red material which is believed to be a new form of RuF_5 (chapter 5).

Efforts to prepare volatile rhodium fluorides in dynamic systems have not been very successful. The hexafluoride has not

previously been obtained in a flow system and attempts to prepare the pentafluoride by direct fluorination of the metal powder at low temperatures have produced only small quantities. The new preparative procedure has produced a volatile brown vapour which has the physical properties attributed to RhF_6 together with larger quantities of a deep red liquid which appears to be RhF_5 . Both compounds are exceptionally powerful oxidative fluorinating agents and definitive characterization has been difficult. Nevertheless, it is clear that the new preparative method produces high yields of volatile rhodium fluorides.

2.4.9. Conclusion

It was possible to transfer all the metals except palladium from the boat into the collection traps. Thus, it may be possible to use dynamic fluorination to separate a mixture of P.G.M.'s.

The next step is to try to fluorinate a mixture of P.G.M's.

2.5. Initial Fluorination of a mixture of P.G.M's

2.5.1. Preparation of P.G.M. Mixture

A mixture of P.G.M's was prepared with the following ratio:-

Pt	100
Pd	200
Rh	13
Ru	15
Os	3
Ir	3

This ratio was chosen because it is a close approximation to that commonly obtained in ores.

2.5.2. Fluorination

The mixture was loaded into a nickel boat and placed in the reactor. The glassware was then assembled as shown in figure 2.3, the line was passivated as previously discussed and the metal was fluorinated for 2 hours. Each trap was then sealed, its contents hydrolysed and the hydrolysis products and residue in the reactor were sent for analysis to Johnson Matthey Technology centre.

2.5.3. Results

	Pt(mg)	Pd(mg)	Rh(mg)	Ru(mg)	Ir(mg)
Residue from boat	46	938	9	2	1
Residue from reactor	28	---	22	16	1
Trap 1 0°C	103	---	9	12	---
Trap 2 -78°C	145	---	6	10	6
Trap 3 -183°	48	---	4	9	6
Total	369	938	50	49	14

Total metal out (except Os) = 1.420g

Metal in (-Os)= 1.475g.

The results are very encouraging since, the majority of each metal with the exception of palladium, was removed from the boat as a volatile fluoride. It should be noted that the proportions of each metal left in the boat bears a close resemblance to the ease of production of the volatile fluorides, a much higher percentage of rhodium being left in the boat than Ir, Pt, or Ru. From these results it appears likely that if the fluorination is allowed to continue for 5-6 hours only palladium will remain in the boat.

Chapter 3

Analysis of Platinum Group Metal Fluorides

Chapter 3

Analysis of Platinum Group Metal Fluorides

3.1. Introduction

After each fluorination the products were characterized using a variety of techniques and as much spectroscopic data as possible was compiled for each. It was hoped that a method could be found to clearly identify each of the fluorides, so that when a mixture of metals was fluorinated, the fluorides collected in each fraction could be easily identified.

3.2. Mass Spectrometry

3.2.1. Introduction

Mass spectrometry was a very useful technique. It was used to study hexafluorides and pentafluorides and provided a good method for assessing the purity of the products as well as providing definitive identification. The natural abundances of the isotopes of the P.G.M's are shown in table 3.1.

3.2.2. Hexafluorides

The hexafluorides were admitted into the mass spectrometer directly from the storage cans via a copper spray-on tube with a Teflon end, which acted as an electrical insulator. Fluorine, followed by several doses of the hexafluoride was passed down the tube and pumped out through the mass spectrometer to season the tube and the ionization chamber of the mass spectrometer before the spectra were recorded.

This method worked well for OsF_6 , IrF_6 and PtF_6 and good spectra were obtained for each (figure 3.1, 3.2, 3.3, and table 3.2). Unfortunately, a spectrum of RuF_6 could not be obtained using this method. RuF_6 is very reactive and cannot be stored in nickel storage cans at room temperature as it will rapidly decompose. It is therefore taken directly from the quartz collection vessels.

Before entering the mass spectrometer the RuF_6 attacked the Teflon tip producing spectra which showed only the fragmentation pattern of a $(\text{CF}_2)_n$ chain. The Teflon tip was replaced with a quartz tip, and the RuF_6 was taken directly from the quartz collection vessel into the mass spectrometer, but it was still not possible to obtain spectra of RuF_6 . Peaks due to SiF_4 , RuO_4 , WF_6 and $(\text{CF}_2)_n$ were observed. The SiF_4 and RuO_4 were probably formed due to attack of the RuF_6 on the silica. The WF_6 is thought to result from the RuF_6 fluorinating the tungsten filament and $(\text{CF}_2)_n$ may be formed via attack of RuF_6 on the Teflon o-rings inside the mass spectrometer. Therefore, although RuF_6 must be reaching the source, no spectrum is observed because of its powerful oxidative fluorinating ability and rapid decomposition.

It was anticipated that the MF_5^+ ion would be the most abundant, and this is the case for OsF_6 and PtF_6 . However, the IrF_4^+ ion appears to be the most abundant species in the IrF_6 case. This is probably due to the relative stabilities of the MF_5^+ and MF_4^+ species and the kinetics of the reactions in the mass spectrometer.

3.3.3. Pentafluorides

Attempts were made to obtain mass spectra of RuF_5 , OsF_5 , IrF_5 and PtF_5 . It was expected that signals due to the monomeric, dimeric, trimeric and tetrameric species would be observed for RuF_5 [27,28,60]. However, the tetrameric species for IrF_5 , OsF_5 and PtF_5 would be outside the mass range of the spectrometer, hence, these would not be observed.

It has previously been reported that monomeric, dimeric and trimeric species have been observed for PtF_5 [27,28,60], using molecular beam mass spectrometry, but a signal due to PtF_6^+ is also observed. It is known that PtF_5 is very unstable and rapidly decomposes under vacuum to PtF_6 and PtF_4 and this may explain the presence of the PtF_6^+ ion. It seems unlikely that polymeric species would be observed in the present study as the PtF_5 is vapourised prior to its entrance into the spectrometer and because only very small amounts enter the mass spectrometer, all the PtF_5 would decompose to PtF_6 and PtF_4 before reaching the source.

**Table 3.1 Natural Abundancies of the Isotopes of the Platinum
Group Metals (Percentage).**

Ruthenium	Rhodium	Palladium
96 5.51	103 100	102 1.0
98 1.57		104 11.0
99 12.72		105 22.2
100 12.62		106 27.3
101 17.07		108 26.7
102 31.61		110 11.8

Osmium	Iridium	Platinum
184 0.018	191 37.3	192 0.78
186 1.59	193 62.7	194 32.9
187 1.64		195 33.8
188 13.3		196 25.3
189 16.1		198 7.21
190 26.4		
192 41.0		

Figure 3.1 Mass Spectrum of OsF₆ (Conditions 70ev, 4kV, 70°C)

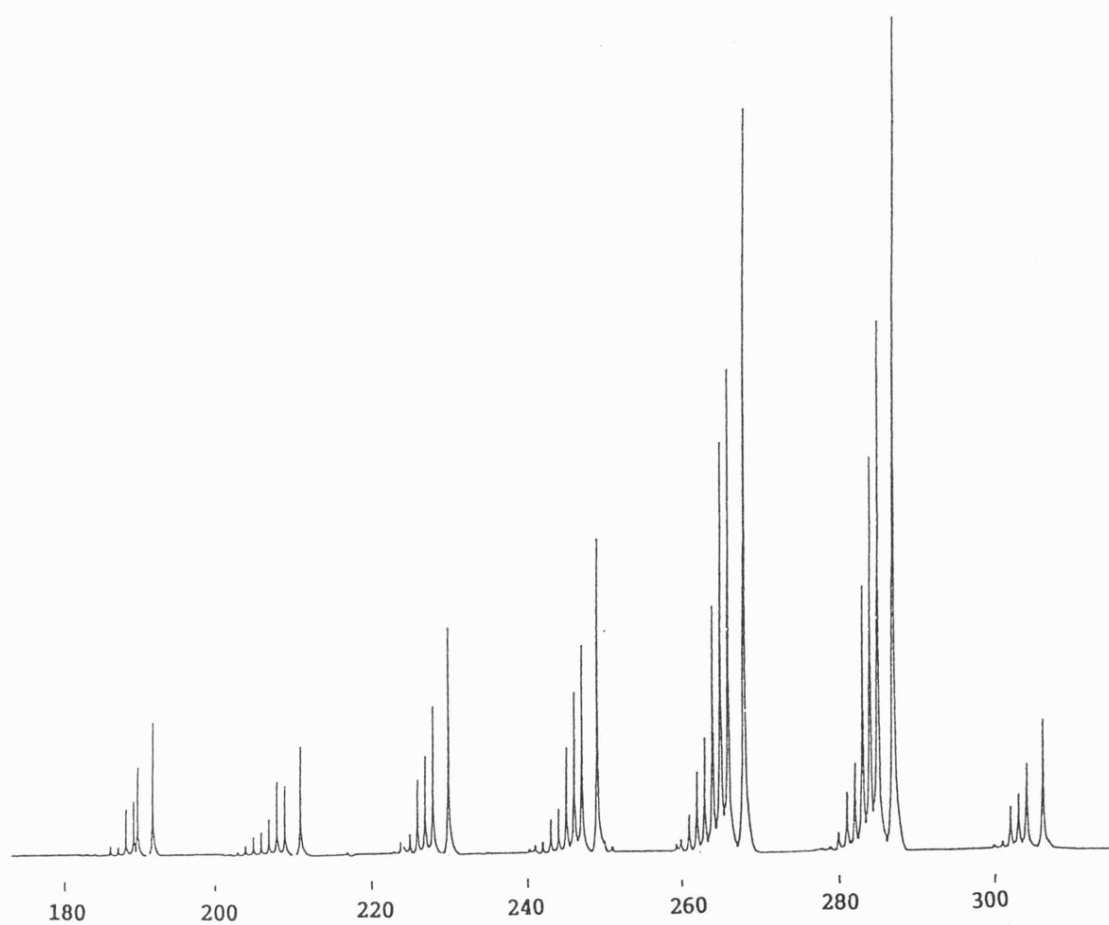


Figure 3.2 Mass Spectrum of IrF₆ (Conditions 70eV, 4kV, 70°C)

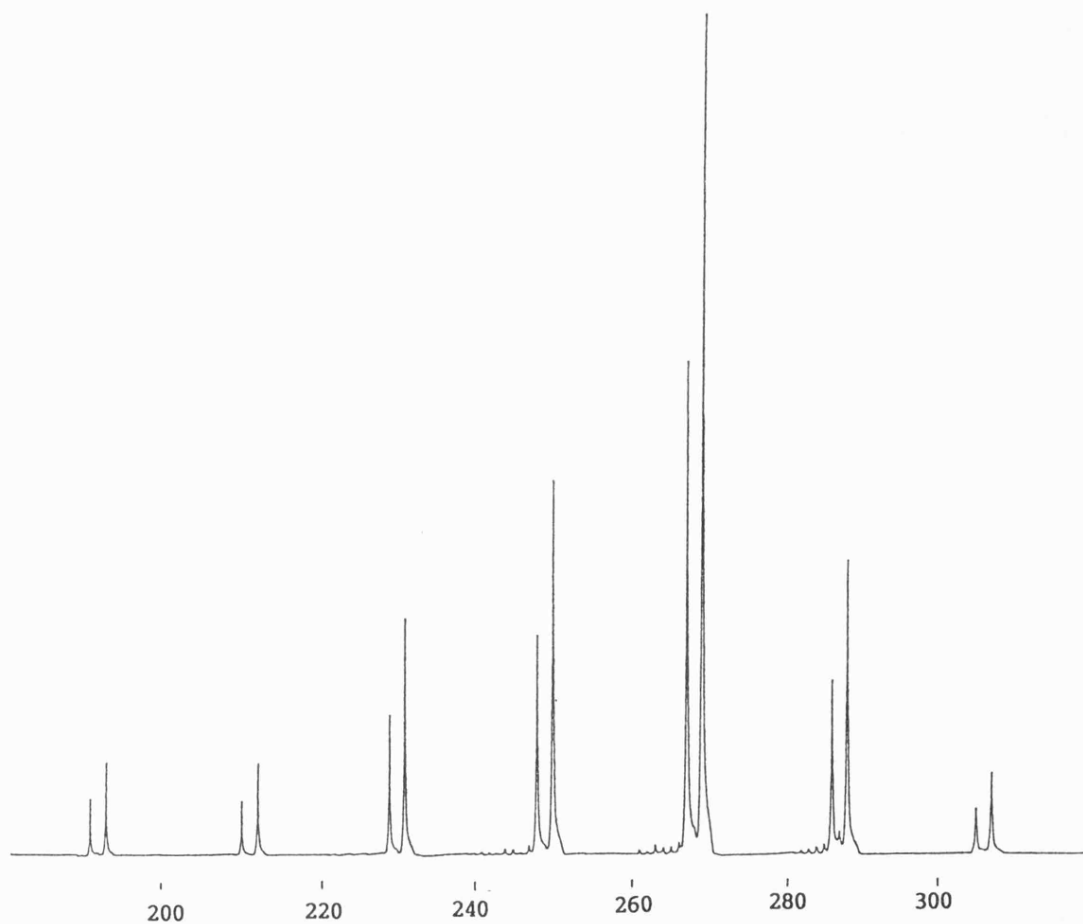


Figure 3.3 Mass Spectrum of PtF₆ (Conditions 70eV, 4kV, 70°C)

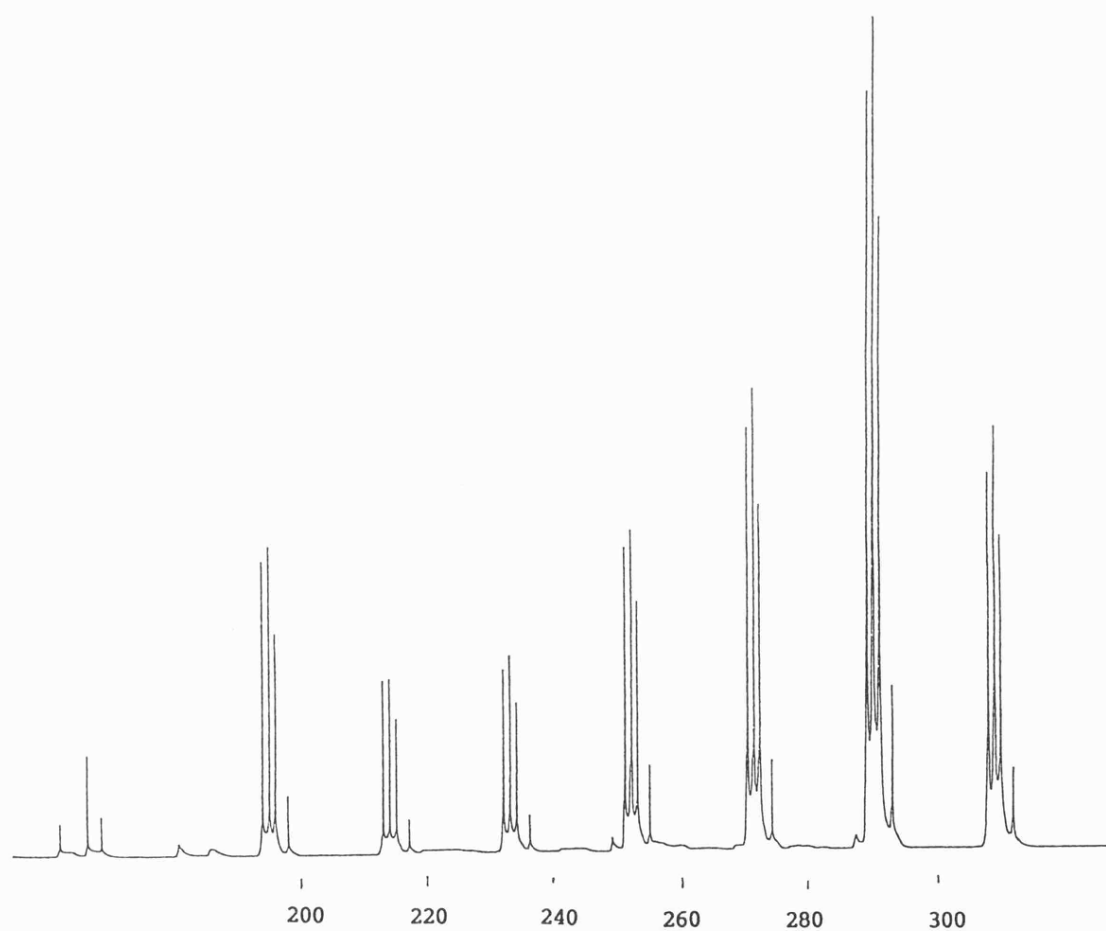


Table 3.2 Relative Abundancies of the Ions of the Hexafluorides

% Relative abundance (largest peak in each being 100%)

	OsF ₆ [*]	IrF ₆ [*]	PtF ₆ [*]
M ⁺	16.0	11.4	37.5
MF ⁺	13.1	11.0	21.4
MF ₂ ⁺	27.6	28.3	23.7
MF ₃ ⁺	37.9	44.9	38.6
MF ₄ ⁺	89.4	100	55.3
MF ₅ ⁺	100	35.4	100
MF ₆ ⁺	15.8	9.0	50.8

* all recorded at 70eV, 4kV and 70°C

The pentafluoride was placed in the mass spectrometer and the source temperature was increased until a good spectrum was observed. At 90°C good spectra of RuF_5 were obtained and the monomeric, dimeric, trimeric and tetrameric species were observed (figure 3.4). Good spectra of OsF_5 and IrF_5 were also obtained at 120 and 140°C respectively, each showing signals due to monomeric, dimeric and trimeric species (figure 3.5 and 3.6). Several samples of each pentafluoride were studied and the resulting spectra were reproducible, (tables 3.3, 3.4, 3.5).

The acceleration voltage at which these spectra were run gave highest sensitivity at 4kV, whilst, the mass range was greatest at 2kV. Thus, in order to detect the tetrameric species, spectra were recorded at 2kV, but to obtain good sensitivity and to detect impurities, samples were run at 4kV. It can be shown from these results that RuF_5 exists as a tetramer in the gaseous state. However, the occurrence of vapour phase trimeric, dimeric or monomeric species is uncertain, since, it is possible that these species result from fragmentation of the RuF_5 tetramer within the mass spectrometer. Similar conclusions are drawn for OsF_5 and IrF_5 , but, since the mass range was limited the tetramer, cannot be observed. It can only be concluded, therefore, that OsF_5 and IrF_5 exist as polymeric structures in the gas phase.

By running the spectra at much higher temperatures it was anticipated that an increase in the concentration of monomeric and a reduction in the concentration of the polymeric species would occur. However, at 210°C, very little difference was observed for RuF_5 or OsF_5 , but when IrF_5 was studied significant differences were observed. No trimeric species were found and only tiny traces of the dimeric species were recorded. The electron energy was reduced from 70eV to 50eV to check if this was partly responsible for the fragmentation, but the intensities remained the same. It, therefore, seem likely that at 210°C, IrF_5 is virtually monomeric.

