

# Purification of Uranium Hexafluoride by Non-Aqueous Means

A Thesis presented for the degree of  
Doctor of Philosophy  
in the  
Faculty of Science  
of the  
University of Leicester  
by

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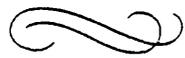


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*Dedicated to the Memory of  
Eric and Phyllis*



*Your love and encouragement  
will remain forever*

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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 1983 and September 1987. The work has not been submitted, and is not currently being submitted, for any other degree at this or any other university.

Date: .Sept. 17th. 1987

Signed:  .....

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# CHAPTER 1

Comparative Chemistry of the Hexafluorides  
of Uranium, Molybdenum and Tungsten

## 1.1 INTRODUCTION

The history of uranium is only 200 years old. In 1789 Martin H. Klaproth discovered pitch blende and in 1841 Eugene M. Peligot obtained pure uranium for the first time.

Elemental fluorine was produced for the first time in 1886. Because of its high reactivity, chemical reactions with many substances, among them that of metallic uranium, were soon established; Moisson even succeeded in producing uranium hexafluoride [1]. Otto Ruff, at the beginning of the century, was working on volatile fluorine compounds and characterised, in the 6th. group of the periodic system of elements, the unexpectedly volatile hexafluorides of molybdenum, tungsten, and finally uranium [2].

Ruff made extensive studies on the chemical and especially the physical properties of uranium hexafluoride. Considering that these investigations were made approximately 75 years ago, the results are remarkable. For example, Ruff determined 56°C as the sublimation point of uranium hexafluoride and today the accepted value is 56.54°C. Most of his other results have proved to be correct also; the only exception being the reaction of uranium hexafluoride with hydrogen [see Section 1.3.1].

Some 30 years after its discovery, uranium hexafluoride became the subject of great chemical interest when the United States of America poured large amounts of time and money into the development of the gaseous diffusion process for enriching  $U^{235}$  for a nuclear bomb and, later, for nuclear power. During the Second World War, an immense amount of work, the 'Manhattan Project', was carried out on its physical properties. The chemical behaviour of uranium hexafluoride was only investigated as far as necessary for the operation of a gaseous

diffusion process. Due to the nature of the 'Manhattan Project', all the work was subjected to very strict classification; much was not published in the open literature until some years after the end of the War and, doubtless, there is still much left which has yet to be declassified.

Uranium hexafluoride is a very important chemical in the nuclear fuel cycle even though it does not play any direct rôle in nuclear power generation. Since uranium hexafluoride is the most volatile of all known uranium compounds, it is an ideal working medium for physical processes in which separation of isotopes takes place. This separation or the enrichment of  $U^{235}$  is essential for nuclear power reactors of the AGR and PWR design, since these require a concentration of 2-3%  $U^{235}$ , instead of the natural abundance of 0.7% used in older Magnox reactors for reasons of neutron economy. The two major industrial enrichment processes (gaseous diffusion and centrifugation) employ uranium hexafluoride. An additional important advantage of uranium hexafluoride is that natural fluorine only has one single isotope.

More efficient and economically viable processes are constantly being sought for the production and purification of uranium hexafluoride. After the enrichment of uranium hexafluoride, it has to be converted to uranium dioxide,  $UO_2$ , from which reactor fuel is made.

Fig. 1.1 shows a systematic representation of the three main routes by which uranium hexafluoride is industrially produced. Each involves many highly costly steps. A possible alternative economical process for uranium hexafluoride production is shown in Fig. 1.2 and involves the direct fluorination of the concentrated uranium ore at high temperature. However, the problem with this process is the separation of uranium hexafluoride from other volatile fluorides [Step 3]. Due

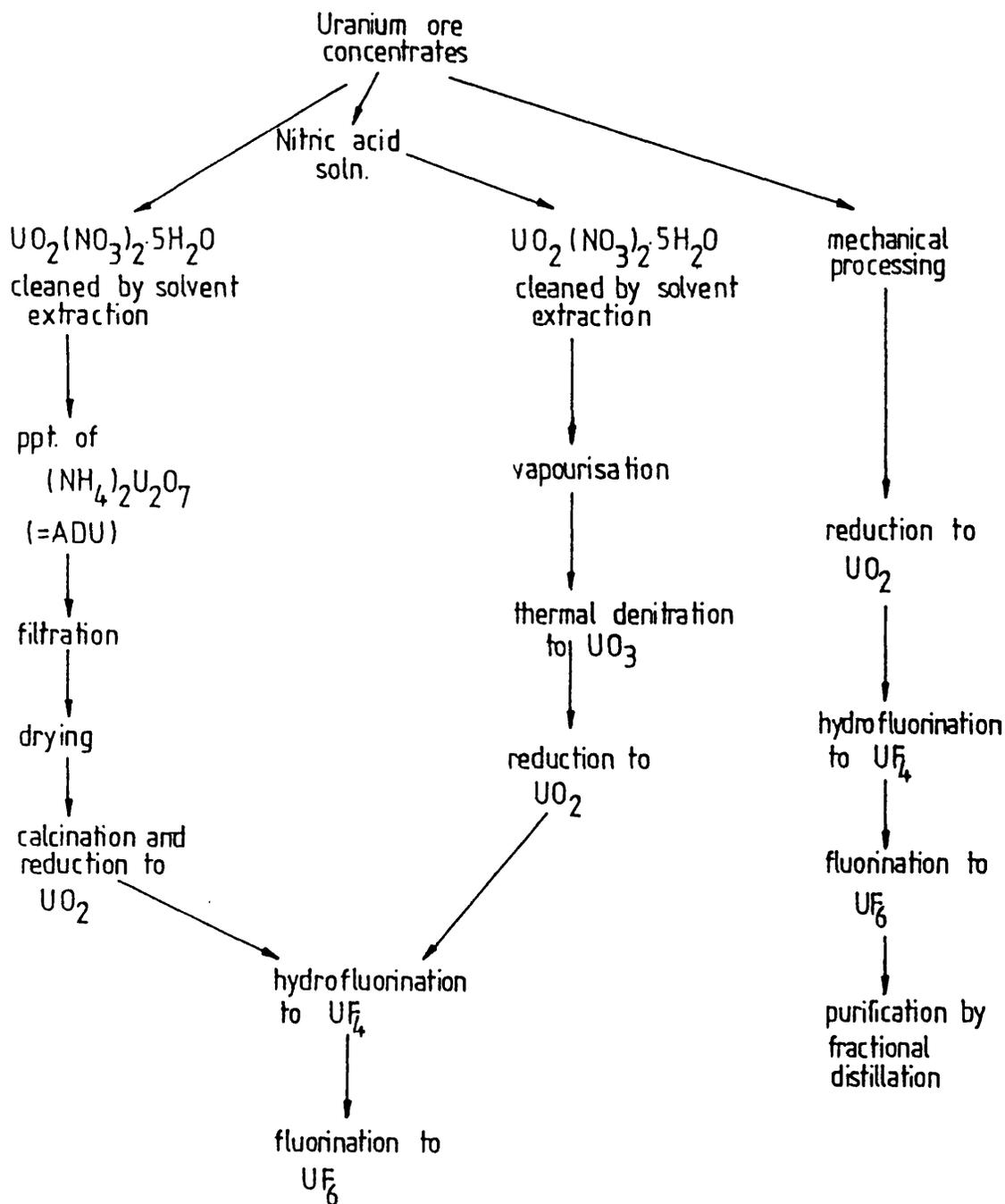


FIGURE 1.1

Technically applied procedures for  $UF_6$  production.

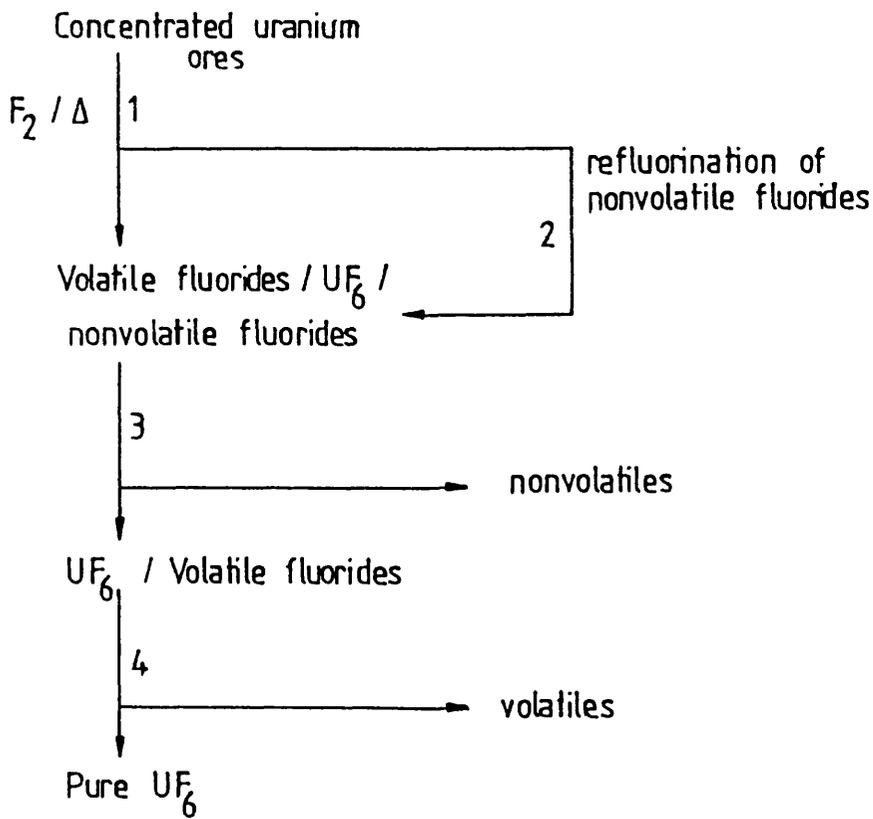


FIGURE 1.2

A possible alternative method for the production of  $UF_6$ .

to the many similarities between the hexafluorides of molybdenum, tungsten and uranium, which are all first members of their respective hexafluoride series, no effective method has been found by which pure uranium hexafluoride can be obtained from a mixture of these hexafluorides. However, any volatile fluorides more chemically reactive than uranium hexafluoride can be removed by means of specific chemical reactions.