Attempts were also made to record the spectra of PtF_5 (table 3.6.). Unfortunately, the spectra obtained were similar to those obtained for PtF_6 , no polymeric species were observed and peaks due

Figure 3.4 Mass Spectrum of RuF_5 (Conditions 70eV, 90°C)

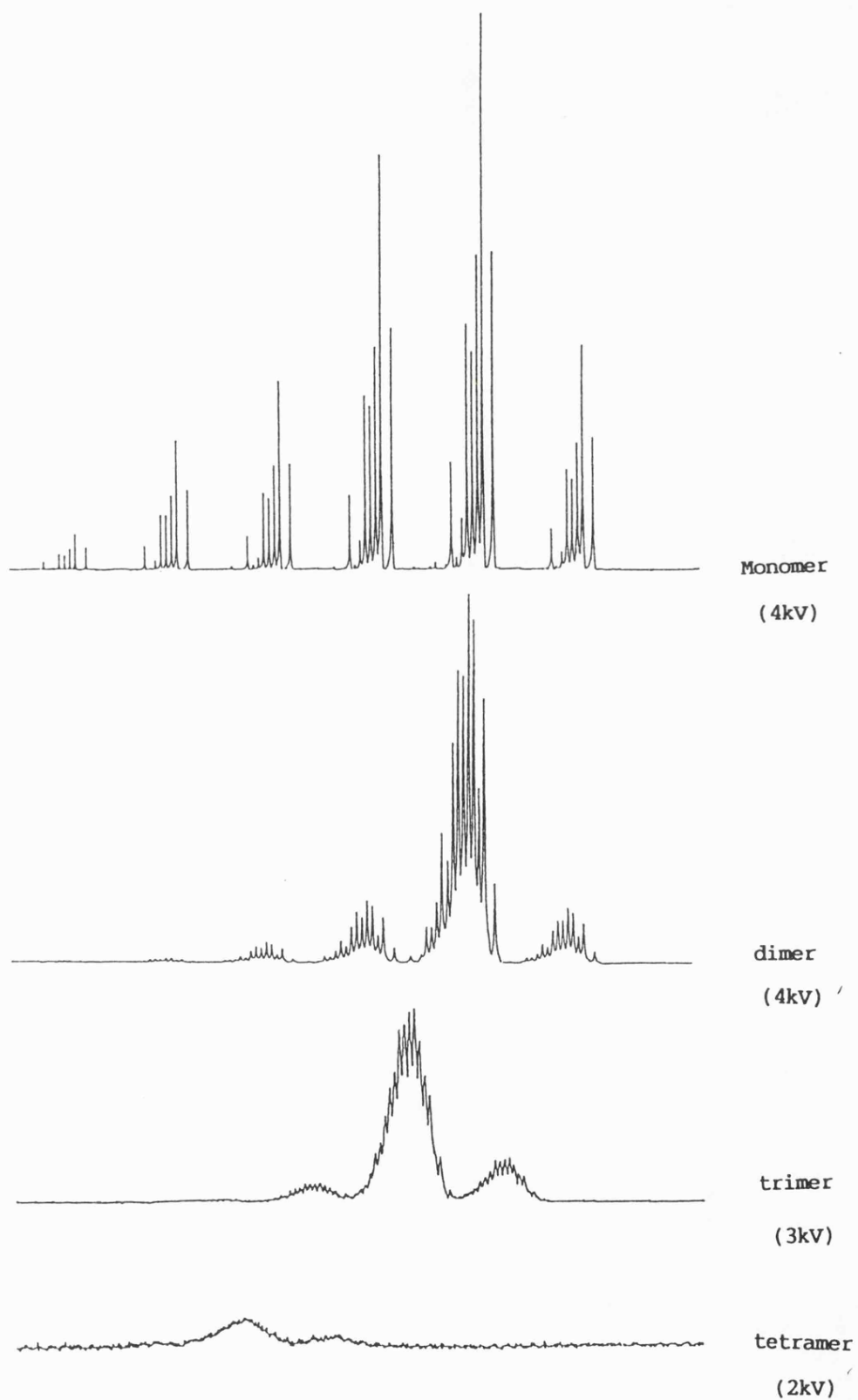


Figure 3.5 Mass Spectrum of OsF_5 (Conditions 70eV, 120°C)

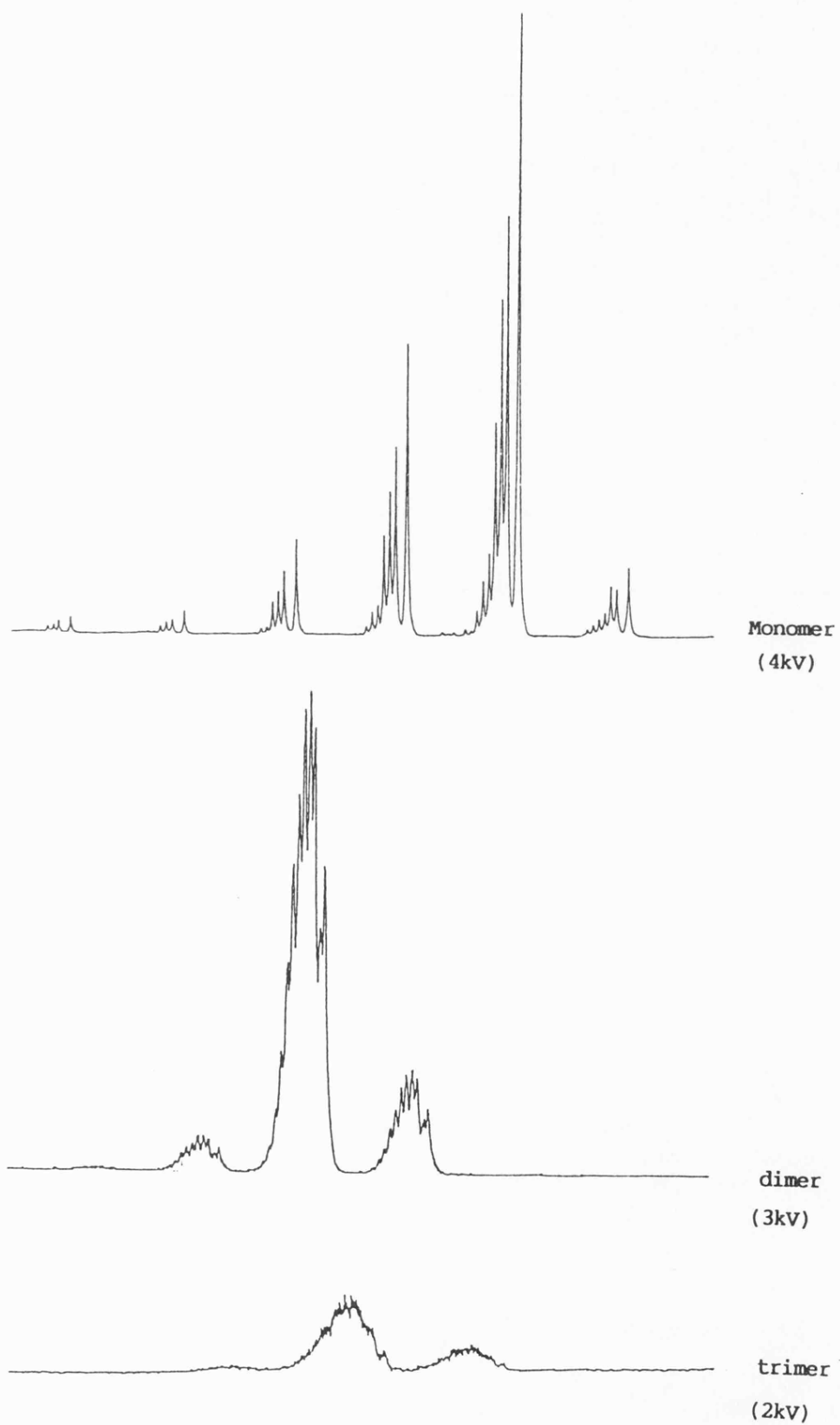


Figure 3.6 Mass Spectrum of IrF₅ (Conditions 70eV, 140°C)

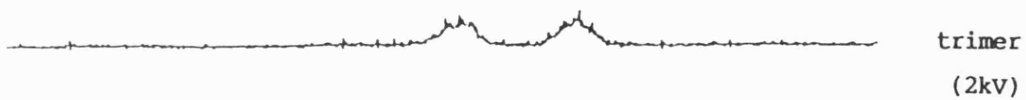
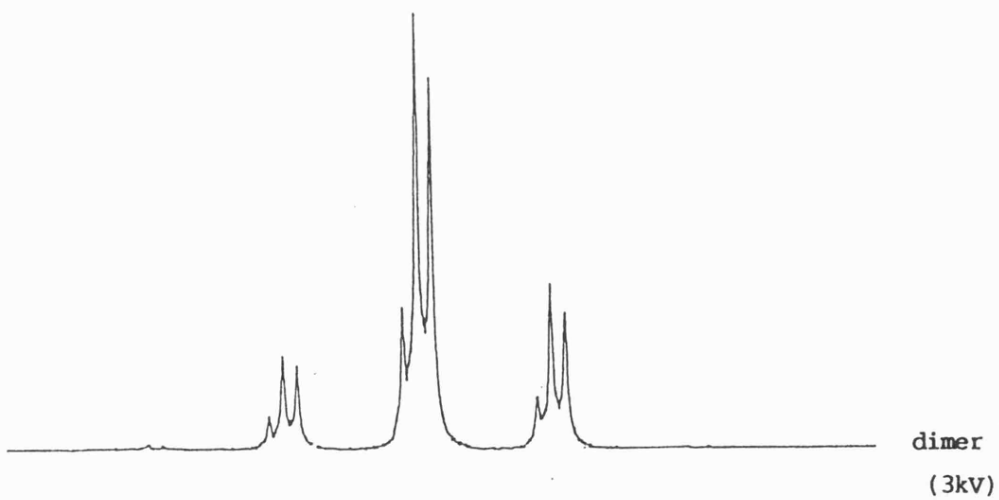
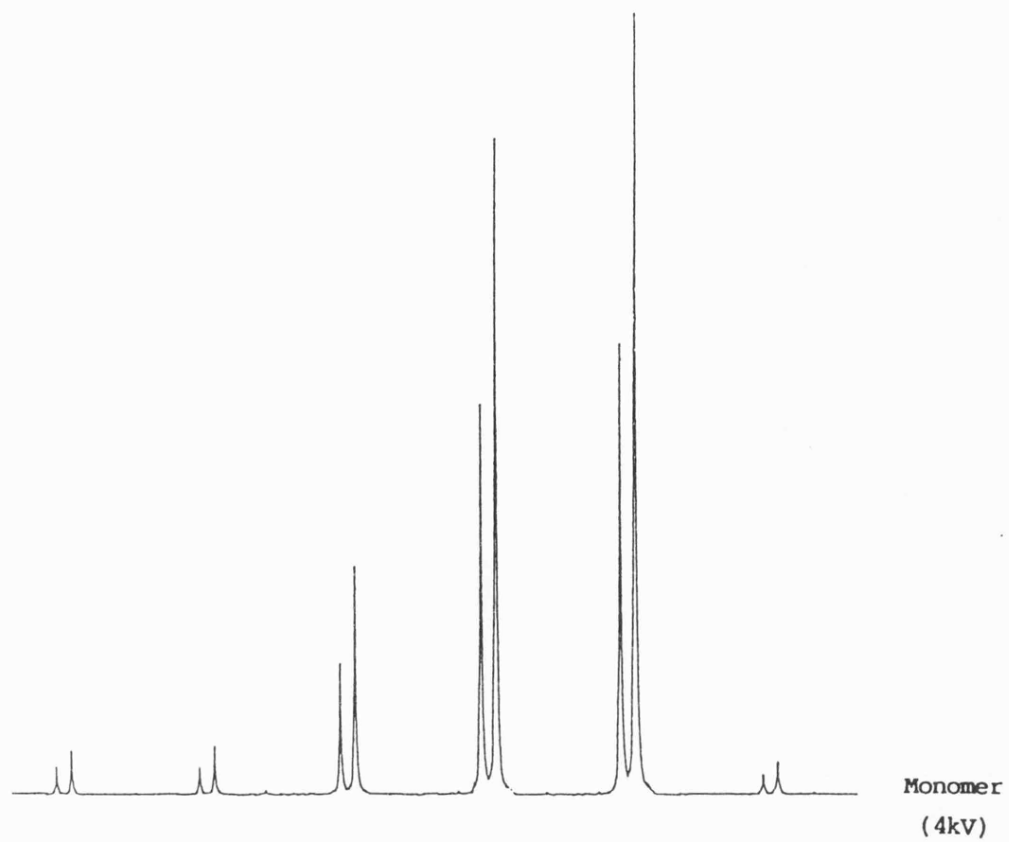


Table 3.3 Mass Spectroscopic Data For (RuF₅)₄

% Relative Intensity (Highest peak = 100%)

	90°C 4kV		90°C 3kV		90°C 2kV	
Ru ⁺	5.8	6.5	6.2	6.1	5.3	6.1
RuF ⁺	19.5	23.7	20	25.3	19.2	20.0
RuF ₂ ⁺	28.7	34.4	28.9	35.8	26.7	30.0
RuF ₃ ⁺	69.9	74.4	68.9	80.5	60.5	70.2
RuF ₄ ⁺	100	100	100	100	100	97.7
RuF ₅ ⁺	4.0	40.9	49.7	41.4	48.9	40.9
Ru ₂ F ₆ ⁺						1.4
Ru ₂ F ₇ ⁺	3.2	3.7	---	7.4	3.0	6.1
Ru ₂ F ₈ ⁺	10.3	11.2	8.3	17.2	10.5	17.4
Ru ₂ F ₉ ⁺	65.5	65.8	85.5	92.1	74.8	100
Ru ₂ F ₁₀ ⁺	10.3	10.0	15.9	13.9	16.5	11.6
=====						
Ru ₃ F ₁₃ ⁺			2.8	4.7	1.1	3.7
Ru ₃ F ₁₄ ⁺			26.2	29.8	18.4	37.7
Ru ₃ F ₁₅ ⁺			6.2	8.8	4.9	6.9
=====						
Ru ₄ F ₁₉ ⁺						2.8
Ru ₄ F ₂₀ ⁺						0.7

==== Limit of mass range

Table 3.4 Mass Spectroscopic Data for (OsF₅)₄

% Relative Intensity (Highest Peak = 100%)

	4kV			3kV	2kV
	60°C	100°C	120°C	120°C	120°C
Os ⁺	6.5	8.7	2.8	2.6	2.8
OsF ⁺	2.4	5.9	3.5	3.2	3.5
OsF ₂ ⁺	14.4	15.1	15.1	14.6	14.4
OsF ₃ ⁺	53.2	49.0	46.6	45.3	44.2
OsF ₄ ⁺	100	100	100	100	100
OsF ₅ ⁺	9.7	11.1	11.1	10.0	13.0

=====

Os ₂ F ₈ ⁺	3.2	4.4
Os ₂ F ₉ ⁺	43.5	56.3
Os ₂ F ₁₀ ⁺	9.4	10.7

=====

Os ₃ F ₁₄ ⁺	13.5
Os ₃ F ₁₅ ⁺	1.4

=====

==== Limit of mass range

Table 3.5 Mass Spectroscopic Data for (IrF₅)₄

% Relative Intensity (Highest Peak =100%)

	140°C			210°C	
	4kV	3kV	2kV	3kV	2kV
Ir ⁺	5.6	7.0	10.4	15.05	26.5
IrF ⁺	6.1	7.0	7.9	14.6	12.4
IrF ₂ ⁺	28.9	26.0	28.6	36.9	32.7
IrF ₃ ⁺	84.1	75.6	71.9	100	100
IrF ₄ ⁺	100	100	100	56.8	62.8
IrF ₅ ⁺	4.2	6.3	5.5	0	0
=====					
Ir ₂ F ₈ ⁺		9.5	6.8	0	0
Ir ₂ F ₉ ⁺		44.9	27.5	1.7	2.7
Ir ₂ F ₁₀ ⁺		17.2	10.9	0	0
		=====		=====	
Ir ₃ F ₁₄ ⁺			3.0		
Ir ₃ F ₁₅ ⁺			3.0		
			=====		=====

===== Limit of mass range

Table 3.6 Comparison of the Mass Spectroscopic Data of
 $(\text{PtF}_5)_4$ and PtF_6

% Relative Intensity (Highest Peaks = 100%)

ion	PtF_5			PtF_6
	4kV			4kV
	60°C	70°C	110°C	70°C
Pt^+	32.8	41.2	52.5	37.5
PtF^+	19.7	22.7	29.5	21.4
PtF_2^+	24.6	26.8	32.2	23.7
PtF_3^+	34.4	40.0	47.1	38.6
PtF_4^+	49.2	55.1	61.7	55.3
PtF_5^+	100	100	100	100
PtF_6^+	68.9	54.9	54.4	50.8

to PtF_6^+ ion were observed. On removal of the sample from the source, a yellow powder (PtF_4) remained in the capillary. Thus, it appears that the PtF_5 decomposes to PtF_6 and PtF_4 , before it reaches the source of the spectrometer.

3.3 Infrared Spectroscopy

3.3.1 Introduction

Infrared spectra of all the P.G.M. hexafluorides have been previously recorded and analysed [31,37,49,51-54,71,73,94,101,103]. In the present work, infrared spectroscopy has been used as an aid to determining the purity of each hexafluoride. Very little infrared data has been recorded for the pentafluorides. Data has been published for osmium and iridium pentafluoride [64,65] and the infrared spectrum of RuF_5 has been recorded (table 3.7)[163].

Table 3.7 Infrared spectra of Osmium, Iridium and Ruthenium pentafluoride (cm^{-1}).

OsF_5	IrF_5	RuF_5
Thin film (196°C)	Thin film (196°C)	Room temp.
		750 s,sh
712 m,sh	715 s,sh	715 vs
619 s	699 s,sh	
	678 vs	
657 s	642 vs	657 vs
530 s	533 m,br	525 s,br

The spectra recorded were of poor quality and, due to the complexity of the structures of the compounds, no group theoretical analysis has been attempted on them. In the present study efforts were made to obtain better quality spectra which would aid spectral assignment.

3.3.2 Hexafluorides

In the gas phase the P.G.M. hexafluorides have O_h symmetry, and each molecule is therefore expected to show two infrared active fundamentals of T_{1u} symmetry in the regions $700\text{--}750\text{ cm}^{-1}$ and $200\text{--}300\text{ cm}^{-1}$. In the present work the gas cell was fitted with AgCl windows. These have an infrared window above only 400 cm^{-1} and thus, we would expect to see only one infrared fundamental. Table 3.8 shows the values obtained in this work for the ν_3 fundamental and those previously recorded. Figure 3.7 shows a typical spectrum for a P.G.M. hexafluoride. This was recorded with only 1mm Hg pressure of the hexafluoride in the cell. In order to look for impurities in the samples further spectra were recorded with higher pressures of hexafluoride in the cell.

Table 3.8 Infrared fundamentals for P.G.M. Hexafluorides (cm^{-1}).

	ν_3 (Present work)	ν_3 (Previous work)
RuF_6	733	735 [73]
OsF_6	719	720 [51,53]
IrF_6	718	718 [94]
PtF_6	705	705 [54]

In all cases the samples were found to be pure. Small traces of OsO_4 (peak at 960 cm^{-1}) were observed in an early spectrum of OsF_6 , but, after the cell had become well seasoned by the OsF_6 , no sign of the OsO_4 appeared. Therefore, the OsO_4 must have formed from the hydrolysis of the OsF_6 on the interior surfaces of the cell. In all cases peaks due to ClF_3 were observed; these occurred at $1273(\text{s})$, $1022(\text{m})$ and $957(\text{m})\text{ cm}^{-1}$ [164]. The ClF_3 is undoubtedly due to attack of the hexafluorides on the AgCl windows.

When 20mm Hg pressure of the hexafluoride was introduced into the cell, bands were observed for the $(\nu_1+\nu_3)$ and $(\nu_2+\nu_3)$ combinations. This is in accord with previous work (Table 3.9). The spectra of OsF_6 showed a broadening of the $(\nu_2+\nu_3)$ combination with

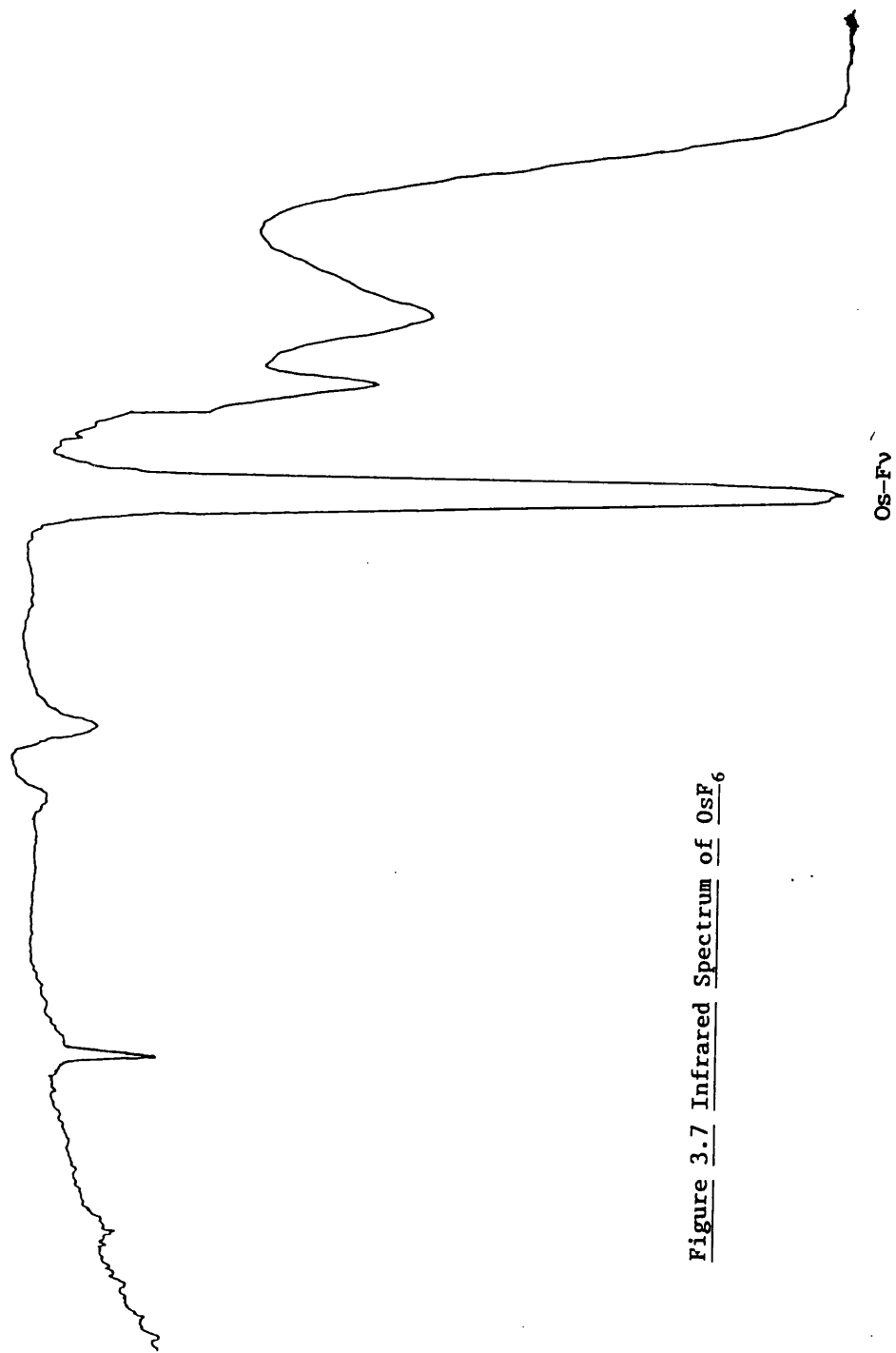


Figure 3.7 Infrared Spectrum of OsF_6

an accompanying loss of intensity. In the case of RuF_6 the broadening is so severe that no peak was observed. This phenomenon is due to the Jahn-Teller effect [165,166] which has been previously discussed several times in connection with the hexafluorides [73,103,51].

Table 3.9 Combination Bands of the P.G.M. Hexafluorides (cm^{-1}).

	Present		Previous		
	$(\nu_1+\nu_3)$	$(\nu_2+\nu_3)$	$(\nu_1+\nu_3)$	$(\nu_2+\nu_3)$	
RuF_6	1411	----	1410	----	[73]
OsF_6	1450	1350	1453	1352	[51]
IrF_6	1420	1365	1425	1364	[94,103]
PtF_6	1360	1306	1360	1306	[51]

It should be noted that the ν_3 fundamentals were also very broad being about 40cm^{-1} wide at the base line. Under closer examination the ν_3 fundamentals in OsF_6 and IrF_6 were found to be triplets. The peak positions are listed in Table 3.10. This is probably due to the rotational effects of the molecule giving PQR splitting. If this is the correct assumption, much sharper peaks should be found in the matrix isolated infrared spectra since, here the individual molecules will be held at 14K in an inert matrix and no rotational motion will be possible.

Table 3.10 ν_3 Fundamentals of P.G.M. Hexafluorides (cm^{-1})

	ν_3		
OsF_6	712	718	725
IrF_6	713	718	725

3.3.3 Pentafluorides

Attempts were made to record the infrared spectra of RuF_5 and OsF_5 . The powdered samples were placed between two dry KBr discs in the dry box, then compressed in a cell holder and quickly taken to the spectrometer. However, air and moisture immediately began to attack the samples at the edges of the plate and the whole sample decomposed before analysis was complete. A special plate holder was therefore designed (chapter 6) to hold the KBr discs in an atmosphere of dry nitrogen. This proved more successful and permitted infrared spectra to be recorded (Table 3.11). As with the previous work, a broad band is observed between $500\text{--}530\text{ cm}^{-1}$, this can be assigned as the $\nu(\text{M-F-M})$ stretching mode. Due to the complexity of the structure, none of the other bands have been definitively assigned, although tentative assignments can be made. The bands at $\sim 700\text{ cm}^{-1}$ may be due to the axial terminal Ru-F stretches and those at $600\text{--}650\text{ cm}^{-1}$ to the equatorial Ru-F stretches.

Table 3.11 Infrared spectra of OsF_5 and RuF_5 .

OsF_5	RuF_5
720 m	735 m,sh
665 s,sh	705 s
645 s,br	655 m
620 m	580 m,br
525 m,sh	515 s,br

The spectra were not of good quality, and so it was decided to attempt to obtain spectra using matrix isolation infrared spectroscopy. Here the sample is sprayed as a vapour on to a cold window (14K) with a large excess of an inert gas (N_2 or Ar). The sample is immediately frozen in an inert matrix and, since no decomposition occurs, the spectra can be recorded at high resolution. The spectra obtained should be of much better quality as the peaks should be much sharper. This will aid spectral assignment. Matrix isolation will also enable us to ascertain whether the pentafluoride is polymeric in the vapour phase. The sample is sprayed into the spectrometer as a vapour (chapter 4) and is immediately frozen on the window.

3.4 X-ray Powder Diffraction

X-ray powder diffraction photography was used as a fingerprinting method for the pentafluorides. The photographs obtained were compared with existing data to ascertain if the samples were pure. It was noted that when RuF_5 and RhF_5 , prepared in the static system, were studied spurious lines were observed in the photographs. These lines were identified as being due to unreacted metal. However, the RuF_5 prepared in the dynamic system was found to be pure, no unidentifiable lines being observed. Attempts were made to record the powder pattern of PtF_5 . However, the pattern obtained was identical to that of PtF_4 , thus, the PtF_5 must have decomposed in the X-ray beam to PtF_6 and PtF_4 . No lines due to PtF_6 would be observed as this would be present as a vapour.

X-ray powder diffraction was also used to study the hexafluorides of Pt, Ir, and Os. The hexafluoride was distilled into a pre-seasoned capillary, cooled in liquid nitrogen, the capillary was sealed using a micro-burner and allowed to warm to room temperature. Enough hexafluoride must be distilled into the capillary to leave a solid sample when the sample warms to room temperature and exerts a vapour pressure of 200mmHg. The powder patterns obtained confirm that the hexafluorides have a cubic structures at room temperature [8,31,48,126].

3.5 Raman Spectroscopy

3.5.1 Hexafluorides

Previously, the gas phase spectra of some of the P.G.M. hexafluorides have been recorded [54,103]. In the present work it was decided to cool the hexafluoride in a cryostat to a temperature at which the solid state spectra could be recorded. No attempt was made to record the spectra of PtF_6 , RuF_6 or RhF_6 . It was not possible to transfer RuF_6 or RhF_6 into capillaries as they are too reactive. Although, PtF_6 can be distilled into a capillary, it is dark red and so will decompose in the laser light.

Attempts were made to record the Raman spectra of IrF_6 . A small amount of IrF_6 was distilled into a capillary, cooled under liquid nitrogen and sealed using a micro-burner. The capillary was then loaded into a cryostat (figure 6.6) and cooled to 94–98K. The sample was found to decompose easily at laser powers above 80mW but, if the laser power was kept low, typically 50mW, good quality spectra were obtained.

The factor group analysis has been carried out for MF_6 and an attempt has been made to assign the results. The hexafluorides are known to have O_h molecules, with C_s site symmetry and a $D_{2h}^{16} = \text{Pnma}$ space group [8].

Table 3.12. Correlation Table for MF_6 in the Solid State

A. Internal Modes

			x4
Molecules	Site	Unit cell	
O_h	$C_s(xz)$	D_{2h}^{16}	
ν_1, A_1g	A'	$Ag + B_2g + B_1u + B_3u$	
ν_2, Eg	$A' + A''$	$Ag+B_1g+B_2g+B_3g+A_1u+B_1u+B_2u+B_3u$	
ν_3, T_2g	$2A' + A''$	$2Ag+B_1g+2B_2g+B_3g+A_1u+2B_1u+B_2u+2B_3u$	
$\nu_{3,4}, 2T_1u$	$2(2A' + A'')$	$2(2Ag+B_1g+2B_2g+B_3g+A_1u+2B_1u+B_2u+2B_3u)$	
ν_6, T_2u	$A' + 2A''$	$Ag+2B_1g+B_2g+2B_3g+2A_1u+B_1u+2B_2u+B_3u$	

There should be 12 Raman active internal fundamentals, $2A_1g$, $4Eg$, and $6T_2g$.

B. Lattice Modes

Molecules \longrightarrow Site \longrightarrow Unit cell

O_h

$C_s(xz)$

D_{2h}^{16}

3 Transⁿ T_1u $2A' + A''$ $2A_g + B_1g + 2B_2g + B_3g + A_1u + 2B_1u + B_2u + 2B_3u$

3 Rotⁿ T_1g $A' + 2A''$ $A_g + 2B_1g + B_2g + 2B_3g + 2A_1u + B_1u + 2B_2u + B_3u$

There should be 6 Raman active translations and 6 Raman active rotations. Attempts can be made to assign the peaks (table 3.13).

Attempts were also made to record the Raman spectra of OsF_6 , but these proved unsuccessful, the OsF_6 rapidly decomposing in the laser beam at all available powers.

Table 3.13 Assignment of Raman Data of Iridium Hexafluoride

A. <u>Lattice Modes</u> (cm^{-1})		Assignment
19.7 (m)	}	Translations
26.7 (s)		
30.3 (s)	}	
35.2 (s)		
45.6 (m/w)		
53.7 (w)	}	Rotations
61.2 (s)	}	
66.0 (m/w)		
69.5 (w)	}	
75.5 (m)		
84.0 (w)		
92.0 (w)	}	
B. <u>Internal Modes</u> (cm^{-1})		
220.2 (w)	}	ν_5 , T_2g , but the spread of frequencies is too great to be accounted for by factor group splitting alone, components of ν_4 have show through due to site selection rules (267.0(s)= ν_5)
267.0 (s)		
279.0 (w)	}	
288.6 (w)		
299.0 (w)	}	
643.2 (m)	}	ν_2 , Eg. (2 of the 4 allowed components)
647.8 (m)	}	
693.9 (w)	}	Combination bands
696.0 (vw)	}	
702.2 (vs)	}	ν_1 , A_1g (702.2 Ag, 707.4 B_2g)
707.4 (m)	}	
1344.8 (m)	}	Combination bands.
1349.4 (w)		
1403.5 (w)	}	
1431.4 (w)		
1437.4 (w)		
1475.4 (w)	}	

Chapter 4

Matrix Isolation Spectroscopy

Chapter 4

Matrix Isolation Spectroscopy

4.1 Introduction

In the present study, matrix isolation has been used to permit high resolution spectroscopic studies of the extremely reactive P.G.M. fluorides to be undertaken with minimal corrosion and contamination problems. The sample is frozen at 10-14K in an inert matrix, the ratio of sample to matrix gas being about 1:1000. Hence, individual molecules of the fluorides are isolated and decomposition does not occur.

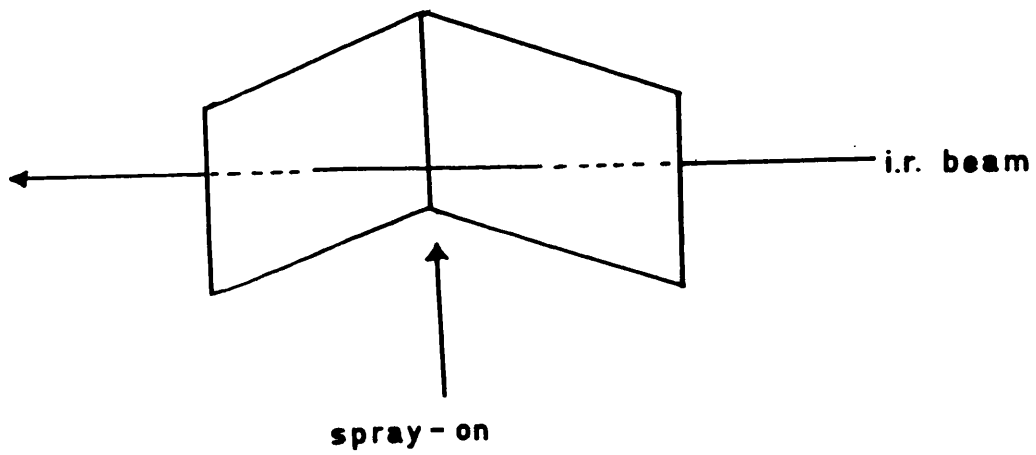
It is vital when carrying out matrix isolation studies to ensure that the sample is well isolated in the matrix gas. To achieve this, samples must be sprayed on slowly. The hexafluorides must be cooled to a temperature at which their vapour pressures are low enough to allow slow spray-on, whilst the pentafluorides require heating. The spray on rate can be monitored using infrared spectroscopy because it is possible, using a triangular CsI window (figure 4.1) to scan a narrow region of the spectrum repeatedly while spraying on the sample. Once the deposition rate has been established the same conditions are used to spray the sample on to the LiF window, used to record the u.v.-visible spectrum.

4.2. Hexafluorides

4.2.1. Preparation of Samples

The preparation of Os, Ir, and Pt hexafluorides was described in chapter 2. Rhenium hexafluoride was prepared by direct fluorination of the metal in a pre-fluorinated nickel reactor. To prevent contamination with the heptafluoride a 5% excess of the reduced metal sponge was heated (300°C) with 5atms. of fluorine.

Figure 4.1 Triangular Window



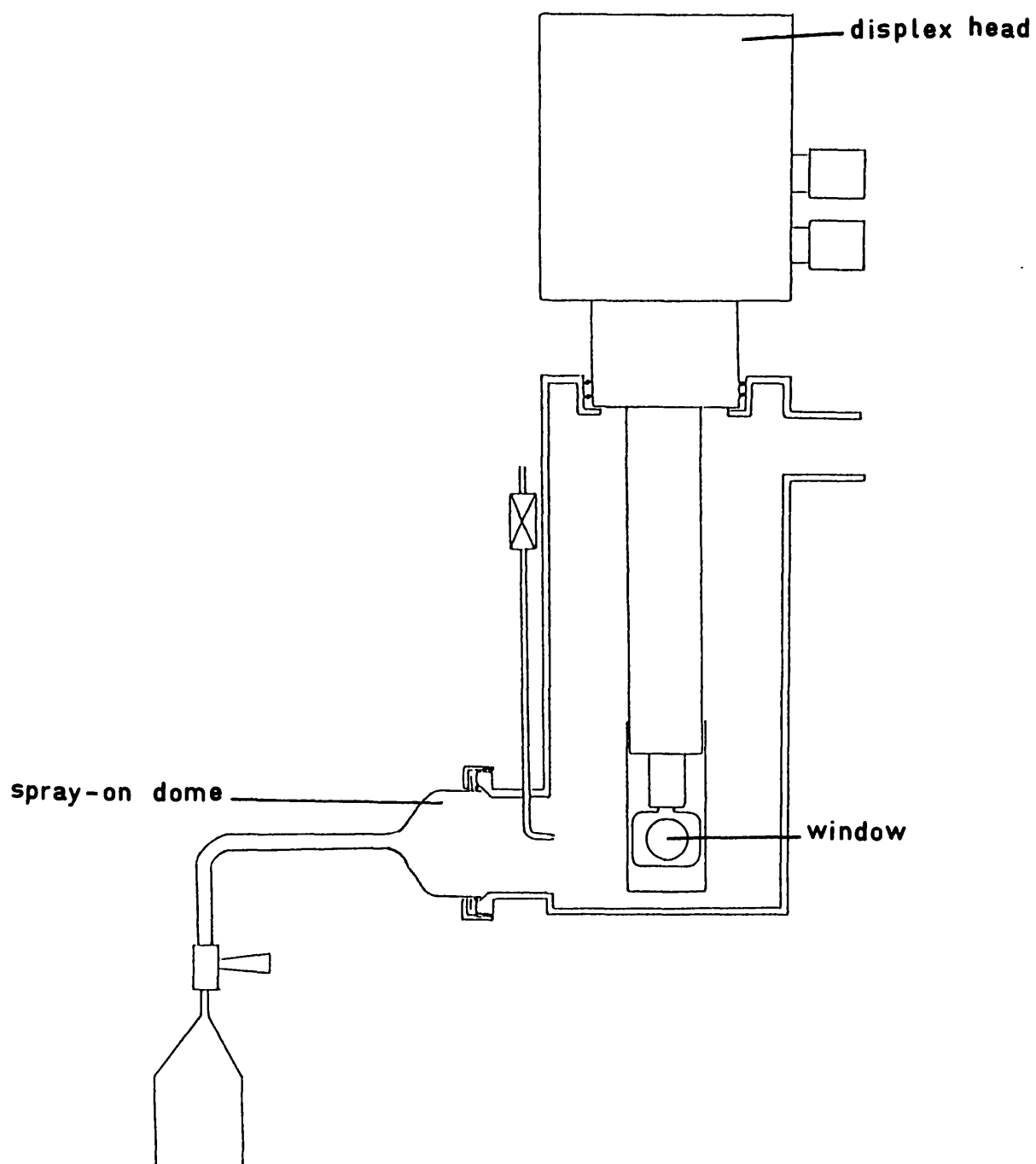
Samples of ReF_6 , OsF_6 , IrF_6 and PtF_6 were stored in pre-seasoned nickel cans fitted with Hoke bellows valves. These were sprayed directly from the can down a copper spray-on tube (figure 4.2). The rate at which the samples were sprayed onto the cold window was controlled using slush baths, ReF_6 , OsF_6 , IrF_6 and PtF_6 were maintained at 190, 195, 200, 232K respectively.