However, before seeking means by which pure uranium hexafluoride might be obtained from mixtures of volatile fluorides, a thorough survey of the literature must be made.

### 1.2 TYPES OF REACTIONS EXHIBITED BY HEXAFLUORIDES

There are currently 17 hexafluorides reported which fall into three categories:-

- ( i ) Group VI non-metal hexafluorides of sulphur, selenium and tellurium.
- ( ii ) The single rare gas hexafluoride of xenon.
- (iii) Thirteen metal hexafluorides.

The metal hexafluorides themselves can be divided into four further categories:-

- (a) First row transition series: chromium ( $3d^0$ ).
- (b) Second row transition series: molybdenum ( $4d^0$ ), technetium ( $4d^1$ ), ruthenium ( $4d^2$ ), and rhodium ( $4d^3$ ).
- (c) Third row transition series: tungsten ( $5d^0$ ), rhenium ( $5d^1$ ), osmium ( $5d^2$ ), iridium ( $5d^3$ ), and platinum ( $5d^4$ ).
- (d) Actinide transition series: uranium ( $5f^0$ ), neptunium ( $5f^1$ ), and plutonium ( $5f^2$ ).

The chemical characteristics of a particular hexafluoride can be evaluated in terms of three main criteria:-

<u>Chemical Characteristics</u>	<u>Related Predominant Property of the Hexafluorides</u>
Fluorination efficiency	Compound dissociation energy
Fluorine addition	Fluoride ion affinity
Oxidation	Electron affinity

The predominant chemical characteristic of the hexafluorides of uranium, molybdenum and tungsten is their fluorination efficiency. They are highly reactive compounds and their chemical reactions take place mainly in the heterogenous phase; the reaction products are usually non-volatile insoluble mixtures.

The types of possible reactions for the three hexafluorides are shown in Fig. 1.3.

#### 1.2.1 Oxidative Fluorination (reaction type Ib1, Fig. 1.3)

The relative reactivity and fluorinating behaviour of the hexafluorides can be estimated to some extent by comparing their first and second bond dissociation energies [Chapter 5].

#### 1.2.2 Exchange Reactions (reaction type Ia1, Fig. 1.3)

The fluorine atoms in the hexafluorides can be partially or completely substituted by other highly electronegative groups; the oxidation state of the central metal atom remains unchanged. The most important reactions of this type are the partial F/O exchange reactions leading to the formation of oxide fluorides.

#### 1.2.3 Oxidation Reactions (reaction type II, Fig. 1.3)

Uranium hexafluoride has an electron affinity of between 118-129 kcal/mol [Table 2.6] and is capable of extracting electrons from NO, NO<sub>2</sub>, I<sub>2</sub>, and various metals by the formation of fluorouranates(V); UF<sub>6</sub><sup>-</sup>. The oxidation effect and its electron affinity is similar to that of molybdenum hexafluoride, but it is higher than that of tungsten

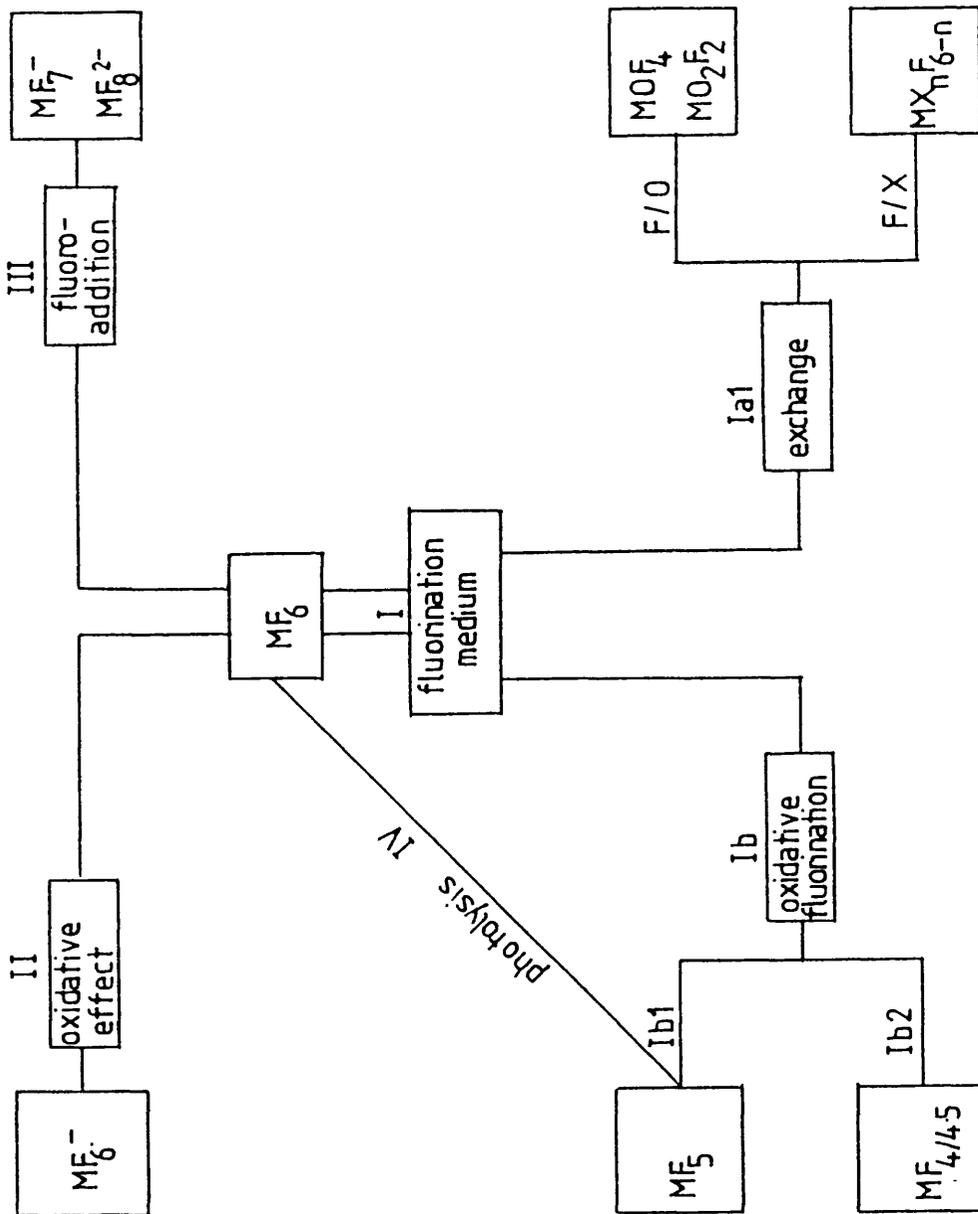


FIGURE 1.3

Possible reactions of the hexafluorides of uranium, molybdenum, and tungsten.

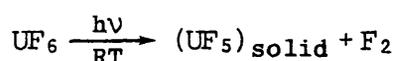
hexafluoride (electron affinity 88-118 kcal/mol) which cannot oxidise NO or NO<sub>2</sub>. Simple oxidation reactions are rare for uranium hexafluoride since, in most cases, oxidative fluorination is the dominant reaction.

#### 1.2.4 Fluoroaddition Reactions (reaction type III; Fig. 1.3)

The fluoride ion affinity of the hexafluorides determines the ease with which they undergo fluoroaddition reactions with Lewis bases such as KF, RbF, NO<sub>x</sub>F (x=1,2), NH<sub>4</sub>F, N<sub>2</sub>H<sub>6</sub>F<sub>2</sub> to form the relevant fluorouranate(VI), molybdate(VI) or tungstate(VI). Uranium, molybdenum and tungsten hexafluorides have comparable fluoride ion affinities which are higher than those of the chalcogenide hexafluorides where there is no tendency for fluorine addition.