Unfortunately, RuF_6 is more unstable than the other hexafluorides and must be stored at -196° as it will decompose quickly at room temperature. Thus, it was sprayed on to the window directly from the quartz trap along a quartz tube. Initial experiments failed but it was later found to be possible to obtain a spectrum of RuF_6 using special conditions, which permitted the spray-on tube to be pre-seasoned with F_2 and ClF_3 . The quartz collection trap was attached to a specially constructed tube (figure 4.3), which was connected to the main vacuum manifold via a Chemcon connector. The apparatus was evacuated, heated to about 80°C , and repeatedly seasoned, first with fluorine and then with ClF_3 . The tube was then re-evacuated and sealed at A. The apparatus was connected to the matrix rig and the dome evacuated to 10^{-7}mmHg . The displacer head was then rotated causing the end of break-seal A to shatter, break seal B was then broken using nickel balls and the nitrogen inside (600mmHg) was pumped away. The Dewar of liquid nitrogen was lowered from around the trap and the RuF_6 was sprayed on to the cold window. The rate at which the sample was sprayed on to the window was controlled by raising and lowering the Dewar.

4.2.2 Infrared Spectroscopy

The vibrational fundamentals of ReF_6 , OsF_6 , IrF_6 , PtF_6 and RuF_6 have been reported previously [53-55,73] and the main reasons for carrying out matrix isolation infrared studies were, firstly to check sample purity, and secondly to establish suitable deposition conditions in preparation for further spectroscopic work. All five hexafluorides have O_h symmetry, and each molecule is thus expected to show two infrared active fundamentals (T_{1u} symmetry). The spectra in argon and nitrogen matrices showed characteristic absorptions in the regions $700\text{--}750\text{ cm}^{-1}$ and $200\text{--}300\text{ cm}^{-1}$ due to these modes.

Figure 4.2 Matrix Rig



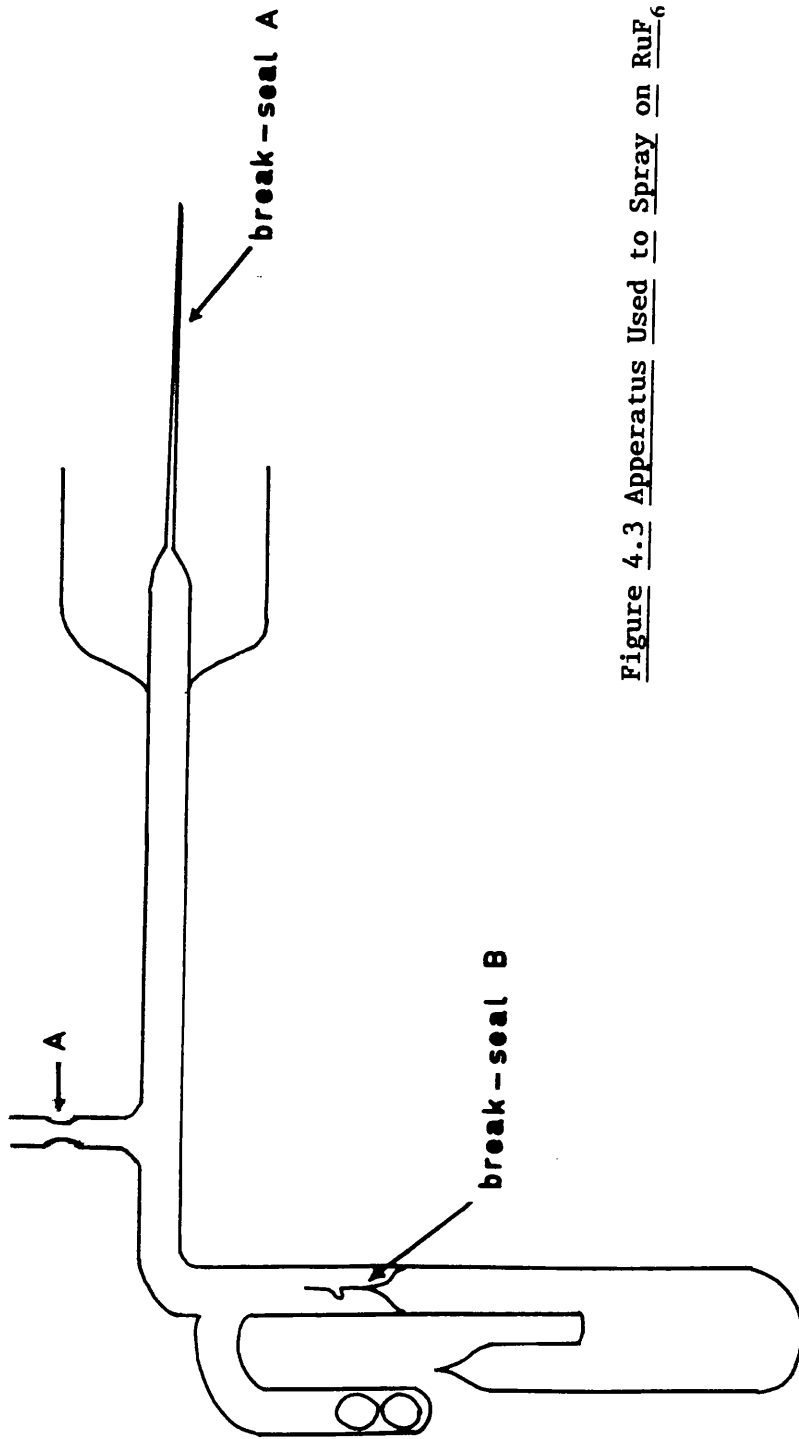


Figure 4.3 Apparatus Used to Spray on RuF₆

Figures 4.4 and 4.5 show typical survey spectra obtained from these hexafluorides. Table 4.1 compares the gas phase and matrix data.

Matrix spectra obtain from ReF_6 , IrF_6 , PtF_6 and RuF_6 indicate that the samples were essentially free from impurities. However, in the case of OsF_6 , OsO_4 was found to be present (band at *ca.* 960cm^{-1}). This, almost certainly arises from hydrolysis in those parts of the spray on system which cannot be adequately seasoned. Fortunately, as deposition proceeds, the growth of this impurity diminishes, and its formation can be eliminated by passing OsF_6 through the spray-on tube prior to cool-down.

Examination of the T_{1u} stretching modes under higher resolution revealed band splittings which were too large to be accounted for simply by metal isotope effects. Thus, for OsF_6 and RuF_6 in nitrogen two components were observed at 724.9 , 712.3 cm^{-1} and 736.5 and 726.5 cm^{-1} respectively with an approximate intensity ratio 1:2. This splitting may be due to a lifting of the T_{1u} degeneracy. There are two possible explanations for this, one being that the origin of these splittings lies in static Jahn-Teller distortions [51], the other that it is a result of matrix perturbations [164].

Iridium hexafluoride in argon shows an almost equal doublet at 719.3 , 716.0 cm^{-1} , but here and in some of the other systems studied, the splitting is probably due to multiple trapping sites.

These infrared studies established the conditions under which the title compounds could be satisfactorily isolated in low temperature matrices. They were generally carried out prior to the u.v.-visible experiments and usually immediately afterwards in order to check the integrity of the sample.

4.2.3 U.V.-Visible Spectroscopy

Introduction

Electronic spectra were recorded over the range *ca.* $190\text{--}900\text{nm}$ ($52\,000\text{--}11\,000\text{cm}^{-1}$) for Re, Os, Ir and Pt hexafluorides isolated in nitrogen matrices at 12K. Several u.v.-visible experiments were performed on each compound, and reproducibility between runs was

Figure 4.4 I.r. Spectra of Matrix-isolated Hexafluorides

(a) ReF_6 in N_2 , (b) OsF_6 in N_2 , (c) IrF_6 in N_2 , (d) PtF_6 in Ar

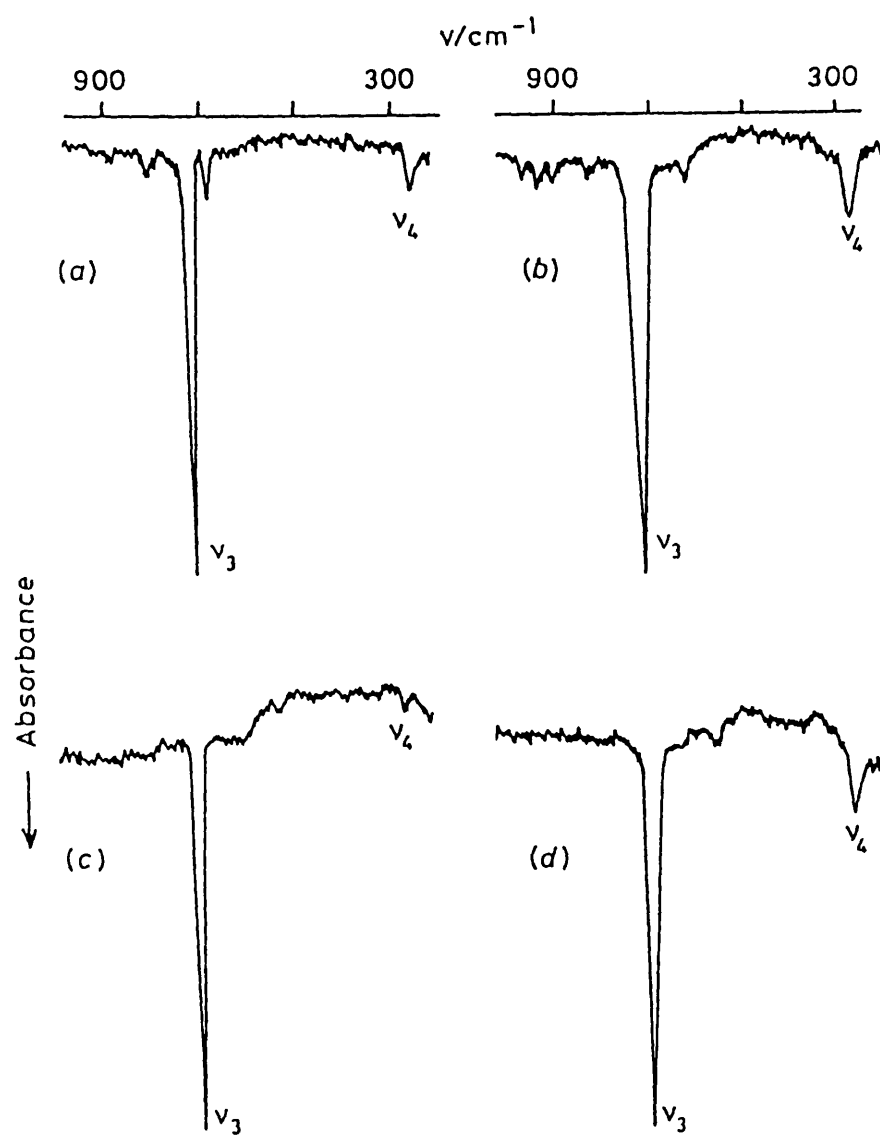
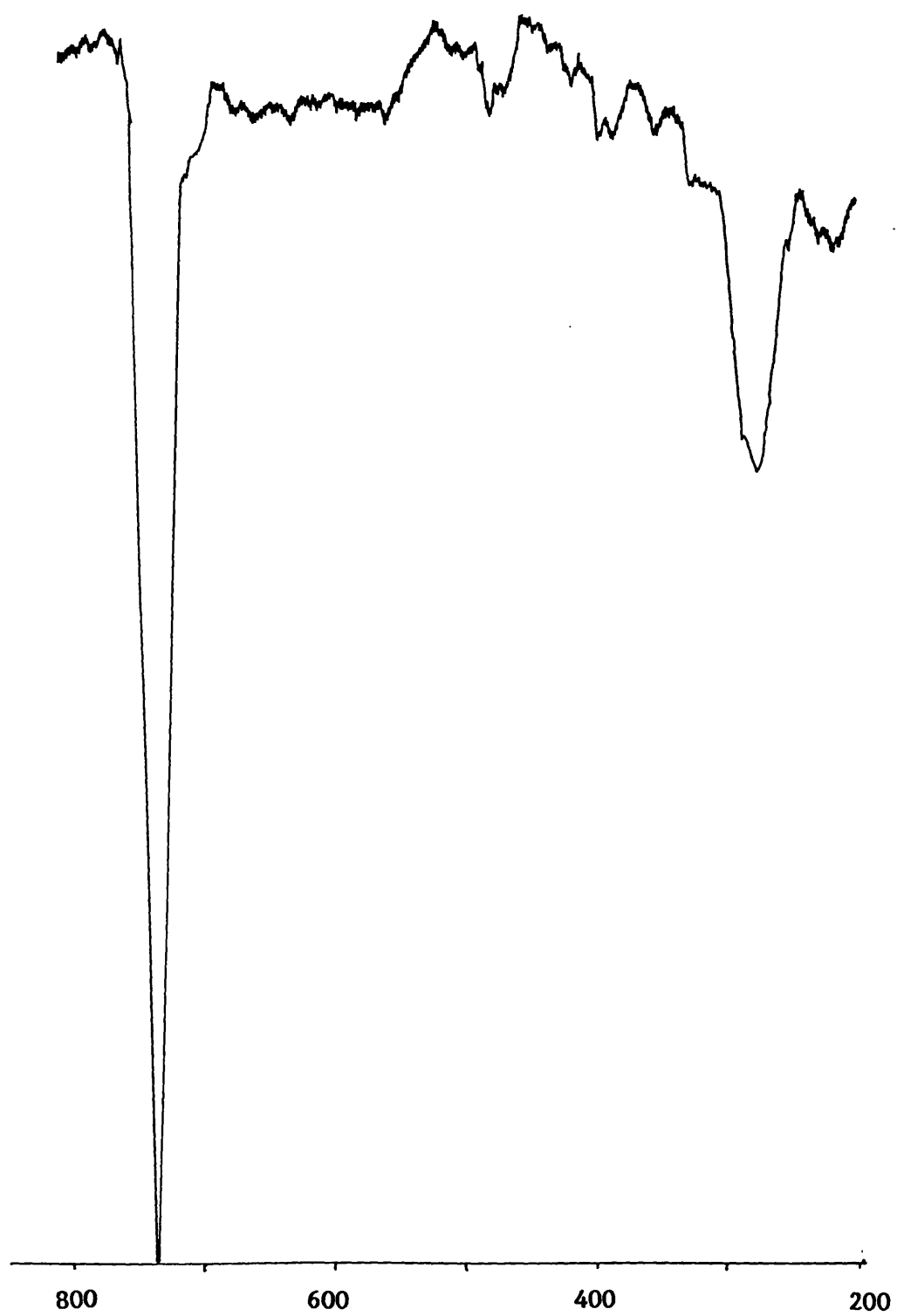


Figure 4.5 I.r. Spectra of Matrix-isolated RuF_6 in N_2



**Table 4.1 Principle Infrared Absorptions (cm⁻¹) of P.G.M.
Hexafluorides**

<u>Compound</u>	<u>Gas Phase</u>	<u>N₂ Matrix</u>	<u>Ar Matrix</u>	<u>Assignment</u>
ReF ₆	715	716.4, 712.7	719.4, 714.0	ν_3 (T _{1u} stretch)
	257	262.7	258.6	ν_4 (T _{1u} stretch)
OsF ₆	720	724.9, 712.3	726.5, 712.2	ν_3
	268	266.2	273.8, 260.4	ν_4
IrF ₆	719	719.1, 717.2	719.3, 716.0	ν_3
	276	279.1	283.3	ν_4
PtF ₆	705	704.4	705.2	ν_3
	273	273.8	274.2	ν_4
RuF ₆	735	733.0, 719.1	----	ν_3
	275	275.0	----	ν_4

excellent. In order to record the complete spectrum deposits were examined at various stages during deposition. The very intense bands in the u.v. were detectable after a relatively short spray-on time (ca. 10 mins), but, thicker deposits were needed to observe the sharp, weak bands at low energy. Unfortunately, it was not possible to measure absolute values for the absorption coefficient of any of the bands.

Many of the more intense bands showed extensive vibrational structure which could be satisfactorily resolved using second derivative recording. The spectra are shown in figures 4.6 and 4.7. This matrix data was compared with previous data and assignments made in table 4.2.

Three types of electronic transitions are expected for these molecules: intra-configurational bands arising from a redistribution of electrons within the spin-orbit split t_{2g} levels; d-d transitions between the t_{2g} and e_g levels; and charge transfer (c.t.) transitions $F(\pi \text{ or } \sigma) \longrightarrow M(t_{2g} \text{ or } e_g)$.

Theoretical treatment of the spectra of 5d elements is difficult, since, the large spin orbit coupling means that relativistic effects must be explicitly considered in addition to ligand-field components. Here assignment of the intra-configurational bands, which appear as weak, sharp, features at low energy, are based on the strong field O^* double group approach of Allen and Warren [167].

The charge transfer bands may be assigned via a molecular orbital approach [168,169]. In the present study Jørgensen's model will be used [170]. Jørgensen has proposed that the charge transfer bands in many hexahalide species may be rationalised in terms of the expression; $\Pi(X) \longrightarrow t_{2g}(M) = V + KD + q(A-E)$, where A and D are related to the corresponding Racah parameter, E represents the variation in orbital energy with occupation number (q), and V and K are parameters dependent upon the metal (primarily oxidation state and atomic number) and ligand. The applications of this model to MF_6 and MF_6^{n-} spectra has been discussed by Allen and Warren [167]. A second approach is to use the orbital electronegativity concept [171], which can be expressed as $\Pi(X) \longrightarrow t_{2g}(M) = 30\,000 [X_{opt}$

Figure 4.6 U.v.-visible Spectra of Matrix Isolated ReF_6 and OsF_6 :
 (a) ReF_6 in N_2 (b) ReF_6 in N_2 after prolonged deposition, (c) OsF_6
 in N_2 (inset: 200–300nm region with derivation recording), (d) OsF_6
 in N_2 after prolonged deposition.