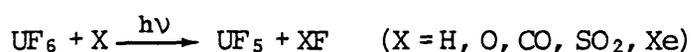
#### 1.2.5 Photolysis (reaction type IV; Fig. 1.3)

Uranium hexafluoride can be generated by the thermal fluorination of uranium tetra- or pentafluoride in the temperature range 200-400°C [10]. By the photoactivation of fluorine, uranium hexafluoride is observed at ambient temperatures [11]. Recently it was shown that uranium hexafluoride can be dissociated photochemically on a laboratory scale by UV light.



In the photolysis reactor, uranium pentafluoride formation and uranium hexafluoride dissociation takes place simultaneously [12,13,15].

The photochemical instability of gaseous uranium hexafluoride accounts for the photoactivation of a number of exothermic, but kinetically hindered reactions [14,20,21,36,47] :-



However, studies [14] have failed to determine the reduction role of either O or Xe in such reactions. The photolysis of a MoF<sub>6</sub>-CO mixture yields the pentafluoride, whereas no reduction occurs for tungsten hexafluoride under similar conditions [89].

## REACTIONS OF URANIUM, MOLYBDENUM, AND TUNGSTEN HEXAFLUORIDES

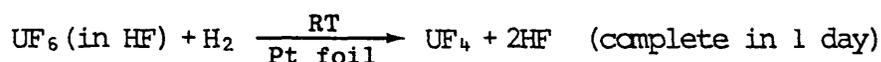
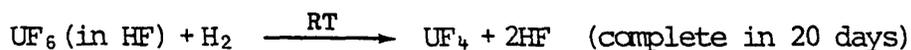
### 1.3 ELEMENTS [Table 1.1]

#### 1.3.1 Hydrogen

Thermodynamic considerations suggest that hydrogen is the only gaseous element which might react with uranium hexafluoride at ambient temperatures. The reaction:-



is exothermic (69.8 kcal/mol), but is strongly hindered; its activation energy being 50.2 kcal/mol [16]. Ruff and Heinzelmann [2] reported that uranium hexafluoride is, indeed, reduced by hydrogen at room temperature. But attempts to repeat their work have failed; however, the conditions under which Ruff et al. were working at the beginning of the century must be taken into account before dismissing their study of the UF<sub>6</sub>-H<sub>2</sub> system. The uranium hexafluoride used was probably contaminated with HF, and platinum from the production of hydrogen was probably also present. Both would have acted as catalysts; the presence of HF and platinum foil having been shown to have catalytic effects on the UF<sub>6</sub>-H<sub>2</sub> system [13,19].



A solution of uranium hexafluoride in liquid hydrogen fluoride is reduced by hydrogen in the presence of gold plates to give β-UF<sub>5</sub> at room temperature [13]. Here an activation of the UF<sub>6</sub> molecules on

TABLE 1.1

Reactions of UF<sub>6</sub>, MoF<sub>6</sub>, WF<sub>6</sub>, with the 'Elements'

	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
H <sub>2</sub>	$\text{UF}_6 + \text{H}_2 \xrightarrow{650^\circ\text{C}} \text{UF}_4 + 2\text{HF}$ [16,17,106-108] $\text{UF}_6 + \text{H}_2 \xrightarrow[\text{R.T.}]{\text{AHF}} \text{UF}_4 + 2\text{HF}$ complete in 20 days $\text{UF}_6 + \text{H}_2 \xrightarrow[\text{R.T.}]{\text{Pt foil, AHF}} \text{UF}_4 + 2\text{HF}$ complete in 1 day [19] $\text{UF}_6 + \text{H}_2 \xrightarrow[\text{R.T.}]{\text{Au plates}} \beta\text{-UF}_6$ [13] $2\text{UF}_6 + \text{H}_2 \xrightarrow[\text{R.T.}]{\text{UV light}} 2\beta\text{-UF}_6 + 2\text{HF}$ [20-24]	$\text{MoF}_6 + 3\text{H}_2 \xrightarrow{500-1200^\circ\text{C}} \text{Mo} + 6\text{HF}$ MoF <sub>3</sub> , MoF <sub>4</sub> , MoF <sub>5</sub> vapours are observed during the reaction [26,28,35]	$\text{WF}_6 + 3\text{H}_2 \xrightarrow{300-900^\circ\text{C}} \text{W} + 6\text{HF}$ [27,30-33] used for the coating of tungsten films on materials
C (graphite)	$\text{UF}_6 + \text{C} \xrightarrow[1-25 \text{ atm.}]{800-1200 \text{ K}} \text{UF}_5, \text{UF}_4, \text{CF}_4, \text{ and other carbon fluorides}$ [34,41] UF <sub>6</sub> + C:- intercalation compounds are formed at R.T. e.g. C <sub>9.1:0.5</sub> UF <sub>6</sub> $\xrightarrow{500^\circ\text{C}}$ C <sub>8.6</sub> UF <sub>4</sub> , CF <sub>4</sub> [41] The intercalation compound formed is highly dependent upon the graphite used, pressure of UF <sub>6</sub> [39-42]	MoF <sub>6</sub> + C:- intercalation compounds are formed at R.T [44-46] e.g. C <sub>5</sub> MoF <sub>6</sub> , C <sub>7</sub> MoF <sub>6</sub> , C <sub>8</sub> MoF <sub>6</sub> [43]	WF <sub>6</sub> + C:- intercalation compounds are formed at R.T [45,46]
S	$2\text{UF}_6 + \text{S} \xrightarrow{130^\circ\text{C}} 2\text{UF}_4 + \text{SF}_4$ static system In flow systems, S <sub>2</sub> F <sub>2</sub> is also observed [2,36,48]		$2\text{WF}_6 + 3\text{S} \xrightarrow[10 \text{ hrs.}]{300^\circ\text{C}} 2\text{WSF}_4 + \text{SF}_4$ [49]
Si	$4\text{UF}_6 + \text{Si} \xrightarrow[1-3 \text{ days}]{\text{AHF}} 4\beta\text{-UF}_6 + \text{SiF}_4$ [21,88] UF <sub>6</sub> + solid Si:- no reaction [36]	$4\text{MoF}_6 + \text{Si} \xrightarrow{\text{AHF}} 4\text{MoF}_5 + \text{SiF}_4$ [18,88]	WF <sub>6</sub> + Si $\longrightarrow$ No Reaction [88]

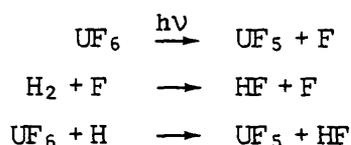
TABLE 1.1 (Continued) .....

	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
I <sub>2</sub>	$3\text{I}_2 + 20\text{UF}_6 \xrightarrow[1-10 \text{ hrs.}]{100-200^\circ\text{C}} 10\text{U}_2\text{F}_9 + 6\text{IF}_5$ <p>[51]</p> $\text{I}_2 + \text{UF}_6 \xrightarrow{\text{IF}_5} \text{I}_2^+ \text{UF}_6^-$ <p>[52,53]</p> <p style="margin-left: 100px;">UF<sub>5</sub> ↙</p>	$\text{MoF}_6 + \text{I}_2 \xrightarrow{\text{MeCN}} \text{MoF}_6\{\text{I}(\text{NCOMe})_2\}$ <p>[54]</p> <p>I<sub>2</sub> dissolves readily in MoF<sub>6</sub> without reaction [98]</p>	
Na; Cs	$\text{UF}_6 + 2\text{Na} \xrightarrow{200^\circ\text{C}} \beta\text{-Na}_2\text{UF}_6$ <p>[109]</p> $\text{UF}_6 + 2\text{Cs} \xrightarrow{\text{rapid reaction}} \text{Cs}(\text{CsUF}_6)$ <p>Drum process:- Na reduces UF<sub>6</sub> to U metal [110,111]</p>		

the bare oxide free surface is assumed to take place.

The reduction on a technical scale can only be carried out at temperatures in excess of 650°C [17].

Under the influence of UV light,  $\beta$ -UF<sub>5</sub> is formed at room temperature [22-24]. The following mechanism has been proposed from studies of UF<sub>6</sub>-H<sub>2</sub>/HF chemical lasers [22,23,24] :-



Gaseous hydrogen chloride can also have catalytic effects on the UF<sub>6</sub>-H<sub>2</sub> system in the presence of liquid hydrogen fluoride [13]. Pilot plant studies for uranium enrichment using a separating nozzle, in which a UF<sub>6</sub>-H<sub>2</sub> mixture were used as an operating medium showed that uranium hexafluoride -hydrogen mixtures can be kept at temperatures below 110°C for long periods of time if kept in "Al Mg 3" containers [25].

Molybdenum and tungsten hexafluorides are both reduced to the metal by hydrogen at elevated temperatures [26-30]. The reduction of molybdenum hexafluoride occurs at temperatures above 500°C [28,29] and is thought to occur in two stages:-

- (i) MoF<sub>3</sub> is formed initially via the reduction of molybdenum hexafluoride by hydrogen.
- (ii) Reduction of MoF<sub>3</sub> by hydrogen at temperatures >500°C produces MoF<sub>3-x</sub> complexes, which subsequently disproportionate to Mo and MoF<sub>3</sub>.

Molybdenum tetrafluoride and pentafluoride vapours observed during the MoF<sub>6</sub>-H<sub>2</sub> reaction [28] are thought to result from side reactions between MoF<sub>3</sub> and MoF<sub>6</sub>.

The reduction of tungsten hexafluoride by hydrogen is used extensively

for the deposition of tungsten films on various materials [27,30]. Tungsten deposition does not occur below 300°C and lower tungsten fluorides are only observed at temperatures between 300 and 900°C when the  $WF_6$ - $H_2$  contact time is small [27]. Many kinetic studies have been made on the  $WF_6$ - $H_2$  system [31-33]. The rate of deposition for static systems is proportional to the pressure of the hexafluoride and to the operating temperature [34].

Studies have also been made on the simultaneous deposition of molybdenum and tungsten films from the hydrogen reduction of a mixture of the hexafluorides [35].

### 1.3.2 Carbon

The gaseous hexafluorides are reduced when heated with amorphous carbon. A variety of carbon fluorides are formed, including carbon tetrafluoride [36,37]. Sorption is reported to take place with graphite or activated carbon with the formation of intercalation compounds. Uranium and molybdenum hexafluorides both form intercalation compounds with graphite at room temperature [38-46], whereas intercalation of tungsten hexafluoride only occurs in the presence of liquid chlorine, fluorine or hydrogen fluoride [45,46].

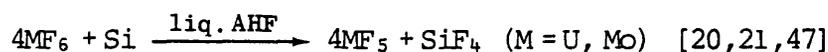
A compound of the type  $C_{9.1 \pm 0.5}UF_6$  which dissociates at 500°C into  $C_{8.6}UF_4$  and  $CF_4$  has been reported [41]. It is a weak fluorinating agent (e.g. with naphthalene in methylene chloride small amounts of monofluoronaphthalene were observed [41]). The dependences of time, temperature and pressure on the rate of uranium hexafluoride intercalation with various types and grades of activated carbon [38-42] have shown that both reduction and sorption occur. This conclusion is supported by another report in which an intercalation compound of nominal formula  $C_{13}UF_6$  was obtained [39], but was found to contain both

uranium(IV) and uranium(VI) fluorides.

The interaction of molybdenum hexafluoride with graphite yields compounds of the type  $C_5MoF_6$ ,  $C_7MoF_6$  and  $C_8MoF_6$  [43], depending upon the conditions employed.

### 1.3.3 Silicon

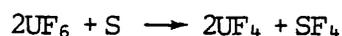
At room temperature the attack of uranium and molybdenum hexafluorides on compact silicon is negligible [36], but if they are condensed directly onto silicon powder there is a chance of an explosion. However, in liquid anhydrous hydrogen fluoride, silicon powder reduces both hexafluorides within a few days according to the equation:-



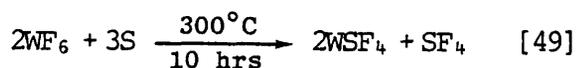
Tungsten hexafluoride is not reduced by silicon either directly or in hydrogen fluoride.

### 1.3.4 Sulphur

Uranium hexafluoride is reduced to the tetrafluoride by elemental sulphur at elevated temperatures in both static and flow systems [2,36,48].



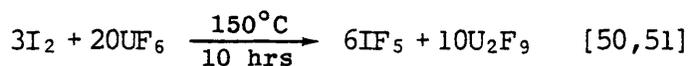
Tungsten thiotetrafluoride is reported to be formed from the direct interaction between stoichiometric quantities of tungsten hexafluoride and elemental sulphur at 300°C for 10 hours according to the equation:-



### 1.3.5 Iodine

Metallic iodine and uranium hexafluoride (molar ratio 3:20) react

in autoclaves between 100° and 200°C for 1-10 hours according to the equation:-



If the reaction is repeated in ~~iodine pent~~ <sup>iodine pent</sup> at ambient temperatures,  $I_2^+UF_6^-$  is observed as an interim product during the reduction of uranium hexafluoride to the pentafluoride,  $\beta$ - $UF_5$  [52,53]. Iodine is oxidised by molybdenum hexafluoride in acetonitrile at room temperature forming bisacetonitrile iodine(I) hexafluoromolybdate(V);  $MoF_6\{I(NCMe)_2\}$  [54].

#### 1.4 HYDRIDES [Table 1.2]

Uranium hexafluoride is slowly reduced by hydrogen chloride at 200°C, but substantially faster at 300°C, to form uranium tetra-, penta- or intermediate fluorides, depending upon the temperature and the pressure of uranium hexafluoride [55,56].

Uranium chloride fluorides;  $UCl_nF_{6-n}$  ( $n = 1, 2$ ) have recently been observed from a  $^{19}F$  nmr spectroscopic study of the interaction between liquid hydrogen chloride and solid uranium hexafluoride at temperatures between -114 to -80°C [57]. These dark red compounds are unstable at higher temperatures. Uranium(VI) chloride fluorides have been shown to be thermodynamically unstable at room temperature with respect to decomposition into a lower fluoride and to the evolution of chlorine [58]. Thus, if the reaction of  $UF_6$  with HCl is correctly interpreted, it suggests that uranium hexafluoride should be reduced by hydrogen chloride at room temperature via the decomposition of the initially formed thermally unstable uranium(VI) chloride fluoride. This does not appear to be the case. The  $UF_6$ -HCl system clearly requires further investigation.

TABLE 1.2

Reactions of UF<sub>6</sub>, MoF<sub>6</sub>, WF<sub>6</sub>, with Hydrides

	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
HCl	$UF_6 + 2HCl \xrightarrow{300^\circ C} UF_4 + 2HF + Cl_2$ <p>[55]</p> $UF_6(s) + HCl(l) \xrightarrow{-80 \text{ to } -114^\circ C} UCl_nF_{6-n}$ <p>n = 1, 2 [57]</p>		
HBr	$UF_6 + HBr \xrightarrow{65^\circ C} \alpha-, \beta-UF_5, U_2F_9, HF, Br_2$ <p>annealed to 200°C in the presence of UF<sub>6</sub> α-UF<sub>5</sub> [59, 60]</p>		
H <sub>2</sub> S	$3UF_6 + H_2S \xrightarrow{RT} 3UF_4 + SF_4 + 2HF$ <p>[61]</p> $UF_6 + H_2S \xrightarrow[RT]{MeCN} UF_4 \cdot MeCN$ <p>[62]</p>		$WF_6 + H_2S \xrightarrow{MeCN} WSF_4 \cdot MeCN$ <p>H<sub>2</sub>S</p> $WS_2F_2 \cdot MeCN$ <p>[63]</p> <p>H<sub>2</sub>S is bubbled through a solution of WF<sub>6</sub> in MeCN</p>
SiH <sub>4</sub>	$UF_6 + SiH_4 \xrightarrow{135^\circ C} UF_4, UF_5, U_2F_9 + SiH_3F$ <p>dependent upon reactant stoichiometry and the temperature [64, 65]</p>		

TABLE 1.2 (Continued) ....

	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
NH <sub>3</sub>	<p> <math>6UF_6 + (8-6n)NH_3 \xrightarrow{-50 \text{ to } -30^\circ C} 6UF_5 \cdot nNH_3 + 6NH_4F + N_2</math>  <math>4UF_6 + 8NH_3 \xrightarrow{0-25^\circ C} 2UF_5 + 2NH_4UF_5 + 4NH_4F + N_2</math> [115]  <math>3UF_6 + 8NH_3 \xrightarrow{100-200^\circ C} 3NH_4UF_5 + 3NH_4F + N_2</math>  <math>NH_3 + UF_6 \xrightarrow{160^\circ C} NH_4UF_6</math>  <math>\xrightarrow{180^\circ C} (NH_4)_2UF_6</math>                      6UF<sub>6</sub> · 7NH<sub>3</sub> has also been observed [66,68,112,113]  <math>NH_3 + UF_6 \xrightarrow{250^\circ C} \beta-NH_4UF_5</math> </p>	<p> <math>MoF_6(g) + NH_3(l) \xrightarrow{-35 \text{ to } -78^\circ C} NH_4F \cdot MoF_5 \cdot 4NH_3</math> mixture                      Reduction of MoF<sub>6</sub> to MoF<sub>5</sub> observed in solid phase at &gt; -130°C [72]                 </p>	<p> <math>WF_6 + 4NH_3 \xrightarrow{RT} WF_5 \cdot (NH_3)_4</math> white hygroscopic solid [69,70,116]  <math>WF_6 + NH_3 \xrightarrow{MeCN} WF_5 \cdot (NH)_MeCN</math>                      [71] <math>NH_4F(s) + [WF_5(NH)]^-</math>                      NH<sub>3</sub>(g) is bubbled through a solution of WF<sub>6</sub> in MeCN                 </p>
NH <sub>2</sub> NH <sub>2</sub>	<p> <math>UF_6 + NH_2NH_2 \xrightarrow{-80^\circ C} \text{explosion}</math>                      reactants diluted with N<sub>2</sub>; 70°C → N<sub>2</sub>H<sub>5</sub>UF<sub>6</sub>  <math>UF_6</math> diluted with Ar bubbled through NH<sub>2</sub>NH<sub>2</sub> → N<sub>2</sub>H<sub>5</sub>UF<sub>6</sub> (N<sub>2</sub>H<sub>5</sub>)<sub>2</sub>UF<sub>6</sub> [73,74]                 </p>	<p> <math>MoF_6 + NH_2NH_2 \xrightarrow{&lt; -80^\circ C} \text{explosion}</math>  <math>\xrightarrow{\text{Ar bubbled through } NH_2NH_2} \text{dark solutions which upon conc. leads to explosion}</math>  <math>MoF_6 + NH_2NH_2 \xrightarrow{MeCN} NH_3, N_2 + \text{lower binary Mo fluorides}</math> [75]                 </p>	<p> <math>WF_6 + NH_2NH_2 \xrightarrow{&lt; -80^\circ C} \text{explosion}</math>                      WF<sub>6</sub> forms only solvates with NH<sub>2</sub>NH<sub>2</sub> in MeCN [75]                 </p>