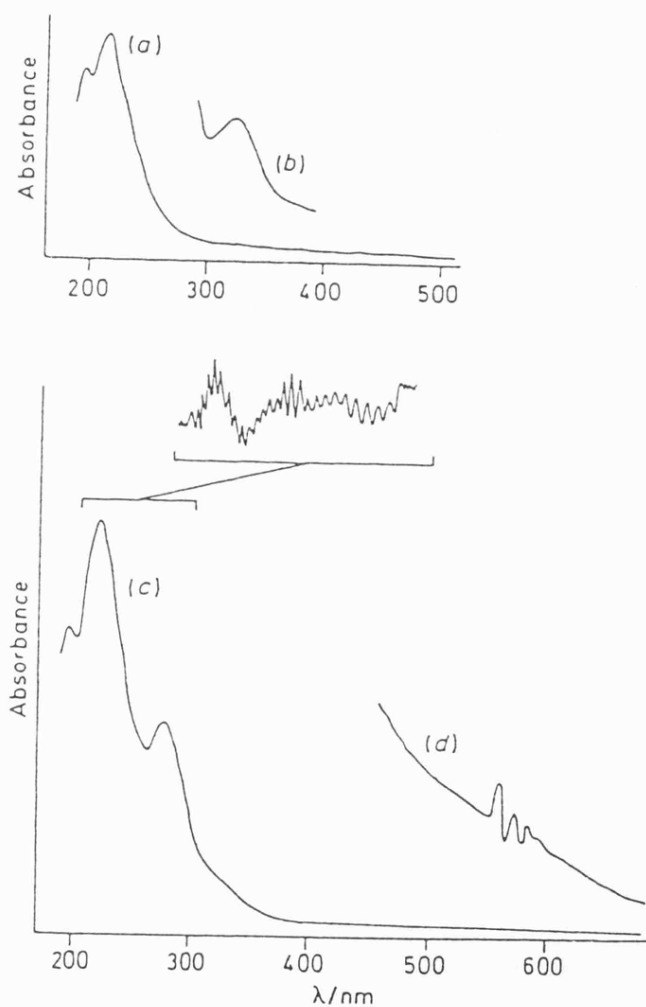


Figure 4.7 U.v.-visible Spectra of Matrix Isolated IrF_6 and PtF_6 :

(a) IrF_6 in N_2 (inset: 200-350nm region with derivation recording),
(b) IrF_6 in N_2 after prolonged deposition, (c) PtF_6 in N_2 (inset:
280-380nm region with derivation recording), (d) PtF_6 in N_2 after
prolonged deposition.

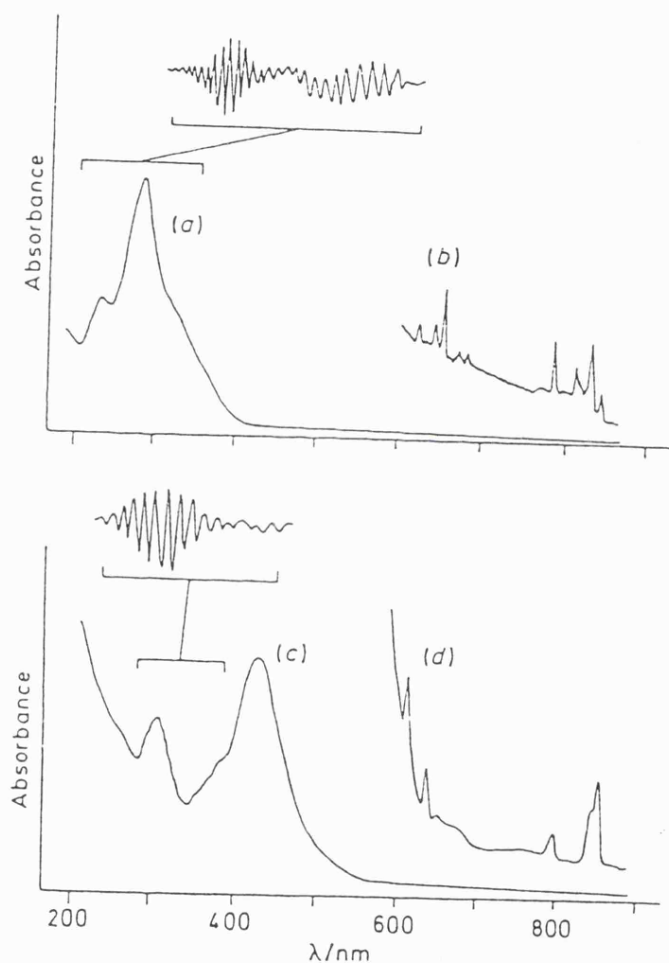


Table 4.2 U.v.-visible Data for P.G.M. Hexafluorides

	Gas Phase [56]	Matrix Isolated [57]	Assignment
ReF ₆	56,404 (700)		
	49,322 (660)	50,700	$\Pi(F) \longrightarrow t_{2g}(Re)$
	47,687	46,800	$\Pi(F) \longrightarrow t_{2g}(Re)$
	32,500	30,190	${}^2T_{2g}(\Gamma_8) \longrightarrow {}^2E_g(\Gamma_8)$
	5,000		${}^2T_{2g}(\Gamma_8) \longrightarrow {}^2T_{2g}(\Gamma_7)$
OsF ₆		> 51,000	$\Pi(F) \longrightarrow t_{2g}(Os)$
		45,435 (630)	$\Pi(F) \longrightarrow t_{2g}(Os)$
	40,800		see text
		36,230 (660)	$\Pi(F) \longrightarrow t_{2g}(Os)$
	35,700		see text
	17,300	17,340	${}^3T_{1g}(\Gamma_3) \longrightarrow {}^1A_{1g}$
	8,500		${}^3T_{1g}(\Gamma_3) \longrightarrow {}^1T_{2g}, {}^1E_g$
	4,300		${}^3T_{1g}(\Gamma_3) \longrightarrow {}^3T_{1g}(\Gamma_4, \Gamma_1)$
	3,930		Hot Band ?
IrF ₆	42,000	43,000	$\Pi(F) \longrightarrow t_{2g}(Ir)$
	35,500	35,700	$\Pi(F) \longrightarrow t_{2g}(Ir)$
	28,200	30,400	$\Pi(F) \longrightarrow t_{2g}(Ir)$
	16,000	16,400	${}^4A_{2g}(\Gamma_8) \longrightarrow {}^2T_{2g}(\Gamma_8)$
	13,000	13,000	${}^4A_{2g}(\Gamma_8) \longrightarrow {}^2T_{2g}(\Gamma_7)$
	9,000		${}^4A_{2g}(\Gamma_8) \longrightarrow {}^2T_{2g}(\Gamma_6, \Gamma_8)$
	6,400		${}^4A_{2g}(\Gamma_8) \longrightarrow {}^2T_{2g}(\Gamma_8)$
PtF ₆	45,000	46,500	$\sigma(F) \longrightarrow t_{2g}(Pt)$
	32,000	32,895	$\Pi(F) \longrightarrow t_{2g}(Pt)$
		26,250	$\Pi(F) \longrightarrow t_{2g}(Pt)$
	25,000	23,500	$\Pi(F) \longrightarrow t_{2g}(Pt)$
	16,000	16,000	${}^3T_{1g}(\Gamma_1) \longrightarrow {}^1A_{1g}$
	12,000	12,000	${}^3T_{1g}(\Gamma_1) \longrightarrow {}^1T_{1g}, {}^1E_g$
	5,400		${}^3T_{1g}(\Gamma_1) \longrightarrow {}^3T_{1g}(\Gamma_3)$
	5,200		${}^3T_{1g}(\Gamma_1) \longrightarrow {}^3T_{1g}(\Gamma_5)$
	3,300		${}^3T_{1g}(\Gamma_1) \longrightarrow {}^3T_{1g}(\Gamma_4)$

(E max/cm⁻¹ and Δν/cm⁻¹)

$(F) - \chi_{\text{opt}}(M^{6+})]$. Corrections may be made for both spin-pairing and relativistic effects but, since, the $\chi_{\text{opt}}(M^{6+})$ values have been derived from the hexafluorides, this is not necessary here.

Results and Discussion

ReF₆

For the d^1 species ReF₆ ($\mu = 0.25\text{BM}$), Moffitt *et.al.* [56] assigned a weak band at *ca.* 5 000cm⁻¹ as the intraconfigurational transition ${}^2T_{2g}(\Gamma_8) \rightarrow {}^2T_{2g}(\Gamma_7)$, and observed a shoulder at *ca.* 32000cm⁻¹ on the rising high-energy absorption. McDiarmid [170] reported bands at 47 687, 49 322 and 56 404cm⁻¹, these were initially assigned as $\Pi(F) \rightarrow \text{Re c.t.}$ and the other members of the Rydberg series. Later all three were assigned [175] as $\Pi(F) \rightarrow t_{2g}(\text{Re})$ c.t. transitions.

In the present studies intense bands are observed at 46 800cm⁻¹ and *ca.* 50 700cm⁻¹ and a weak feature at 30 190cm⁻¹, this weak band being two orders of magnitude less than the band at 46 800cm⁻¹. The band at 30 190cm⁻¹ is assigned as the d-d transition ${}^2T_{2g}(\Gamma_8) \rightarrow {}^2E_g(\Gamma_7)$. This band is very close to the shoulder reported by Moffitt and the other bands are similar to those observed by McDiarmid and are assigned as $\Pi(F) \rightarrow t_{2g}(\text{Re})$ charge transfer.

The d-d band in ReF₆ is much weaker than the charge transfer bands. This indicates that intense absorptions in other MF₆ species should be assigned as $\Pi(F) \rightarrow M \text{ c.t.}$ rather than d-d transitions.

The t_{2g} orbitals in ReF₆ split under spin-orbit coupling into $\Gamma_8(-\frac{1}{2}\xi)$ and $\Gamma_7(+\xi)$. Taking Moffitt's value of 5 000cm⁻¹ for the transition, ξ is estimated to be *ca.* 3 300cm⁻¹. Ignoring configurational interaction between the Γ_8 states in ${}^2T_{2g}$ and 2E_g , the ligand field splitting 10Dq is estimated as *ca.* 28 000cm⁻¹. This parameter [171] is expected to change only slowly through the sequence Re \rightarrow Pt but the c.t. absorptions are expected to move significantly to lower energy. As a result, the d-d bands in the remaining hexafluorides are likely to be obscured by the more intense c.t. absorptions.

OsF₆

For the d² OsF₆ ($\mu = 1.50\text{BM}$) Moffitt *et.al.* [56] identified three intra-configurational bands in the electronic spectra. These originated from the ground state $^3T_{1g} (\Gamma_3)$. Higher energy absorptions at 35 700 and 40 800 cm⁻¹ were also observed. These are assigned as d-d transitions ($t_{2g}^2 \rightarrow t_{2g}^1, e_g^1$). Subsequently Eisenstein [173] confirmed the assignment of the lower energy band but, suggested that the absorptions above 35 000cm⁻¹ were due to charge transfer.

The present spectra of matrix isolated OsF₆ differs significantly from that of Moffitt *et.al.* [56]. Here bands were observed at 36 230, 45 435 and *ca.* 51 000, but no band was observed at 41 000cm⁻¹. Extensive vibrational structure was observed on the 45 435 and 36 230cm⁻¹ bands with average spacings *ca.* 630 and 660 (± 50) respectively. All three high energy bands were assigned as $\Pi (F) \rightarrow t_{2g} (Os)$ c.t. For OsF₆ in the ground state $\nu_1 (Os-F, A_{1g})$ lies at 733cm⁻¹.

The band observed by Moffitt at *ca.* 41 000cm⁻¹ arises from OsO₄ [174]. This is a persistent impurity in osmium fluoride chemistry, its u.v.-visible spectrum showing absorptions at 40 800 and 35 000 cm⁻¹. Thus, the band at 40 800 reported by Moffitt is due to OsF₄ and the band at 35 700cm⁻¹ is a composite of the second OsF₄ band at *ca.* 35 000 and the genuine OsF₆ band at 36 200cm⁻¹.

IrF₆

For the d³ IrF₆ ($\mu = 2.9\text{BM}$) the structured absorptions lying below 20 000cm⁻¹ are assignable as intra-configurational bands arising from a ground state $^4A_{2g} (\Gamma_8)$ [56]. In the present nitrogen matrix work spectra in this region (11 000 - 18 000) show several weak sharp features which agree with the earlier work. The intense bands at 43 400 and *ca.* 35 700cm⁻¹ show vibrational progressions of *ca.* 650cm⁻¹ which correlate with the ground state A_{1g} mode in IrF₆ at 702cm⁻¹, and are assigned as c.t. bands. A distinct, relatively intense shoulder at *ca.* 30 400cm⁻¹ is assigned as $\Pi (F) \rightarrow t_{2g} (Ir)$ c.t. rather than d-d ($^4A_{2g} \rightarrow ^4T_{2g}$) since a bathochromic shift in the lowest energy c.t. band is expected compared to OsF₆. This

latter absorption has been assigned at $36\,200\text{cm}^{-1}$.

PtF₆

PtF₆ is the least stable 5d hexafluoride. Its temperature independent magnetic moment of 1.4BM indicates a ground state $^3T_{1g}(\Gamma_1)$. Moffitt's gas phase spectra [56] showed 3 intra-configurational bands in the region $3\,000 \rightarrow 6\,000\text{cm}^{-1}$, with spin forbidden bands, $^3T_{1g}(\Gamma_1) \rightarrow ^1T_{2g}, ^1E_g$ at *ca.* $12\,000\text{cm}^{-1}$. A third spin forbidden band $^3T_{1g}(\Gamma_1) \rightarrow ^1A_{1g}$ was just evident above $16,000\text{cm}^{-1}$. The present work agreed well with these findings.

The higher energy region of Moffitt's spectrum is unclear. A band is reported at *ca.* $32\,000\text{cm}^{-1}$ and an ill defined maximum at *ca.* $45\,000\text{cm}^{-1}$. A third band lies between $17\,000 - 25\,000\text{cm}^{-1}$.

In the present study a band was observed at $23\,500\text{cm}^{-1}$ with a shoulder at $26\,250\text{cm}^{-1}$, and a rising absorption at $>51\,000\text{cm}^{-1}$ with a shoulder at $46\,500\text{cm}^{-1}$. The $23\,500$, $26\,250$ and $32\,900\text{cm}^{-1}$ bands all show well defined vibrational progressions of 560cm^{-1} . In the ground state, $\nu_1(A_{1g})$ lies at 656cm^{-1} and there is therefore a substantial bond weakening in the excited state in comparison with other hexafluorides in this series.

There is no reliable measurement of $10Dq$ in PtF₆, but based on the value for Re (*ca.* $28\,000\text{cm}^{-1}$) it is possible that the rising absorption at $>51\,000\text{cm}^{-1}$ may correspond to $\Pi(F) \rightarrow eg(Pt)$. The shoulder at $46\,500\text{cm}^{-1}$ may be due to $\sigma(F) \rightarrow t_{2g}(Pt)$ as suggested by Allen and Warren [167]. The band at *ca.* $32\,900\text{cm}^{-1}$ shows a very similar vibrational progression to those at $23\,500$ and $26\,250\text{cm}^{-1}$ and is therefore assigned as $\Pi(F) \rightarrow t_{2g}(Pt)$ c.t. transition.

4.3 Pentafluorides

4.3.1 Preparation of Samples

RuF₅ was prepared via the direct fluorination of ruthenium metal in a dynamic system. However, OsF₅ and IrF₅ cannot be produced by the same method. The IrF₅ was prepared by the direct fluorination of iridium metal in a static reactor using

stoichiometric amounts of iridium and fluorine [104]. OsF_5 was prepared by the reduction of OsF_6 using iodine in iodine pentafluoride [43,59].

The samples were loaded into glass sample tubes fitted with Young valves, and these were glass blown directly on to glass spray-on domes which connected directly into the matrix rig. The samples were electrically heated to about 100°C where they were found to slowly deposit on the matrix window. Unfortunately, large amounts of SiF_4 were also found to deposit on the window (peak at 1025cm^{-1}). This was formed when the pentafluoride attacked the Pyrex tube. This problem was overcome by loading the samples into metal reactors fitted with high temperature Autoclave Engineers valves which allowed high vacuum to be maintained at elevated temperatures.

4.3.2 Results and Discussion

Spectra were recorded for RuF_5 , IrF_5 , OsF_5 and PtF_5 . The spectra for Ru, Os and Ir pentafluorides were very complex (figures 4.8, 4.9, 4.10) and the results are shown in table 4.3. Each of these pentafluorides is known to be tetrameric in the solid state and from the results of the mass spectroscopic studies tetrameric, trimeric, dimeric and monomeric species would be expected in the gaseous phase. Due to the complexity of the tetrameric structure and the uncertainty of the dimeric and trimeric structures, no definitive assignment can be made. However, the peaks at $\sim 700\text{cm}^{-1}$ will be $\nu(\text{M-F})$ of the terminal F atoms, those at $560\text{--}580\text{cm}^{-1}$ will be bridging F-M stretches and those at $280\text{--}320\text{cm}^{-1}$ will be $\delta(\text{M-F})$ deformations. This shows that the vapourisation of the P.G.M. pentafluorides does not only give monomeric species.