Hydrogen bromide reduces uranium hexafluoride in flow systems at 65°C to produce a mixture of  $\alpha$ - and  $\beta$ -UF<sub>5</sub> and U<sub>2</sub>F<sub>9</sub> [59]. Pure  $\alpha$ -UF<sub>5</sub> can be obtained if the fluoride mixture is annealed to 200°C in the presence of uranium hexafluoride. If the interaction between uranium hexafluoride and hydrogen bromide is repeated in anhydrous hydrogen fluoride, reduction to  $\beta$ -UF<sub>5</sub> occurs swiftly at room temperature [60].

Uranium hexafluoride is reduced by hydrogen sulphide at room temperature according to the equation:-



If the reaction is repeated in acetonitrile, a green uranium tetrafluoride adduct, UF<sub>4</sub>.MeCN, is produced and when a large excess of hydrogen sulphide is present a brown complex, UF<sub>4</sub>.2HF.2MeCN is formed [62]. The tungsten thiofluoride acetonitrile adducts, WSF<sub>4</sub>.MeCN and WS<sub>2</sub>F<sub>2</sub>.2MeCN are formed when hydrogen sulphide is bubbled through a solution of tungsten hexafluoride in acetonitrile [63].

Uranium tetra-, penta- or intermediate fluorides are produced from the gas phase reduction of the hexafluoride by silicon tetrahydride, which begins at 135°C [64,65]. The nature of the lower fluoride obtained depends upon the reactant stoichiometry and the temperature.

The reaction between uranium hexafluoride and gaseous ammonia has been reported to yield either ammonium hexafluorouranate(V), NH<sub>4</sub>UF<sub>6</sub> [66], or a mixture of uranium pentafluoride and NH<sub>4</sub>UF<sub>5</sub> [67], whereas the reaction with anhydrous liquid ammonia at -70°C, yields the uranium(V) salt, NH<sub>4</sub>UF<sub>5</sub> [68]. Ruff and Eisner [69] reported the formation of an orange/brown solid from the reaction of tungsten hexafluoride with gaseous ammonia and of a white solid with liquid ammonia; neither product was identified. The orange/brown solid has subsequently been shown by chemical and X-ray analysis to be (NH<sub>3</sub>)<sub>4</sub>.WF<sub>6</sub> [70]. This is

the only product reported to be formed with both gaseous and liquid ammonia. When gaseous ammonia is bubbled carefully into a solution of tungsten hexafluoride in acetonitrile,  $WF_4(NH).MeCN$  is reported to be formed [71]. If more ammonia is bubbled into the solution, ammonium fluoride is precipitated and  $^{19}F$  nmr signals attributable to  $[WF_5(NH)]^-$  have been observed [71]. The reaction of molybdenum hexafluoride with liquid ammonia at temperatures between  $-35$  and  $-78^\circ C$  yields a mixture of  $NH_4F-MoF_5.4NH_3$ . Reduction of the hexafluoride to the pentafluoride has been observed in solid phase reactions at temperatures  $\geq -130^\circ C$  [72]. Infra-red spectra of the complex  $MoF_6(NH_3)_4$  indicate that the  $NH_3$  groups are in the inner coordination sphere.

Pure hydrazine and uranium hexafluoride react explosively at  $-80^\circ C$ , while  $N_2H_5UF_5$  is formed at  $70^\circ C$  if the reactants are diluted with nitrogen [73,74]. If uranium hexafluoride vapour diluted with argon is bubbled through anhydrous hydrazine at room temperature,  $(N_2H_5)_2UF_6$  is formed [74]. Molybdenum and tungsten hexafluorides also react explosively with hydrazine at low temperatures [75]. Slowly bubbling the hexafluorides diluted with argon through hydrazine yields dark solutions. Concentration of the molybdenum solution leads to another reaction and eventually to another explosion. If the reaction between molybdenum hexafluoride and hydrazine is repeated in acetonitrile a vigorous reaction occurs with the evolution of  $N_2$ ,  $NH_3$ , and the formation of lower molybdenum fluorides [75], while tungsten hexafluoride only forms solvates with hydrazine in acetonitrile.

### 1.5 WATER [Table 1.3]

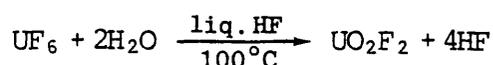
Water vapour reacts with uranium hexafluoride forming a white uranyl fluoride mist. At temperatures below  $60^\circ C$ , uranyl fluoridehydrate,

TABLE 1.3

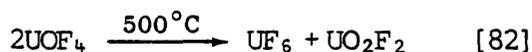
Reactions of UF<sub>6</sub>, MOF<sub>6</sub>, WF<sub>6</sub>, with Water

	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
H <sub>2</sub> O	<p>UF<sub>6</sub> + water vapour → UO<sub>2</sub>F<sub>2</sub>·nH<sub>2</sub>O</p> <p>excess UF<sub>6</sub> + H<sub>2</sub>O <math>\xrightarrow{\text{below } 60^{\circ}\text{C}}</math> UO<sub>2</sub>F<sub>2</sub>(0.7-1.3)H<sub>2</sub>O [2,36,76]</p> <p>UF<sub>6</sub> <math>\xrightarrow[\text{of H}_2\text{O}]{\text{small partial press.}}</math> U<sub>3</sub>O<sub>6</sub>F<sub>8</sub> 160-170°C [78]</p> <p>UF<sub>6</sub> + 2H<sub>2</sub>O <math>\xrightarrow[100^{\circ}\text{C}]{\text{HF}}</math> UO<sub>2</sub>F<sub>2</sub> + 4HF [77]</p> <p>UF<sub>6</sub> <math>\xrightarrow[\text{in HF}]{0.1-0.2\% \text{ H}_2\text{O}}</math> UOF<sub>4</sub> [79,80,81,82]</p> <p>UF<sub>6</sub> <math>\xrightarrow[\text{in HF}]{&gt;0.2\% \text{ H}_2\text{O}}</math> compounds within the range (UOF<sub>4</sub>-UO<sub>2</sub>F<sub>2</sub>) [81,82]</p>	<p>MoF<sub>6</sub> + 2H<sub>2</sub>O → MoO<sub>2</sub>F<sub>2</sub> + 4HF k = 3 × 10<sup>3</sup> [83]</p> <p>MoF<sub>6</sub> + H<sub>2</sub>O <math>\xrightarrow{\text{HF}}</math> MOOF<sub>4</sub> + 2HF [84]</p>	<p>WF<sub>6</sub> + 2H<sub>2</sub>O → WO<sub>2</sub>F<sub>2</sub> + 4HF k = 6 × 10<sup>3</sup> [83]</p> <p>WF<sub>6</sub> + 2H<sub>2</sub>O <math>\xrightarrow{\text{HF}}</math> H<sub>3</sub>O<sup>+</sup>·WO<sub>2</sub>F<sub>5</sub><sup>-</sup> + HF [84]</p>

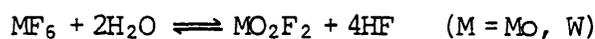
$\text{UO}_2\text{F}_2 \cdot (0.7-1.3)\text{H}_2\text{O}$  is generated from gaseous or liquid water in the presence of an excess of uranium hexafluoride. Uranyl fluoridehydrate cannot be dehydrated in the presence of uranium hexafluoride [2,36,76]. Only at temperatures greater than  $60^\circ\text{C}$  can compounds containing less water be formed. Pure, water-free  $\text{UO}_2\text{F}_2$  can be prepared from the hydrolysis of uranium hexafluoride with a stoichiometric quantity of water in liquid hydrogen fluoride [77].