It was hoped that if the spray-on temperature was raised the spectra would simplify due to a decrease in the amount of tetrameric species and an increase in the amount of lower polymers, until eventually only monomeric species would be observed. RuF_5 and OsF_5 were heated to $\sim 300^\circ\text{C}$ with little change in their spectra, but above this temperature no further growth in the peaks was observed as the pentafluorides decomposed to metal and fluorine. The metal residue being observed to deposit on the walls of the spray-on tube. However, as IrF_5 was heated most of the initial peaks stopped

Figure 4.8 I.r. Spectra of Matrix-isolated $(\text{RuF}_5)_4$

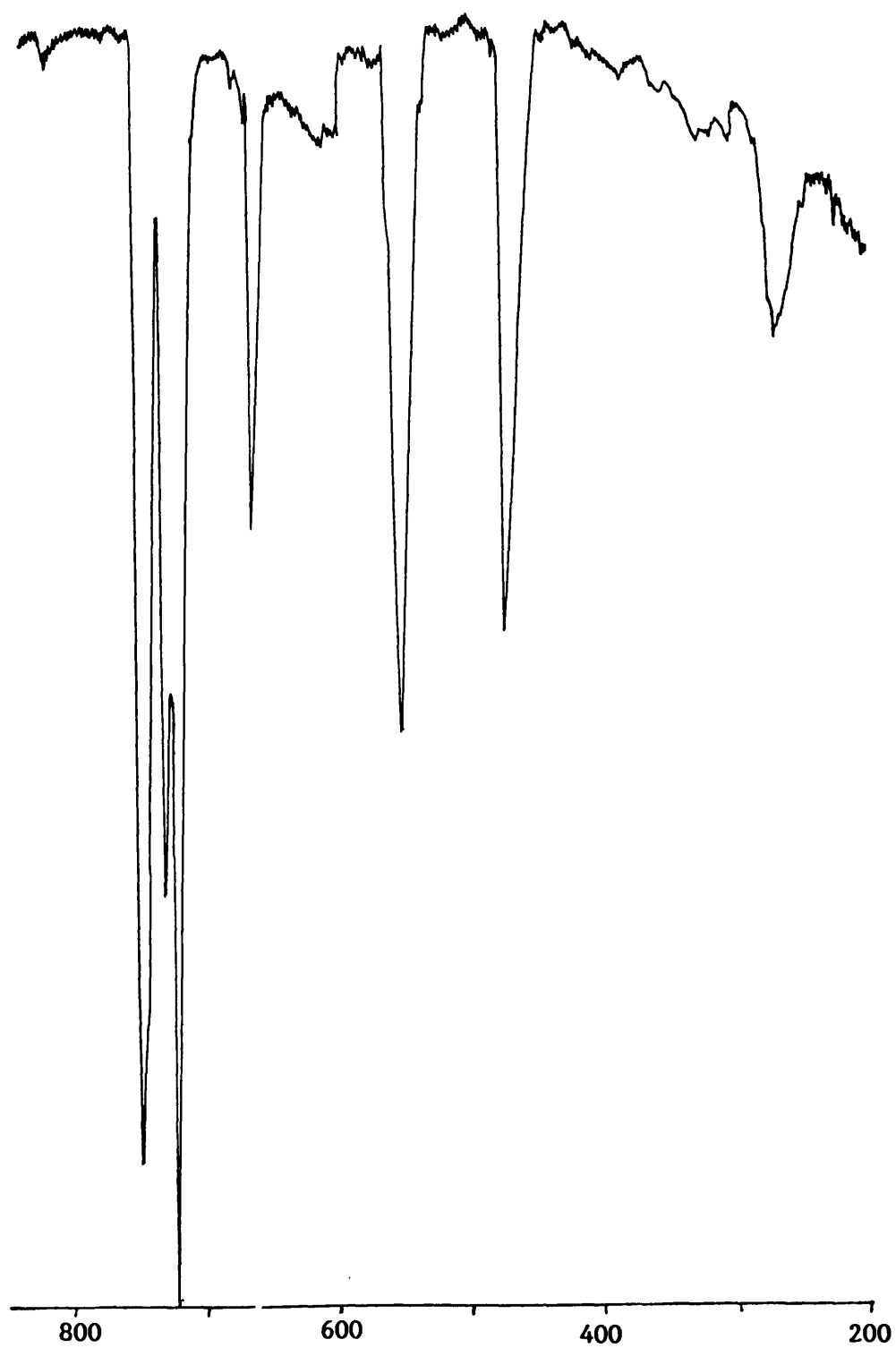


Figure 4.9 I.r. Spectra of Matrix-isolated $(\text{IrF}_5)_4$

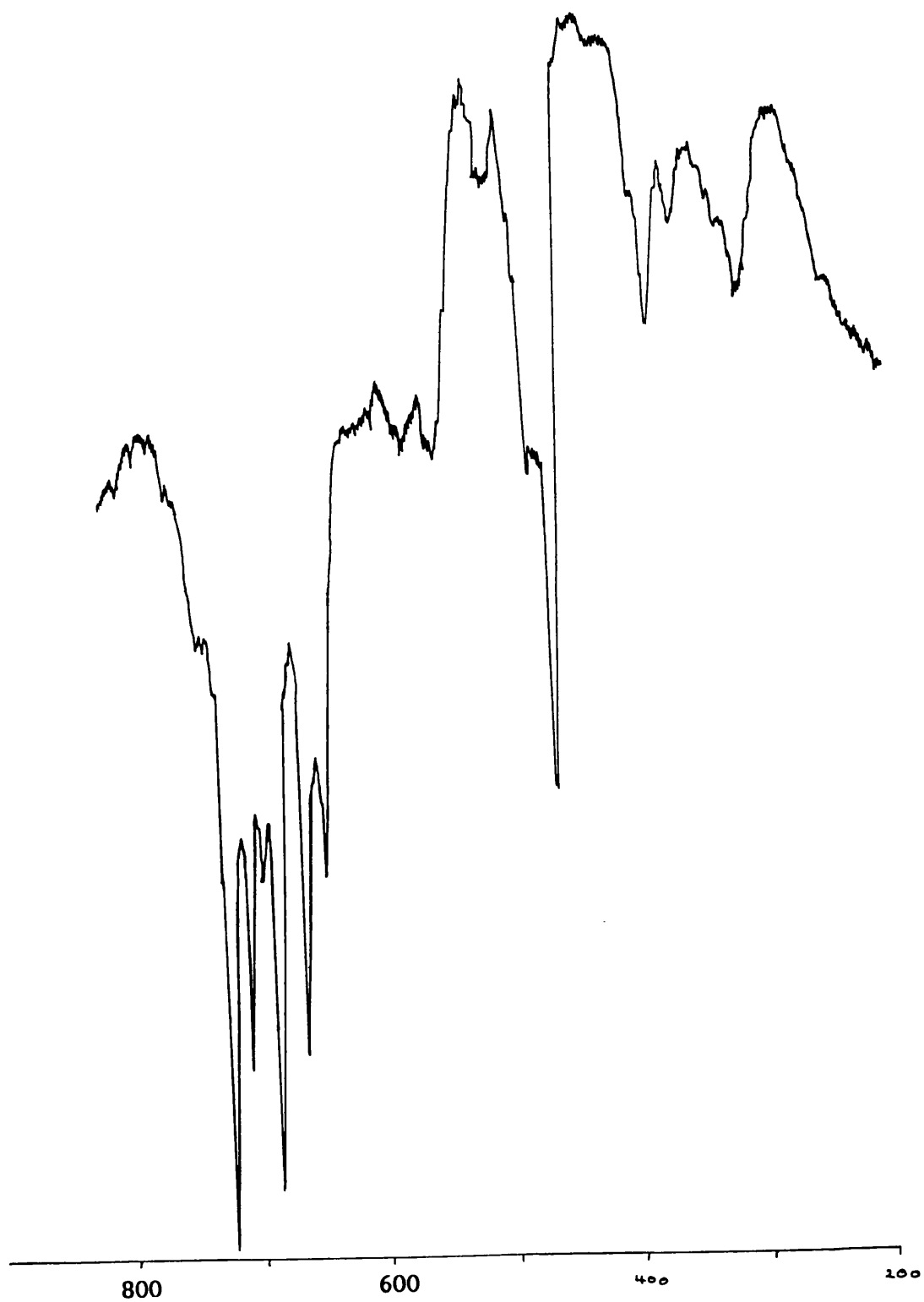


Figure 4.11 I.r. Spectra of Matrix-isolated IrF₅ Recorded at 366°C

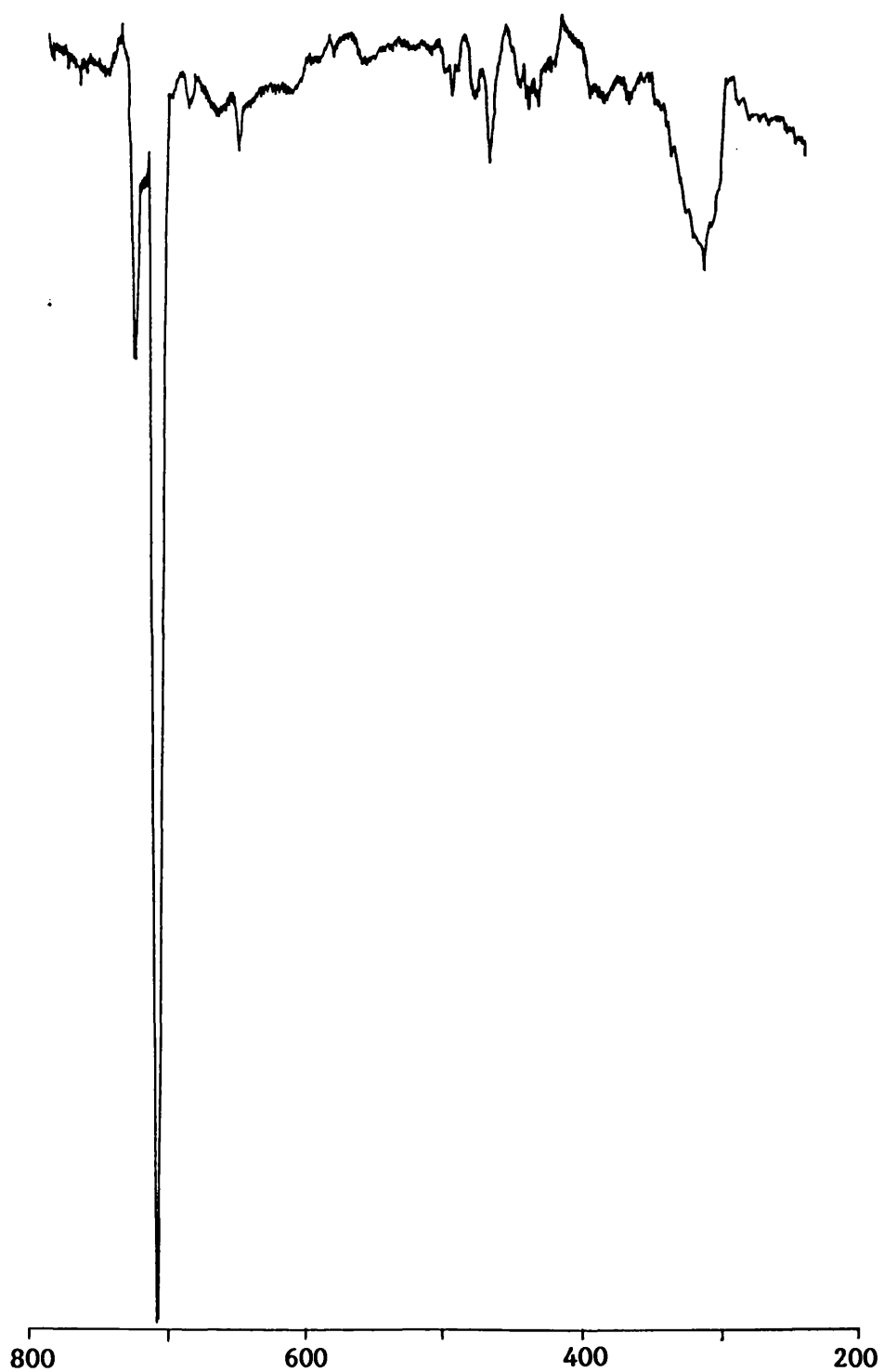
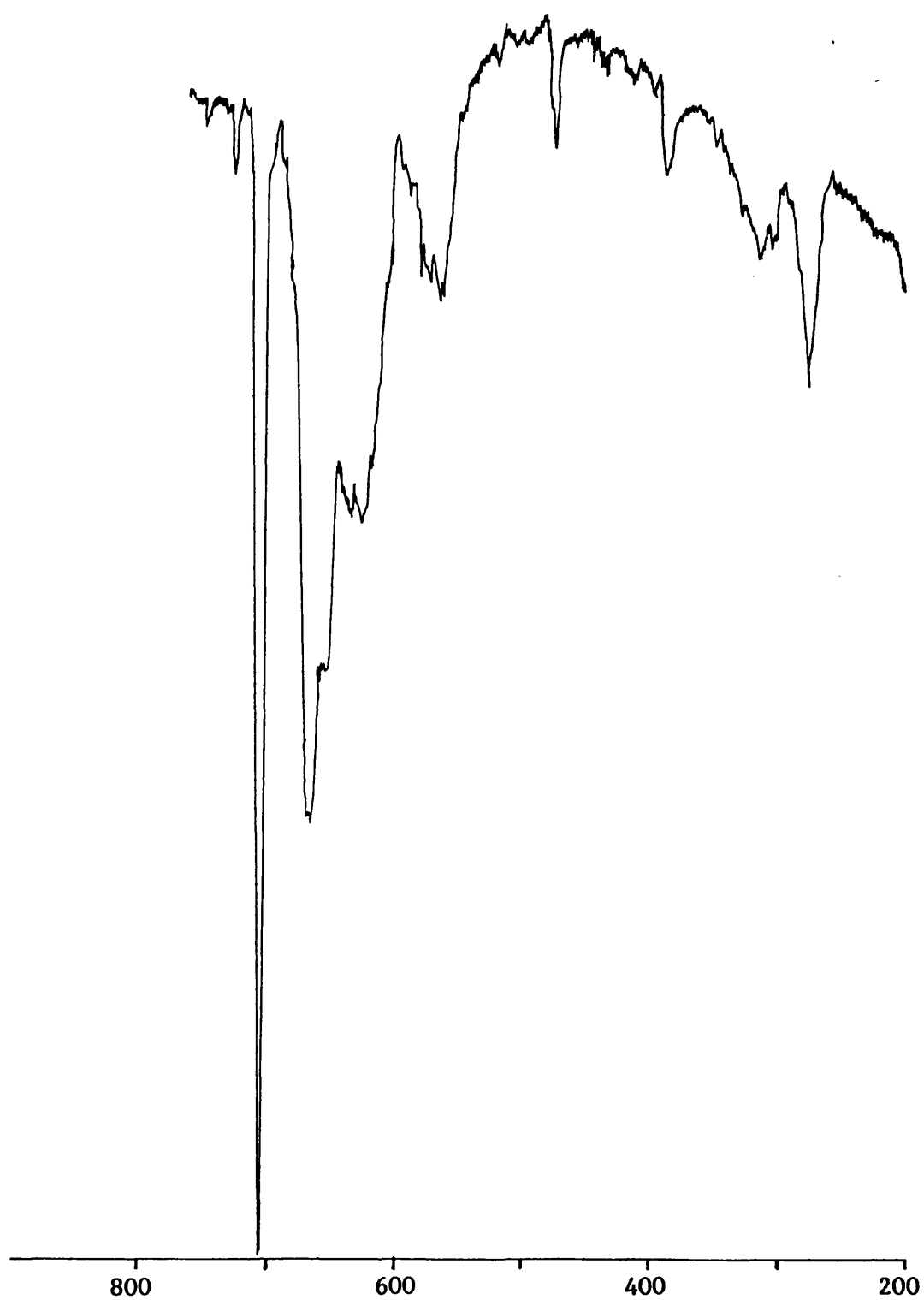


Figure 4.12 I.r. Spectra of Matrix-isolated $(\text{PtF}_5)_4$



Chapter 5

A New Form of Ruthenium Pentafluoride

Chapter 5

A New Form of Ruthenium Pentafluoride

5.1 Introduction

When ruthenium powder was fluorinated in a dynamic system, a red glassy material was observed which had not previously been reported. The compound was found to be extremely difficult to manipulate. Not only is it very sensitive to moisture but it decomposes under dynamic vacuum at room temperature and under static vacuum at temperatures in excess of 35°C to $(\text{RuF}_5)_4$. The red compound is deposited in flow fluorinations of ruthenium metal on the glass side arm of the collection apparatus alongside the green pentafluoride. Before investigations of the red product were carried out it had to be separated from the green $(\text{RuF}_5)_4$. The glassware was assembled as shown in figure 5.1, pumped out, fluorinated and the break-seal to trap A broken. The whole apparatus was held under static vacuum and trap A was warmed to about 26–27°C. Heating was continued over a period of 3–4 days until, gradually, the red material moved along the glass tubing leaving most of the green pentafluoride in trap A. It was impossible to obtain total separation since, even at room temperature, the green pentafluoride has a vapour pressure of about 2mm Hg, but the red material is sufficiently more volatile than the pentafluoride to obtain reasonably pure samples.

5.2 Infrared Spectroscopy

This red ruthenium decomposed over about ½ hour in a dry box and even when a powdered sample was held between KBr discs in a specially designed holder (chapter 6) which enclosed the sample in an atmosphere of dry nitrogen, the spectra had to be recorded rapidly before decomposition occurred. The peak positions obtained are recorded in table 5.1 and the spectrum is shown in figure 5.2.