Uranium compounds with composition of  $\text{UO}_{1.68}\text{F}_{2.68}$  to  $\text{UO}_{1.61}\text{F}_{2.78}$  (e.g.  $\text{U}_3\text{O}_5\text{F}_8$ , which may be written as  $(\text{UO}_2\text{F}_2)_2\text{UOF}_4$ , and is thermally unstable and decomposes at  $480^\circ\text{C}$  [78]) are generated from the gaseous-phase hydrolysis of uranium hexafluoride under very small partial pressures of water at temperatures between  $160-170^\circ\text{C}$  [78]. The hydrolysis of excess of uranium hexafluoride in a solution of 0.1-0.2%  $\text{H}_2\text{O}$  in liquid hydrogen fluoride at  $20^\circ\text{C}$  leads to the formation of uranium oxide tetrafluoride,  $\text{UOF}_4$  [79,80-82]. The primary product of the hydrolysis is thought to be  $\text{H}_3\text{O}^+\text{UOF}_5^-$  which is soluble in HF and is converted after 10-30 minutes into the HF-insoluble orange solid,  $\text{UOF}_4$ , by treatment with more uranium hexafluoride. If the concentration of water in liquid hydrogen fluoride exceeds 0.2%, more and more oxygen-enriched products, in the form of compounds in the system  $\text{UOF}_4-\text{UO}_2\text{F}_2$ , are obtained in addition to uranyl fluoridehydrate [81,82]. Such impure " $\text{UOF}_4$ " is formed by the hydrolysis of uranium hexafluoride with a 0.7% solution of water in hydrogen fluoride [81,82]. Uranium oxide tetrafluoride cannot be prepared by the gas phase hydrolysis of uranium hexafluoride by water. At elevated temperatures, uranium oxide tetrafluoride disproportionates according to the equation:-



Molybdenum and tungsten hexafluorides are also very sensitive to traces of moisture, but very few studies have been made by comparison with uranium hexafluoride. The metal dioxide difluorides are produced from the direct hydrolysis of the hexafluorides by water according to the equation:-



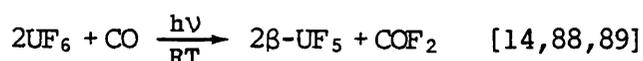
$$\begin{aligned} K &= 3 \times 10^3 \quad (\text{Mo}) \quad [83] \\ &= 6 \times 10^3 \quad (\text{W}) \end{aligned}$$

Recent studies suggest that tungsten oxide tetrafluoride,  $\text{WOF}_4$ , cannot be produced from the hydrolysis of tungsten hexafluoride by water either directly or in hydrogen fluoride [85]. Selig et al. [84] obtained  $\text{H}_3\text{O}^+\text{WOF}_5^-$  and molybdenum oxide tetrafluoride,  $\text{MoOF}_4$ , from the hydrolysis of tungsten and molybdenum hexafluorides in hydrogen fluoride respectively.

The metal oxide tetrafluorides can be more conveniently synthesised from the respective hexafluoride using boron oxide or silicon dioxide [Section 1.6], which may explain why the hydrolysis of molybdenum and tungsten hexafluorides have received so little attention.

#### 1.6 OXIDES [Table 1.4]

Uranium, molybdenum and tungsten hexafluorides do not react spontaneously with  $\text{O}_2$  [2],  $\text{N}_2\text{O}$  [86],  $\text{CO}_2$  [36] and  $\text{ClO}_2$  [87], however, photolysis of a  $\text{UF}_6\text{-O}_2$  mixture by UV light yields  $\beta\text{-UF}_5$  [14]. Uranium pentafluoride can also be synthesised by the photolysis of the hexafluoride in the presence of the fluorine scavenger carbon monoxide, according to the equation:-



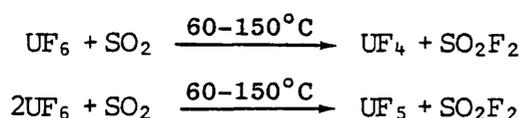
Reactions of UF<sub>6</sub>, MoF<sub>6</sub>, WF<sub>6</sub>, with Oxides

	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
O <sub>2</sub>	$\text{UF}_6(\text{g}) + \text{O}_2(\text{g}) \longrightarrow \text{No Reaction} \quad [2]$ $2\text{UF}_6(\text{g}) + \text{O}_2(\text{g}) \xrightarrow{h\nu} 2\text{UF}_5 + \text{O}_2\text{F}_2 \quad [14]$	No Reaction [69,116]	No Reaction [69,116]
B <sub>2</sub> O <sub>3</sub>	$3\text{UF}_6 + \text{B}_2\text{O}_3 \xrightarrow{\text{AHF}} 3\text{UOF}_4 + 2\text{BF}_3 \quad [96]$	$3\text{MoF}_6 + \text{B}_2\text{O}_3 \xrightarrow{\text{AHF}} 3\text{MoOF}_4 + 2\text{BF}_3 \quad [96]$	$3\text{WF}_6 + \text{B}_2\text{O}_3 \xrightarrow{\text{AHF}} 3\text{WOF}_4 + 2\text{BF}_3 \quad [96]$
CO	$2\text{UF}_6(\text{g}) + \text{CO}(\text{g}) \xrightarrow[\text{UV lamp}]{h\nu} 2\text{UF}_5 + \text{COF}_2(\text{g}) \quad [14,88,89]$	$2\text{MoF}_6(\text{g}) + \text{CO}(\text{g}) \xrightarrow{h\nu} 2\text{MoF}_5 + \text{COF}_2(\text{g}) \quad [89]$	No Reaction [89]
CO <sub>2</sub>	No Reaction [36]	No Reaction [69,116]	No Reaction [69,116]
O <sub>2</sub> F <sub>2</sub>		$\text{MoF}_6(\text{g}) + \text{O}_2\text{F}_2(\text{g}) \xrightarrow[\text{RT}]{\text{RT}} \text{O}_2\text{MoF}_7(\text{s})$ <p>white solid; results not reproducible [117]</p>	$\text{WF}_6(\text{g}) + \text{O}_2\text{F}_2(\text{g}) \xrightarrow[\text{RT}]{\text{RT}} \text{O}_2\text{WF}_7$ <p>white solid; results not reproducible [117]</p>
SiO <sub>2</sub>	$2\text{UF}_6 + \text{SiO}_2 \xrightarrow{\text{HF}} \text{UOF}_4 + \text{SiF}_4$ <p>The slow reaction  <math display="block">4\text{HF} + \text{SiO}_2 \rightleftharpoons \text{SiF}_4 + 2\text{H}_2\text{O}</math> provides a one step stoichiometric controlled partial reduction of UF<sub>6</sub> [10,95]</p>		
SO <sub>2</sub>	$2\text{UF}_6(\text{g}) + \text{SO}_2 \xrightarrow{60-150^\circ\text{C}} 2\text{UF}_5 + \text{SO}_2\text{F}_2 \quad [36,90,91]$ $\text{UF}_6 + \text{SO}_2 \xrightarrow{60-150^\circ\text{C}} \text{UF}_4 + \text{SO}_2\text{F}_2$ $2\text{UF}_6 + \text{SO}_2 \xrightarrow[\text{RT}]{h\nu} 2\text{UF}_5 + \text{SO}_2\text{F}_2 \quad [14]$	No Reaction	No Reaction
		SO <sub>2</sub> was used as the solvent for the preparation of M <sub>2</sub> [MoF <sub>6</sub> ] from MI (M = Na, K, Rb) + MoF <sub>6</sub> [92]	WF <sub>6</sub> /SO <sub>2</sub> mixture:- on long standing traces of thionyl fluoride and tungsten oxyfluorides have been detected [70]

TABLE 1.4 (Continued) . . . .

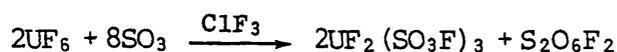
	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
SO <sub>3</sub>	$2\text{UF}_6 + 8\text{SO}_3 \xrightarrow{25^\circ\text{C}} 2\text{UF}_2(\text{SO}_3\text{F})_3 + \text{S}_2\text{O}_6\text{F}_2$ <p style="text-align: center;">[93]</p> $2\text{UF}_6 + 10\text{SO}_3 \xrightarrow[\text{ClF}_3]{-60^\circ\text{C}} 2\text{UF}(\text{SO}_3\text{F})_4 + \text{S}_2\text{O}_6\text{F}_2$ <p style="text-align: center;">[94]</p> $2\text{UF}_6 + 8\text{SO}_3 \xrightarrow{\text{ClF}_3} 2\text{UF}_2(\text{SO}_3\text{F})_3 + \text{S}_2\text{O}_6\text{F}_2$		
CrO <sub>3</sub>		$\text{MoF}_6 + \text{CrO}_3 \xrightarrow{125^\circ\text{C}} \text{CrO}_2\text{F}_2 + \text{unidentified molybdenum oxide fluorides}$ <p style="text-align: center;">[118]</p>	$\text{WF}_6 + \text{CrO}_3 \xrightarrow{125^\circ\text{C}} \text{CrO}_2\text{F}_2 + \text{unidentified tungsten oxide fluorides}$ <p style="text-align: center;">[118]</p>

The differences in the reactivities of the hexafluorides is clearly demonstrated by their differing behaviour with sulphur dioxide. Uranium tetra-, penta- or intermediate fluorides can all be obtained from the reduction of uranium hexafluoride by sulphur dioxide (reaction type Ibl, Fig. 1.3) by varying the stoichiometric ratio of the reactants and the temperature [90,91].



Photolysis of uranium hexafluoride-sulphur dioxide mixtures by UV light produces pure  $\beta$ -UF<sub>5</sub> [14]. Molybdenum hexafluoride does not react appreciably with sulphur dioxide, since it is used as the solvent for the preparation of M<sub>2</sub>[MoF<sub>6</sub>] (M = Na, K, Rb, Cs) from the reaction between the appropriate metal iodide and molybdenum hexafluoride [92]. Upon long standing tungsten hexafluoride - sulphur dioxide mixtures produce very small traces of tungsten oxide fluorides and thionyl fluoride [70].

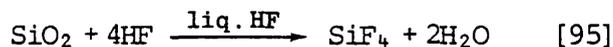
A vigorous reaction occurs between uranium hexafluoride and sulphur trioxide at room temperature with the formation of a blue-green solid, of composition, UF<sub>2</sub>(SO<sub>3</sub>F)<sub>3</sub> and a sulphur oxide fluoride, S<sub>2</sub>O<sub>6</sub>F<sub>2</sub> [93]. The same products are obtained if the reaction is repeated in ClF<sub>3</sub> [94].



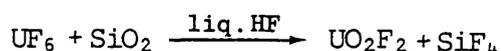
At low temperatures (<-50°C), a beige solid, UF(SO<sub>3</sub>F)<sub>4</sub> has been observed from the reaction between uranium hexafluoride and sulphur trioxide in chlorine trifluoride [94].

An indirect hydrolysis (F/O exchange; reaction type Ial, Fig. 1.3) of uranium hexafluoride is possible using quartz wool, SiO<sub>2</sub>, in liquid hydrogen fluoride; since water is slowly released from the SiO<sub>2</sub>/HF

mixture:-

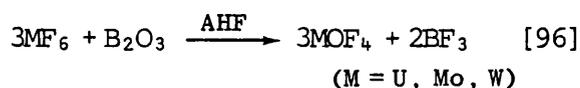


The composition of the hydrolysis product can be controlled by varying the stoichiometric ratio of the reactants. When a large excess of uranium hexafluoride is present, uranium oxide tetrafluoride is obtained, whereas the reaction between equimolar quantities of the hexafluoride and quartz wool in hydrogen fluoride yields pure uranium dioxide difluoride;



Variation of the molar ratio from 2:1 to 1.5:1 at room temperature results in the formation of compounds within the system  $\text{UOF}_4\text{-UO}_{1.5}\text{F}_2$ ; with molar ratios in the range 1.5:1 to 1:1 mixtures of adducts containing  $\text{UO}_{1.5}\text{F}_2$  with  $\text{UO}_2\text{F}_2$  are obtained [10].

A further F/O exchange reaction takes place between boron oxide and the three hexafluorides.



### 1.7 COVALENT CHLORIDES AND BROMIDES [Table 1.5]

The products obtained from the interactions between the hexafluorides of uranium, molybdenum and tungsten with covalent halides are summarised in Table 1.5. In all of the reactions it is thought that, initially, halogen exchange occurs, and that secondary reactions take place, which can be used to explain the observed products [97,98].

A simple halogen exchange (reaction type Ia1; Fig. 1.3) is reported to take place between uranium hexafluoride with excess of boron trichloride and aluminium trichloride [97].

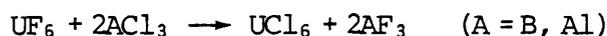


TABLE 1.5

Reactions of UF<sub>6</sub>, MoF<sub>6</sub>, WF<sub>6</sub>, with Covalent Halides

	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
BCl <sub>3</sub>	$\text{UF}_6 + 2\text{BCl}_3 \xrightarrow[\text{(excess)}]{\text{RT}} \text{UCl}_6 + 2\text{BF}_3$ $3\text{UF}_6 + 2\text{BCl}_3 \xrightarrow[\text{(excess)}]{\text{RT}} 3\text{UF}_4 + 2\text{BF}_3 + \text{Cl}_2$ [97]	$\text{MoF}_6 + 2\text{PCl}_3 \xrightarrow[\text{(excess)}]{\text{RT}} \text{MoCl}_5 + 2\text{PF}_3 + \frac{1}{2}\text{Cl}_2$ $\text{MoF}_6 + \text{PCl}_3 \xrightarrow[\text{(excess)}]{\text{RT}} \text{MoF}_5 + \text{Mo}_2\text{Cl}_3\text{F}_6 + \text{PF}_3 + \text{PF}_5$	$\text{WF}_6 + \text{PCl}_3 \xrightarrow{\text{RT}} \text{No Reaction}$ the reactants remain as two immiscible liquids, not reacting up to 150°C [119]
CCl <sub>4</sub>	$\text{UF}_6 + \text{CCl}_4 \xrightarrow[\text{(excess)}]{\text{RT}} \text{UF}_4 + \text{CCl}_{4-y}\text{F}_y + \text{Cl}_2$ $\text{UF}_6 + \text{CCl}_4 \xrightarrow[\text{(excess)}]{\text{RT}} \text{UF}_4 + \text{CCl}_{4-y}\text{F}_y + \text{Cl}_2$ [97]	$\text{MoF}_6 + \text{CCl}_4 \xrightarrow[\text{(excess)}]{\text{RT}} \text{Mo}_2\text{Cl}_3\text{F}_6 + \text{CCl}_3\text{F} + \text{CCl}_2\text{F}_2$ [98,119]           independent of reactant stoichiometry	$\text{WF}_6 + \text{CCl}_4 \xrightarrow{\text{RT}} \text{No Reaction}$ the reactants are miscible not reacting up to 150°C [119]
AlCl <sub>3</sub>	$\text{UF}_6 + 2\text{AlCl}_3 \xrightarrow[\text{(excess)}]{\text{RT}} \text{UCl}_6 + 2\text{AlF}_3$ [97]		
	$3\text{UF}_6 + 2\text{AlCl}_3 \xrightarrow[\text{(excess)}]{\text{RT}} 3\text{UF}_4 + 2\text{BF}_3$		
SiCl <sub>4</sub>	$2\text{UF}_6 + \text{SiCl}_4 \xrightarrow[\text{(excess)}]{25^\circ\text{C}} 2\text{UF}_4 + \text{SiF}_4 + 2\text{Cl}_2$ [97]           independent of reactant stoichiometry	$\text{MoF}_6 + \text{SiCl}_4 \xrightarrow[\text{(excess)}]{\text{RT}} \text{Mo}_2\text{Cl}_3\text{F}_6 + \text{SiF}_4$ slow reaction [98,119]	$\text{WF}_6 + \text{SiCl}_4 \xrightarrow{\text{RT}} \text{No Reaction}$ the liquids are miscible, but do not react up to 120°C [119]
PCl <sub>3</sub>	$\text{UF}_6 + \text{PCl}_3 \xrightarrow[\text{(excess)}]{\text{RT}} \text{UCl}_4 + \text{UF}_4 + (\text{PCl}_3)_2 + \text{PF}_3 + \text{PF}_5$ [97]	$\text{MoF}_6 + \text{PCl}_3 \xrightarrow[\text{(excess)}]{\text{RT}} \text{MoF}_5 + \text{PF}_3 + \text{Cl}_2$ $\text{MoF}_6 + \text{PCl}_3 \xrightarrow[\text{(excess)}]{\text{RT}} \text{Mo}_2\text{Cl}_3\text{F}_6 + \text{MoF}_5 + \text{PF}_3 + \text{PF}_5$ [98,119]	$\text{WF}_6 + \text{PCl}_3 \xrightarrow{\text{RT}} \text{No Reaction}$ the reactants remain as two immiscible liquids not reacting up to 150°C [119]
TiCl <sub>4</sub>	$\text{UF}_6 + \text{TiCl}_4 \xrightarrow[\text{(excess)}]{\text{RT}} \text{UCl}_6 + \text{UF}_4 + \text{TiF}_4 + \text{Cl}_2$ [97]	$\text{MoF}_6 + \text{TiCl}_4 \xrightarrow[\text{(excess)}]{\text{RT}} \text{MoCl}_5 + \text{TiF}_4$ $\text{MoF}_6 + \text{TiCl}_4 \xrightarrow[\text{(excess)}]{\text{RT}} \text{Mo}_2\text{Cl}_3\text{F}_6 + \text{TiF}_4 + \text{Cl}_2$ [98,119]	$\text{WF}_6 + \text{TiCl}_4 \xrightarrow[\text{(excess)}]{\text{RT}} \text{WCl}_6 + \text{TiF}_4$ [119]
	$\text{UF}_6 + \text{TiCl}_4 \xrightarrow[\text{(excess)}]{\text{RT}} \text{UF}_4 + \text{TiF}_4 + \text{Cl}_2$		$\text{WF}_6 + \text{TiCl}_4 \xrightarrow[\text{(excess)}]{\text{RT}} \text{WCl}_6 + \text{TiClF}_3$ 5°C $\text{WF}_5\text{Cl}$ [134]           red solid

TABLE 1.5 (Continued) . . . .