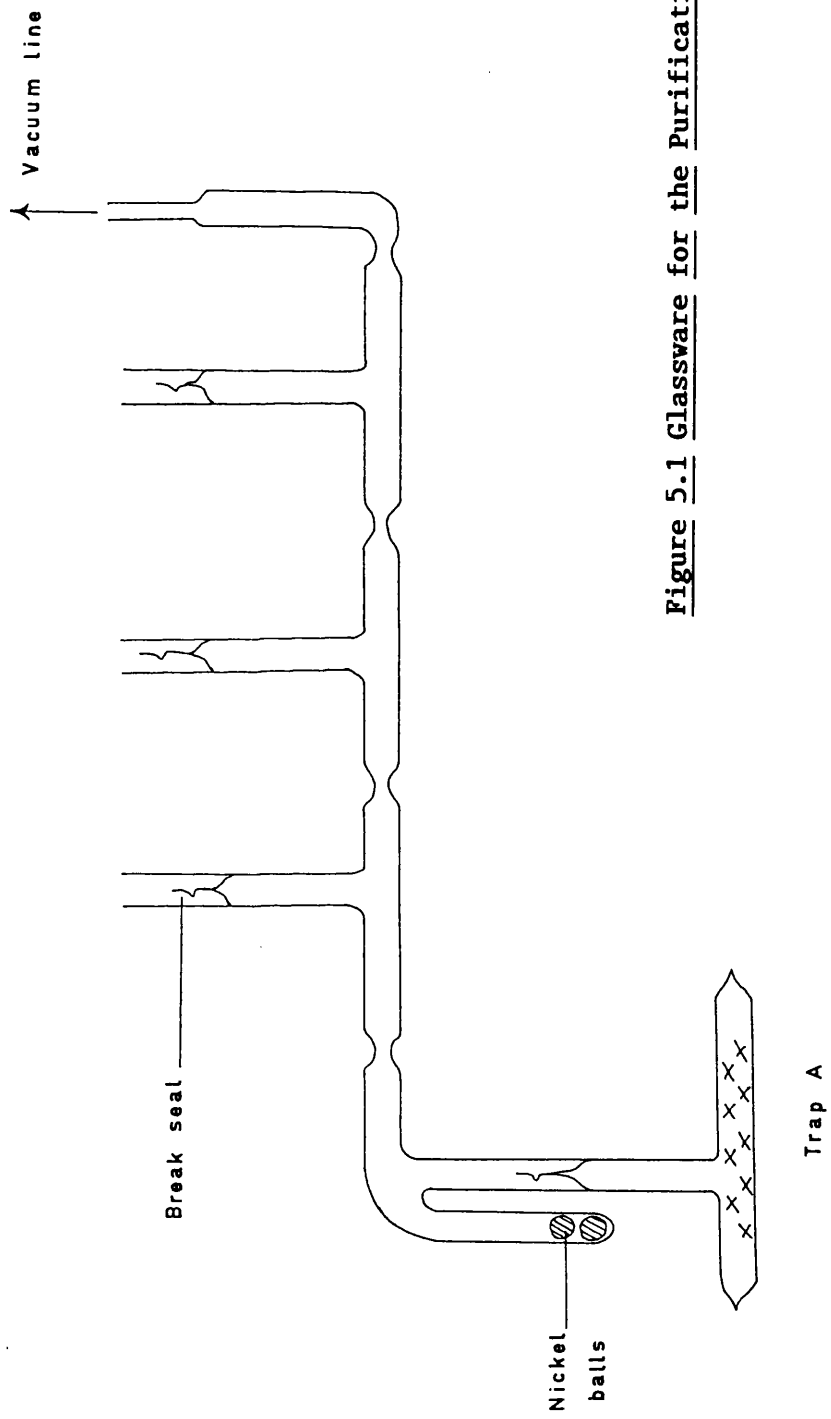


Figure 5.1 Glassware for the Purification of RuF_5

Figure 5.2 Infrared Spectra of $(\text{RuF}_5)_3$

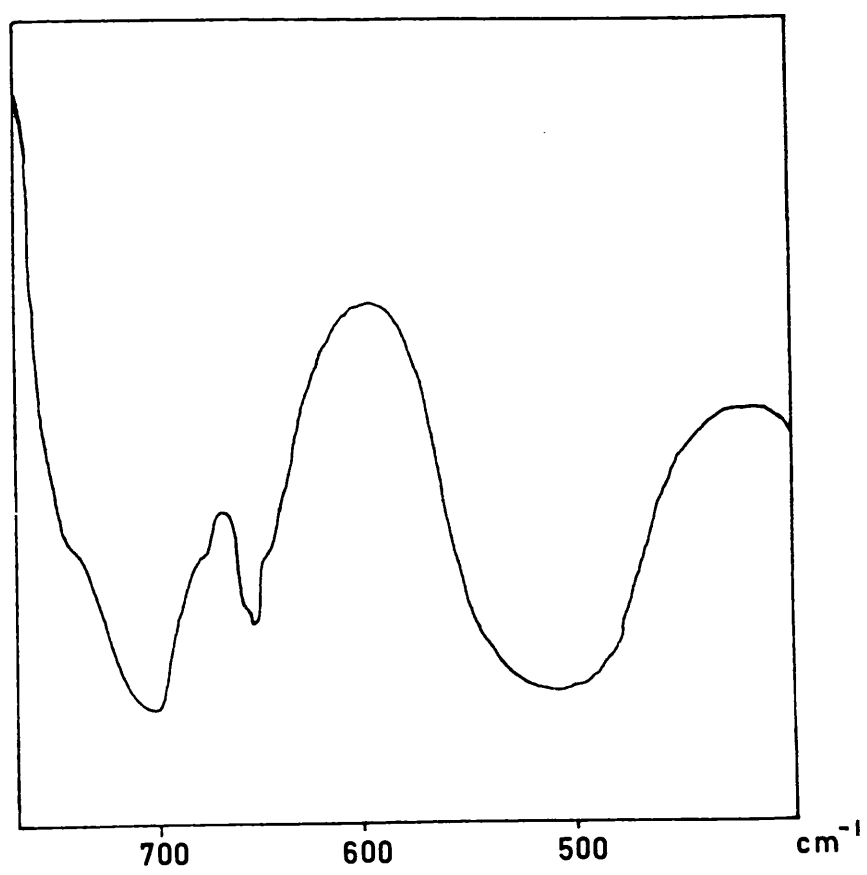


Table 5.1 Infrared Data of Red Ruthenium Pentafluoride.

Frequency (cm-1)	Tentative Assignments
735 m,sh	} Axial terminal Ru-F stretch
700 s	
660 m	} Equatorial terminal, Ru-F stretch
650 m,sh	
510 s,br	Bridging F-atom

No absorptions were recorded in the Ru-O region between 900-1000 cm^{-1} which indicates that the compound is not an oxide fluoride. A close similarity between this spectrum and that of $(\text{RuF}_5)_4$ was noted.

5.3 Mass Spectrometry

Several mass spectra of the red glassy material were recorded. In each case the spectrum was almost identical to that previously recorded for $(\text{RuF}_5)_4$ except that no evidence of a tetramer was observed, neither was there evidence of an oxide fluoride. The absence of fragmentation patterns that could be associated with an oxide fluoride and of the fragmentation pattern of $(\text{RuF}_5)_4$ suggested that the red material might be a trimeric form of RuF_5 , namely $(\text{RuF}_5)_3$. To test this the spectrum of $(\text{RuF}_5)_4$ was repeatedly recorded until conditions were found that maximised the signals due to the tetramer. Identical conditions were utilised to record the spectra of the red ruthenium compound. No signal due to the tetramer was visible but the signal due to the trimer was intense. When the intensity of this signal was increased five times still no evidence of the tetramer signal was detected. Thus it appears likely that the red ruthenium compound is a new crystalline form of ruthenium pentafluoride, probably $(\text{RuF}_5)_3$.

5.4 E.S.R. Spectroscopy

It is known that in RuF_5 there is one unpaired electron on the ruthenium. In $(\text{RuF}_5)_4$ the four single electrons present are expected

to be coupled so that no e.s.r. signal would be observed. However, if the red material is $(\text{RuF}_5)_3$ the single unpaired electron should give an e.s.r. signal.

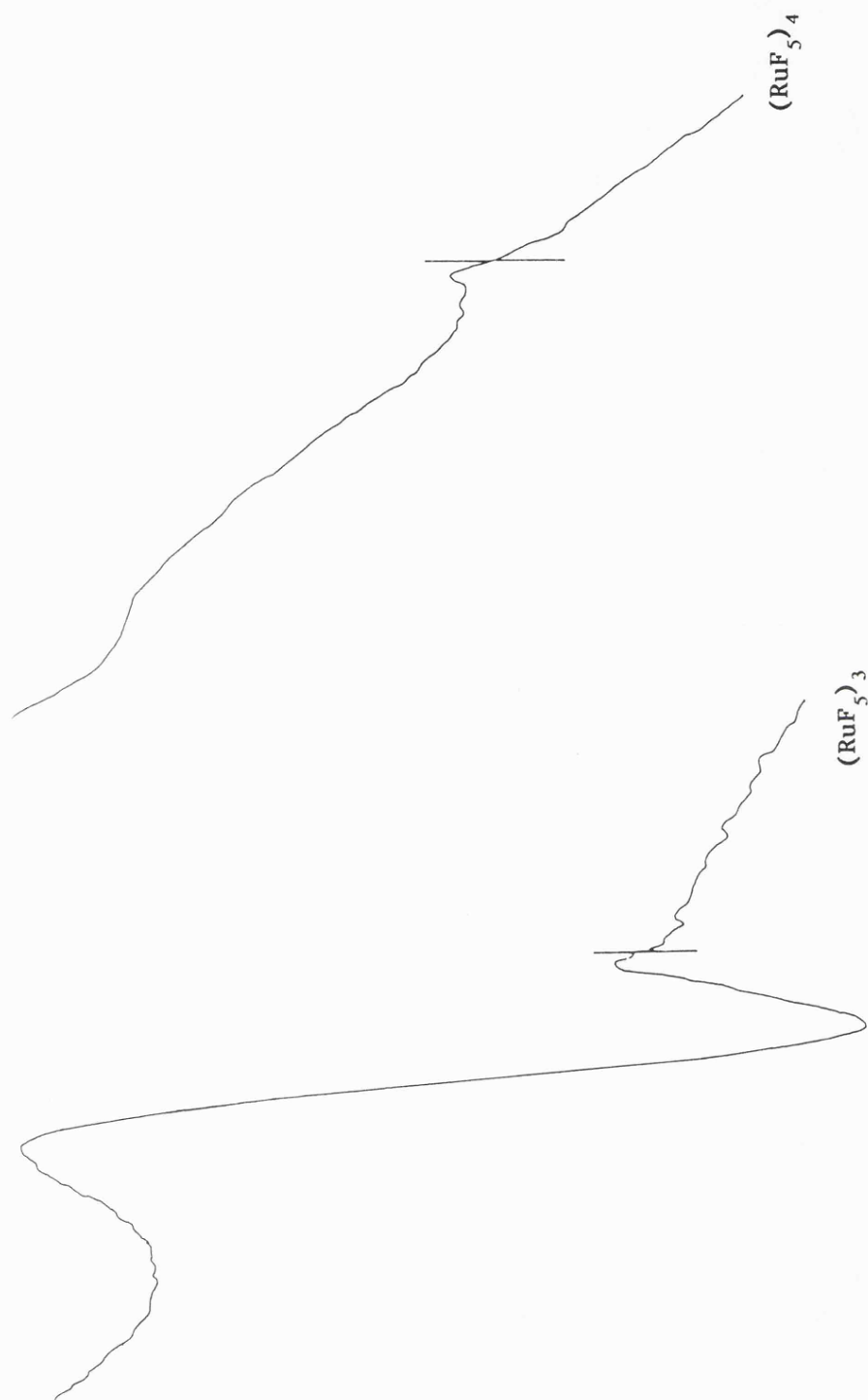
Samples of the green pentafluoride and the red ruthenium compound were loaded into pre-seasoned quartz e.s.r. tubes in a dry box. The samples were both run at liquid nitrogen temperatures and the results are shown in figure 5.3.

A clear signal was recorded for the red compound but no signal was found for the green pentafluoride which constitutes further evidence in support of the theory that the red compound is $(\text{RuF}_5)_3$.

5.5 Conclusion

It seems probably that a new binary fluoride has been prepared and isolated. It is believed that this red material is $(\text{RuF}_5)_3$. This could be confirmed by a x-ray study of a single crystal but as yet no single crystals have been obtained.

Figure 5.3 E.S.R Spectra of $(\text{RuF}_5)_3$



Chapter 6

Experimental

nickel cans fitted with Hoke bellows valves [Model 4171 M2B]. Thermally unstable samples were stored at -196°C in a cryostat [British Oxygen Co. Ltd.] or at -78°C in solid carbon dioxide.

6.2. Vacuum Systems, Reaction Vessels and Flow Systems

Vacuum line or flow line methods were used to prepare all the compounds studied.

6.2.1. Vacuum Line

The vacuum line consisted of a metal manifold with high and low vacuum facilities which formed the basic system (figure 6.1). This was constructed from $\frac{3}{8}$ " o.d, $\frac{1}{8}$ " i.d. nickel tubing [H.Wiggin & Co. Hereford] and argon welded "U" traps ($\approx 25\text{cm}^3$ capacity). The manifold was completed with AE-30 series hard drawn stainless steel needle valves, crosses and tees [Autoclaves Engineers Inc. Erie, Pennsylvania, USA.].

The low vacuum system (10^{-2} mmHg) consisted of a single stage rotary pump [Model PSR/2, NGN Ltd., Accrington, Lancashire] with a large metal trap filled with soda lime (5-10 mesh) between the pump and the manifold. This chemical trap collected any fluorine or volatile fluoride exhausted from the manifold. The low vacuum system served to remove large quantities of gases before opening the manifold to the high vacuum system. The high vacuum (10^{-4} mmHg) was maintained by a single or double stage rotary pump [Genevac type GRS2 or GRD2, General Engineers Co., Radcliff, Lancashire] which was connected to the manifold via a mercury diffusion pump and a liquid nitrogen cold trap (-196°C). Facilities for admission of argon and hydrogen, directly into the manifold from cylinders, were provided and fluorine was introduced to the line from welded nickel cans (1dm^3 capacity) fitted with AE-30 stainless steel needle valves.

Manifold pressure of plus or minus 1 atmosphere (0-1500mmHg) were measured using a stainless steel bourdon tube gauge [type 1F/66Z, Budenberge Gauge Co. Ltd., Broadheath, Greater Manchester]. The vacuum was monitored using a cold-cathode Penning gauge [Model 2A, Edwards High Vacuum Ltd., Crawley, West

- C - Stainless steel cross
- G - Bourdon tube gauge
- N - Nickel "U" trap
- T - Stainless steel "T"
- V - Stainless steel needle valve

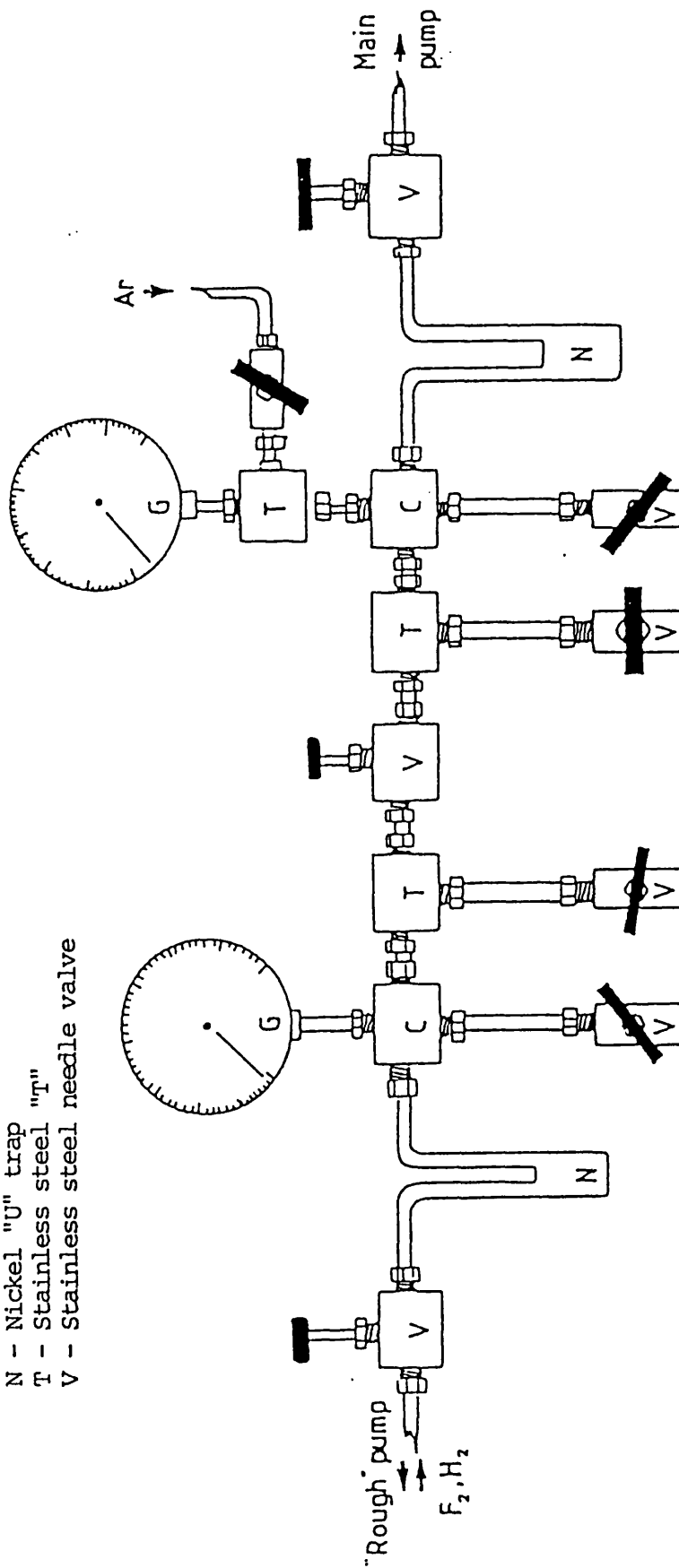


Figure 6.1 The Basic High Vacuum Manifold

Sussex], capable of measuring pressures in the range 10^{-2} to 10^{-6} mmHg.

Leaks in the manifold and in constructed reaction systems were located with a helium leak detector [Edwards High Vacuum Ltd., mass spectrometer model LT 104].

6.2.2 Reaction Vessels

A variety of metal, fluoroplastic, Pyrex or silica reaction vessels could be attached to the vacuum line. Glass reaction systems were designed and fabricated as required and were attached to the manifold by precise $\frac{1}{4}$ " o.d. glass connector to $\frac{1}{4}$ " o.d. stainless steel tubing machined to Autoclave Engineers AE-30 series fittings, by Chemcon Teflon connectors [type STD/4 E1P, Production Techniques Ltd., Fleet, Hampshire] using Teflon compression unions. Greaseless glass valves [Quickfit 'Rotaflo' type TF2/13 and TF6/13 or J.Young, Scientific Glassware Ltd., Acton, London] fitted with Teflon stems were used where glass systems were employed or, alternatively, glass reaction vessels were fitted with Chemcon Teflon needle valves [Type STD/VC 4/P].

Fluoroplastic reactors of $\frac{3}{4}$ " o.d. Kel F with approximately 30cm^3 volume, [obtained from Argon National Laboratory] were fitted with Chemcon Teflon needle valves *via* a stem fabricated from a Teflon FEP block [Trimflex corporation U.S.A] (figure 6.2). Stainless steel or nickel reactors of approximately 30cm^3 volume, employed in thermal reactions, were fitted with gold seals and closed with an AE-30 series stainless steel needle valve (figure 6.3).

6.2.3. Flow Line

The flow line consisted of a metal manifold with a low vacuum facility (figure 6.4). It was constructed of $\frac{3}{8}$ " o.d., $\frac{1}{8}$ " i.d. stainless steel tubing, AE-30 series hard drawn stainless steel needle valves, crosses, tees and elbows [Autoclave engineers Inc., Erie, Pennsylvania, USA.].

Vacuum was obtained using a single stage rotary pump [Model

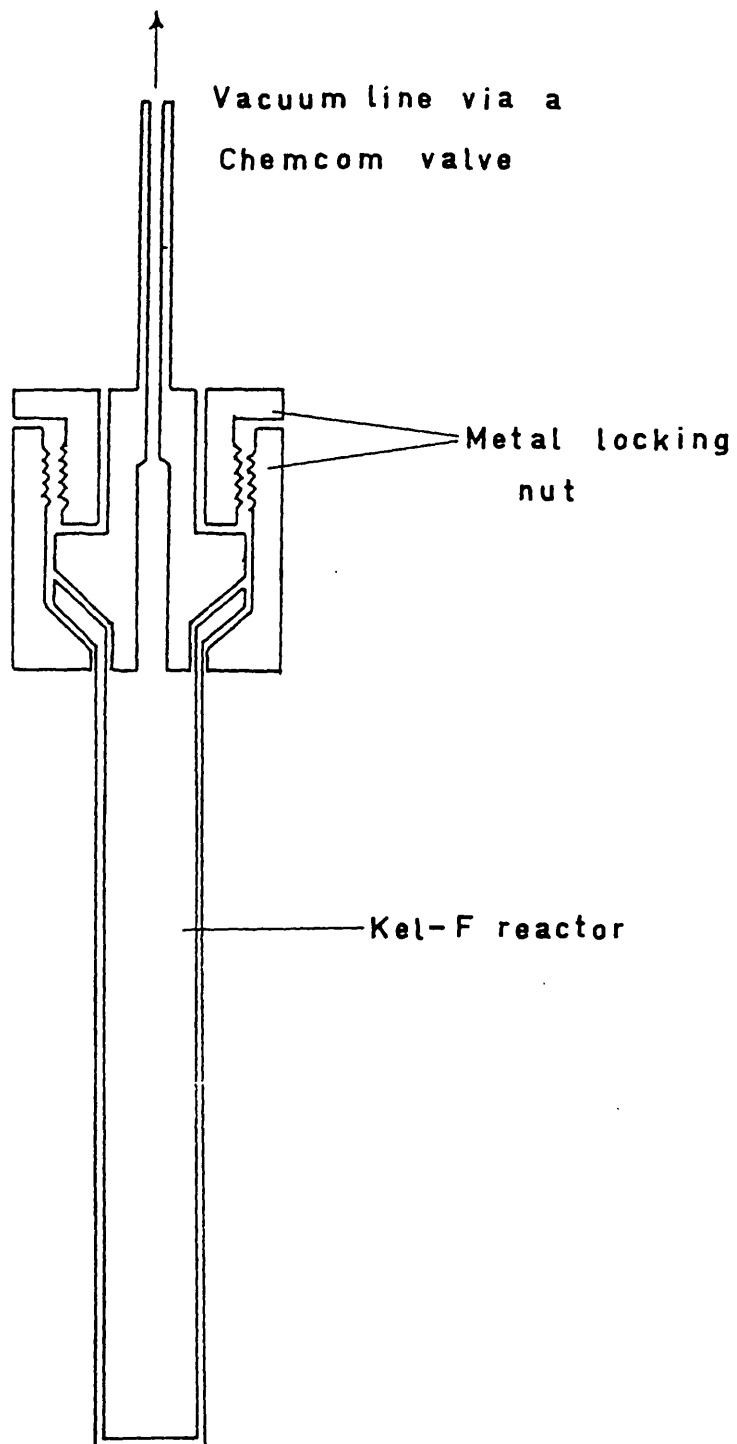


Figure 6.2 Cross-sectional View of a Kel-F Reactor

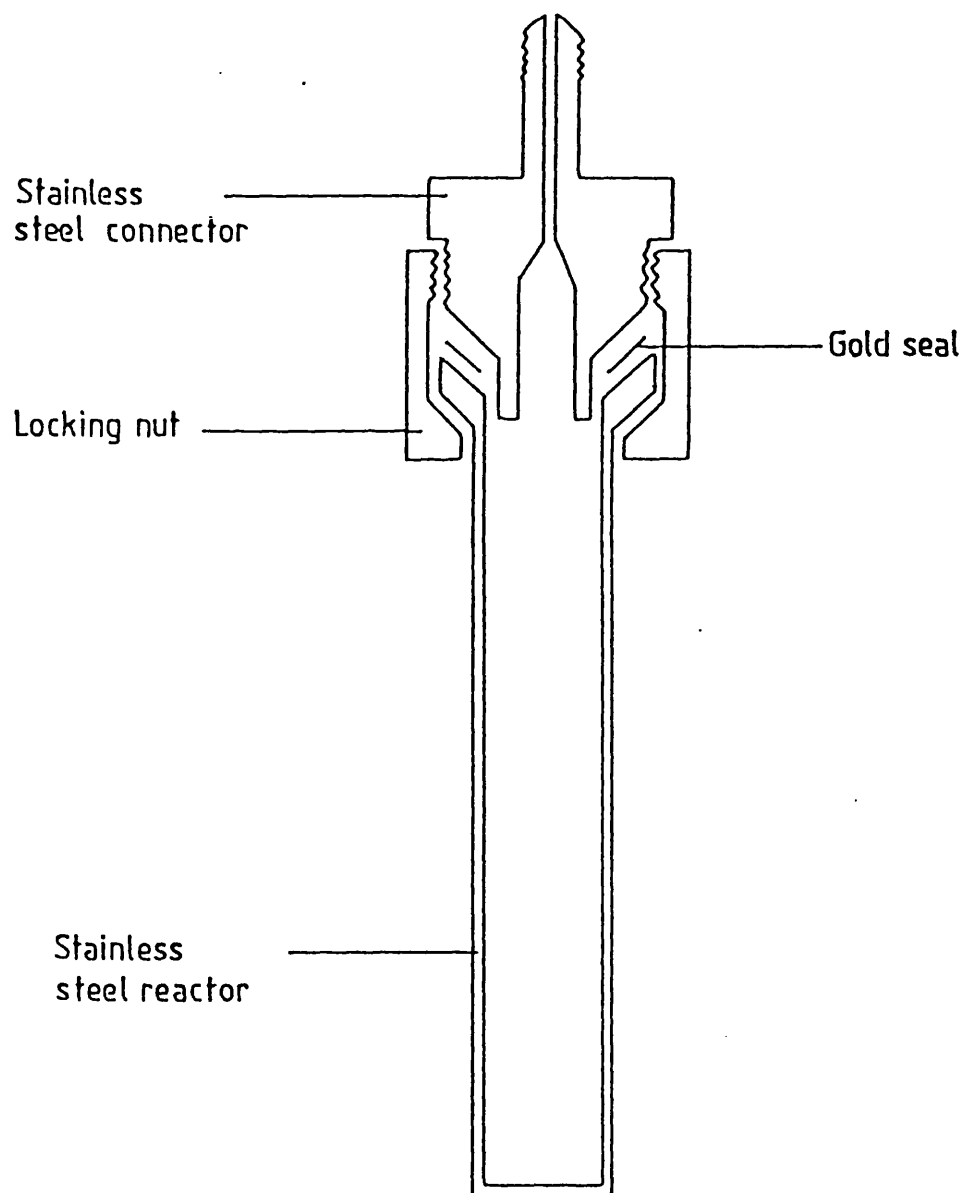


Figure 6.3 Cross-sectional View of a metal reactor

PSR/2, NGN Ltd., Accrington, Lancashire], with a large metal trap filled with soda lime (5-10 mesh) between the pump and the manifold used to collect any fluorine or volatile fluorides exhausted from the manifold. Facilities for the admission of nitrogen, hydrogen and fluorine from cylinders were provided.

Reactions were performed in a copper reaction tube and products were collected in silica or Pyrex traps. The reaction and collection apparatus varied depending on the nature of the products (figures 2.1, 2.2, 2.3). When only volatile hexafluorides were expected a very simple apparatus was sufficient (figure 2.1), but for the fluorination of Ru, Pt, Rh where the pentafluoride was also expected the glassware was modified (figure 2.2) to help the flow of the products from the reactor. Later the glassware was again modified (figure 2.3) in order to trap very reactive less volatile products.

6.3. Characterisation of Products

6.3.1. X-Ray Powder Diffraction

Non volatile samples were ground to a fine powder in a dry box and loaded into seasoned glass capillaries. These were sealed temporarily in the dry box using modelling wax [AD International Ltd., Waybridge] and then sealed using a micro-torch [Model H164/1, Jencons, Hemel Hempstead, Hertfordshire] immediately on removal from the dry box. Volatile samples were condensed from the storage vessels into pre-seasoned capillaries and sealed using a micro torch [model H164/1] whilst the sample was kept at -196°C.

Photographs were taken in a Philips 11.64cm diameter camera, on a Kodirex KD 59T film [Kodak Ltd.]. Nickel filtered Cu-K α radiation (28kV, 18Amps) was used with exposure times of two to five hours.

6.3.2. Infrared Spectroscopy

A Perkin Elmer 580B spectrometer was used to obtain infrared spectra . Solid samples were ground to a fine powder in a dry box

and pressed between discs of KBr ($4000\text{--}350\text{cm}^{-1}$). Highly sensitive samples were held between KBr discs in an atmosphere of dry nitrogen in a specially constructed holder (figure 6.5). Gas phase spectra were obtained using a 10cm path-length copper cell, fitted with AgCl windows ($4000\text{--}400\text{cm}^{-1}$), which could be attached directly to the main manifold. Teflon gaskets provided an air tight seal between the windows and the cell body.

6.3.3. Raman Spectroscopy

Raman spectra were recorded with a Coderg T800 spectrometer, with a 250 mW Ar^+ laser [Model 52, Coherent Radiation Laboratories] which provided 5145 \AA (green) and 4880 \AA (blue) radiation. Solid and volatile samples were contained in Pyrex capillaries, those which were likely to decompose in the beam were run at low temperatures in a cryostat (figure 6.6) [Model DN704 Oxford Instruments Ltd. Osney mead, Oxford].

6.3.4. Matrix Isolated Infrared and Ultra Violet-Visible Spectroscopy

Infrared studies were carried out using a Perkin Elmer 983G spectrometer, and a Matrix rig fitted with CsI optics, whilst u.v.-visible experiments employed LiF optics and a Perkin Elmer 554 spectrometer interfaced with a microcomputer. Details of the spray-on conditions are given in chapter 4.

6.3.5. Mass Spectroscopy

Mass Spectra were recorded on a V.G. Micromass 16B instrument, the samples being introduced directly into the ionising chamber. Solid samples were admitted in glass capillaries mounted on the end of a stainless steel probe. The capillary end was broken off just prior to insertion of the probe. Volatile samples were admitted through a pre-seasoned copper pipe with either a Teflon or Pyrex insulating tip depending on the nature of the sample. In order to minimise decomposition of the sample during passage through the mass spectrometer, the entire system was pre-seasoned by flushing with small amounts of fluorine.

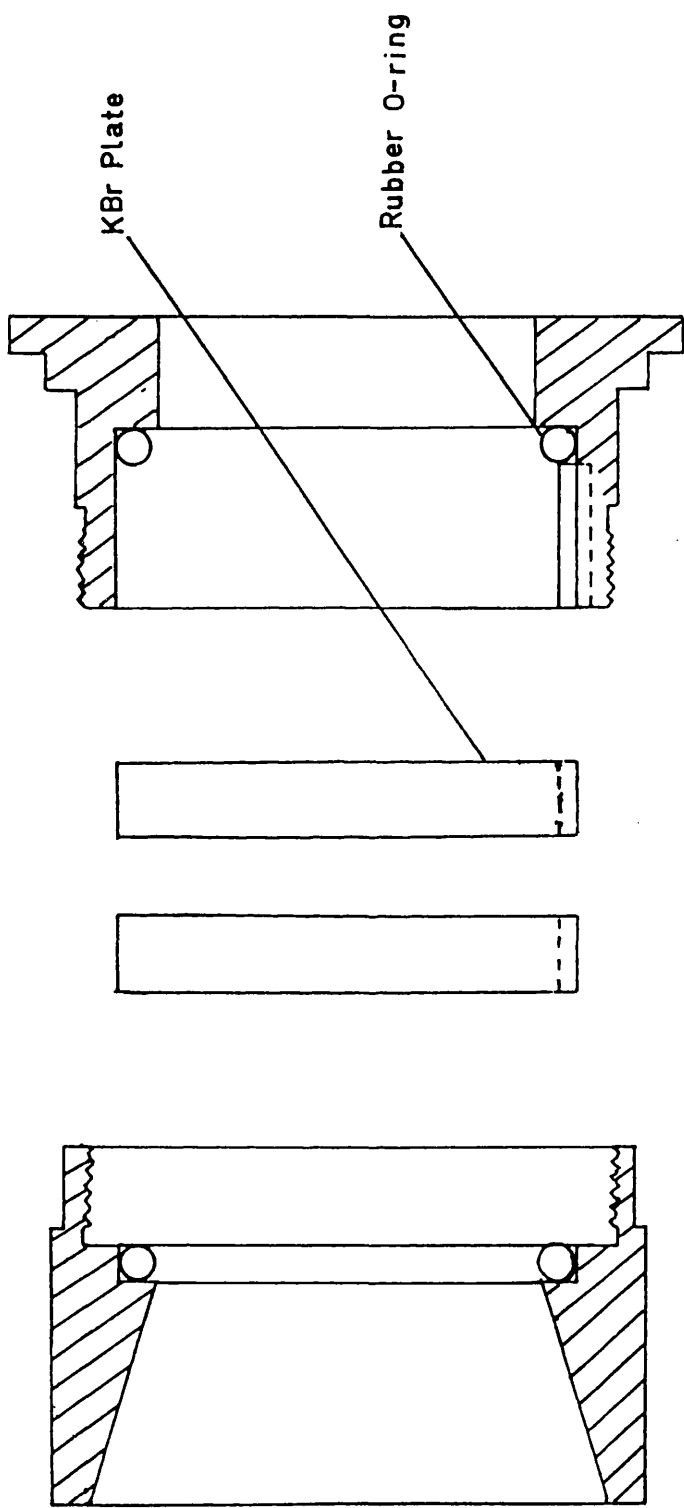
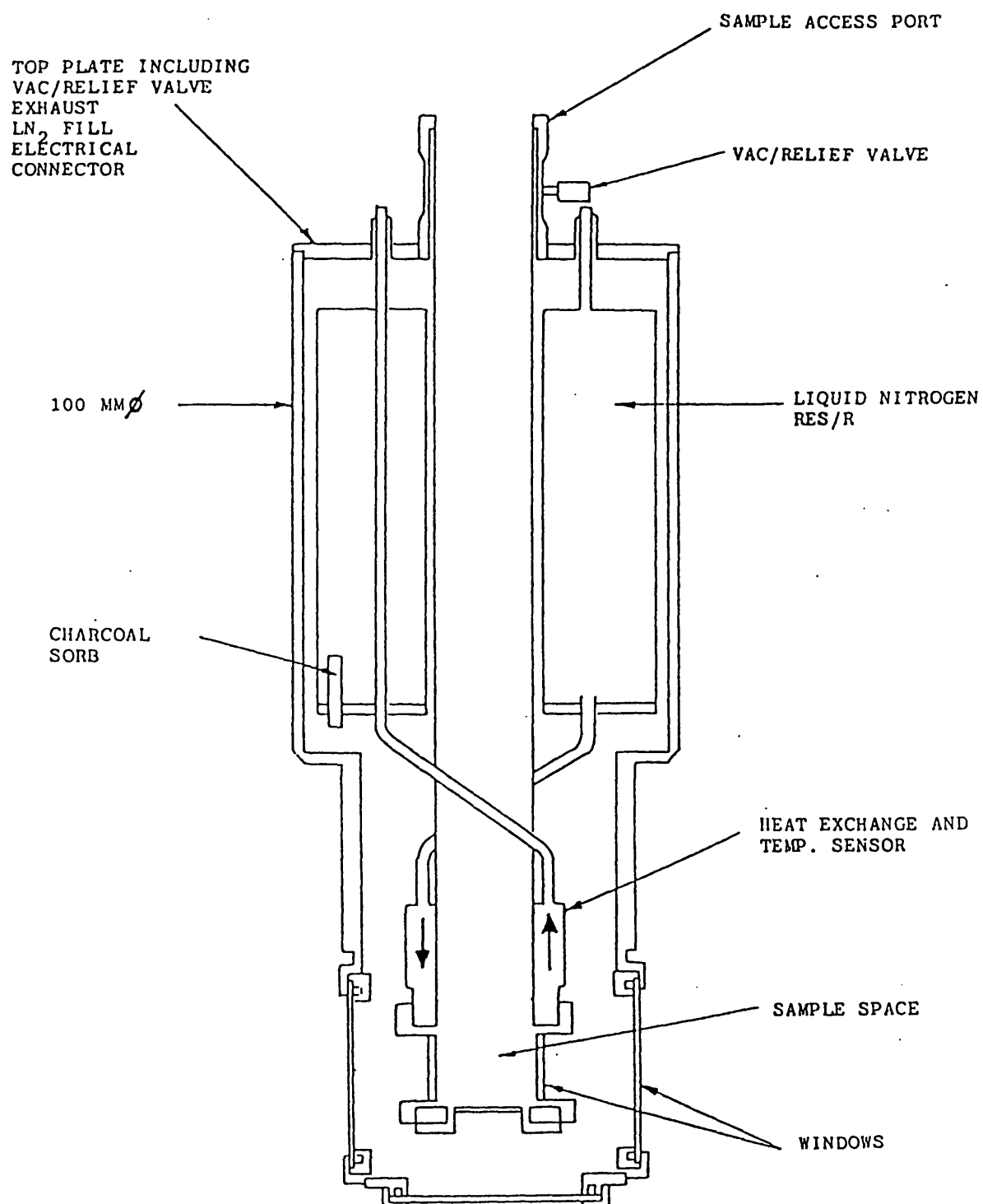


Figure 6.5 Cross-sectional view of an Infrared Plate Holder

Figure 6.6 Liquid Nitrogen Cryostat



6.3.6. Elemental analysis

All elemental analyses were performed by Johnson Matthey Technology Centre. The samples were loaded into pre-seasoned glass tubes in the dry box then evacuated on the manifold and sealed under vacuum.

6.3.7. Electron Spin Resonance Spectroscopy

E.S.R. spectra were recorded on a Bruker ER 200D.

6.4. Chemicals, Sources and Purification Procedures

6.4.1. Starting Materials

Fluorine [99.8% purity, Matherson Gas Products]; for use on the manifold was used without purification from the cylinder. For safety and convenience the gas was transferred to welded nickel cans (1dm³ capacity) when used on the vacuum line.

Chlorine Trifluoride [Fluorochem Ltd.]; was used for seasoning without further purification directly from cylinder.

Metals [Johnson Matthey Spec. Pure Grade]; obtained as fine powders.

Iodine [Aldrich Chemical Co. Ltd.]; purified by vacuum distillation.

6.4.2. Solvents

Iodine Pentafluoride [Ozark Mahoning]; was vacuum distilled from the cylinder into a 3/4" Kel-F tube. To remove traces of iodine approximately 400mmHg of fluorine was distilled onto the IrF₅ and agitated for several hours, periodically more fluorine was added to replace that lost during conversion of iodine to iodine pentafluoride. Reaction was known to be complete when the tube contained a colourless liquid, this was pure iodine pentafluoride.

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ABSTRACT

PREPARATION AND CHARACTERISATION OF THE PLATINUM GROUP METAL FLUORIDES

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An extensive review of the platinum group metal fluorides has been carried out and in the light of this, new preparative routes have been developed and characterisation has been significantly improved.

The preparation of the platinum group metal fluorides in both static and dynamic systems is discussed in chapter two. The fluorinations of ruthenium, rhodium and platinum sponges in dynamic systems proved to be of greatest interest. In these studies large amounts of ruthenium hexafluoride and platinum hexafluoride were produced and traces of rhodium hexafluoride were noted, whereas previously more forcing conditions had been employed in the preparation of these compounds. It is believed that rigorous drying of the flow line and hydrogenation of the metal *in situ* are responsible for the success of this new preparative route.

When ruthenium is fluorinated in the dynamic system ruthenium hexafluoride and tetrameric ruthenium pentafluoride are produced in large quantities, and smaller amounts of a red glassy material is also formed. There have been no previous reports of any red material forming during this reaction. It is now believed that this material is a trimeric form of ruthenium pentafluoride.

The characterisation of these fluorides was carried out using a large variety of techniques, the most useful being mass spectrometry and matrix isolated infrared spectroscopy. Mass spectrometry proved invaluable in the characterisation of the trimeric ruthenium pentafluoride, while matrix isolation enabled good quality infrared spectra of the reactive hexafluorides to be recorded. These techniques were also utilised to give the first insight into the behaviour of the tetrameric pentafluorides in the gas phase. Iridium pentafluoride has been shown to be monomeric at elevated temperatures, under similar conditions ruthenium and osmium pentafluorides decompose to the metal and fluorine. Platinum pentafluoride is known to be unstable at room temperature and thought to decompose to the hexafluoride and tetrafluoride. Using matrix isolation, direct evidence of this has been obtained.