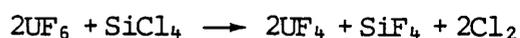
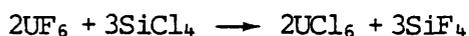
	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
AsCl <sub>3</sub>	$\text{UF}_6 + 2\text{AsCl}_3 \xrightarrow[\text{(excess)}]{\text{RT}} \text{UF}_4 + 2\text{AsF}_3 + 3\text{Cl}_2$ [97] $\text{UF}_6 + \text{AsCl}_3 \xrightarrow[\text{(excess)}]{\text{RT}} \text{UF}_4 + \text{AsF}_3 + \text{Cl}_2$	$\text{MoF}_6 + 2\text{AsCl}_3 \xrightarrow[\text{(excess)}]{\text{RT}} \text{MoF}_5 + 2\text{AsF}_3 + \frac{1}{2}\text{Cl}_2$ $\text{MoF}_6 + \text{AsCl}_3 \xrightarrow[\text{(excess)}]{\text{RT}} \text{Mo}_2\text{Cl}_3\text{F}_6 + \text{AsF}_3$ [98,119]	$\text{WF}_6 + \text{AsCl}_3 \xrightarrow[\text{(excess)}]{\text{RT}} \text{No Reaction}$ [119]
SrCl <sub>4</sub>	$\text{UF}_6 + \text{SrCl}_4 \longrightarrow \text{No Reaction}$ [137]		
SbCl <sub>3</sub>	$\text{UF}_6 + \text{SbCl}_3 \xrightarrow[\text{(excess)}]{\text{RT}} \text{UF}_4 + \text{SbF}_3 + \text{Cl}_2$ [97] $\text{UF}_6 + \text{SbCl}_3 \xrightarrow[\text{(excess)}]{\text{RT}} \text{UF}_4 + \text{SbF}_3 + \text{Cl}_2$ [97]	$\text{MoF}_6 + \text{SbCl}_3 \xrightarrow[\text{(excess)}]{\text{RT}} \text{MoCl}_5 + \text{SbF}_3 + \text{Cl}_2$ [98,119] $\text{MoF}_6 + \text{SbCl}_3 \longrightarrow \text{Mo}_2\text{Cl}_3\text{F}_6 + \text{SbCl}_2\text{F}_3$ [98,119]	$\text{WF}_6 + \text{SbCl}_3 \longrightarrow \text{No Reaction}$ [119]
SOCl <sub>2</sub>	$2\text{UF}_6 + \text{SOCl}_2 \xrightarrow{\text{RT}} 2\beta\text{-UF}_5 + \text{SOF}_2 + \text{Cl}_2$ 2:1 complete in 12 hrs 3:1 complete in 20 hrs (SOClF observed as a transient product [137]		
BBr <sub>3</sub>	$\text{UF}_6(\text{g}) + \text{BBr}_3 \xrightarrow{\text{RT}} \text{UF}_4 + \text{BF}_3 + \text{Br}_2$ [97] independent of reactant stoichiometry		
PBr <sub>3</sub>	$\text{UF}_6 + \text{PBr}_3(1) \longrightarrow \alpha\text{-UBr}_5 + \text{BF}_3$ [136]	$\text{MoF}_6 + \text{PBr}_3 \xrightarrow[\text{(excess)}]{\text{RT}} \text{MoBr}_3 + \text{PF}_3 + \text{PF}_5 + \text{Br}_2$ [98,119]	$\text{WF}_6 + \text{PBr}_3 \xrightarrow[\text{(excess)}]{\text{RT}} \text{WBr}_5 + \text{PF}_3$ slow reaction [119]

The reaction of uranium hexafluoride with phosphorus trichloride is more complex. When the reactants are mixed in stoichiometric amounts the reaction proceeds to produce uranium hexachloride and phosphorus trifluoride [97]. However, when phosphorus trichloride is in excess, the final product of the reaction is  $UCl_4(PCl_3)_x$ ;  $x = 0-1.4$ . The complex is unstable, decomposing to uranium tetrachloride upon slight heating or pumping [97].

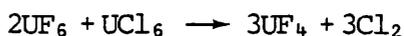
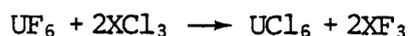
Uranium hexafluoride reacts with uranium hexachloride to produce uranium tetrafluoride [97], according to the equation:-



The above reaction was used extensively by O'Donnell et al. [97] to explain the observation of uranium tetrafluoride in the reactions of excess of uranium tetrafluoride with covalent chlorides such as silicon tetrachloride, antimony trichloride and arsenic trichloride where uranium hexachloride is initially produced, e.g.

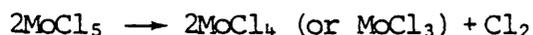
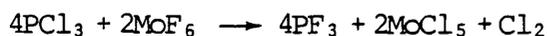


The final products obtained from the reactions of uranium hexafluoride with a trichloride appear to depend upon the comparative rates of the two following reactions:-



The initial reaction between chlorides and the hexafluorides of molybdenum and tungsten is a halogen exchange. In both cases, the highest stable chloride is formed, namely molybdenum pentachloride or tungsten hexachloride [98,119]. Subsequent reactions can take place, but are dependent upon the stoichiometric ratio of the reactants. For example, the following sequence has been proposed to account for the

production of  $\text{MoCl}_5$ ,  $\text{MoF}_5$ ,  $\text{PF}_3$ ,  $\text{PCl}_5$  when an excess of molybdenum hexafluoride and phosphorus trichloride react [98,119]:-



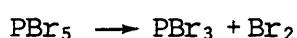
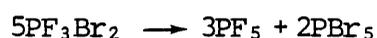
Tungsten hexafluoride is not reduced by phosphorus trichloride at room temperature except in the presence of liquid hydrogen fluoride and even then shaking for several days is required [119].

Carbon and silicon tetrachlorides do not react with tungsten hexafluoride, even when heated to  $120^\circ\text{C}$ , but react slowly with molybdenum hexafluoride forming  $\text{Mo}_2\text{Cl}_3\text{F}_9$  and the respective main group tetrafluoride [98,119]. One of the most interesting features to be noted from Table 1.5 is the common occurrence of the compound  $\text{Mo}_2\text{Cl}_3\text{F}_9$ , which has been formulated as a trinuclear compound  $(\text{Mo}_3\text{Cl}_9^{3+})(\text{MoF}_6^-)_3$  [132]. In all the reactions in which it is produced it is supposed that molybdenum pentachloride is the initial product and that this reacts with an excess of molybdenum hexafluoride to produce  $\text{Mo}_2\text{Cl}_3\text{F}_9$  [132]. Charge transfer reactions have been observed for solutions of tungsten hexafluoride in silicon and carbon tetrachlorides [266].

The reaction of titanium tetrachloride with uranium hexafluoride aroused some interest in the mid-sixties when a curious red complex  $\text{UF}_6 \cdot 2\text{TiCl}_4$  of monoclinic symmetry;  $a_0 = 6.39$ ,  $b_0 = 9.87$ ,  $c_0 = 8.05 \text{ \AA}$ ,  $\beta = 77^\circ 10'$  was reported to be formed when the components are mixed even at liquid air temperatures [133]. This is in contrast to the halogen exchange reaction which occurs between titanium tetrachloride and tungsten hexafluoride [134]. However, later work [97] has shown that the products of the reaction of uranium hexafluoride with titanium tetrachloride are  $\text{UCl}_6$ ,  $\text{UF}_4$ ,  $\text{TiF}_4$  and  $\text{Cl}_2$ , whereas partial halogen

replacement occurs with molybdenum hexafluoride, with the formation of  $\text{Mo}_2\text{Cl}_3\text{F}_6$  [98,119].

Halogen exchange is reported to occur from interactions between phosphorus tribromide and the hexafluorides of molybdenum and tungsten, with the formation of the highest stable bromides of molybdenum,  $\text{MoBr}_3$  and tungsten,  $\text{WBr}_5$  [98,119]. Both phosphorus tri- and pentafluorides are observed in the volatile reaction products from the interaction between phosphorus tribromide and molybdenum hexafluoride, which is consistent with the following series of reactions, each of which is known to occur readily [135]:-



Uranium bromides were not reported to be produced from interactions between uranium hexafluoride and the tribromides of phosphorus and boron due to their 'thermodynamic instability'. Instead, direct reduction to uranium tetrafluoride occurs [97]. However, later work [136] suggests that halogen exchange does occur with the formation of uranium pentabromide. The discrepancies between different workers clearly requires explanation.

### 1.8 IONIC CHLORIDES [Table 1.6]

The order of reactivity of the hexafluorides is reversed when considering their reactions with ionic chlorides, since uranium hexafluoride does not react as readily with Group I chlorides as does molybdenum hexafluoride [Table 1.6] [138].

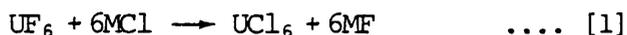
Uranium hexafluoride is reduced by ionic chlorides with the formation

TABLE 1.6

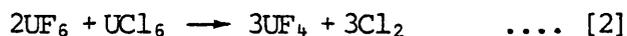
Reactions of UF<sub>6</sub>, MoF<sub>6</sub>, WF<sub>6</sub>, with Ionic Chlorides

	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
MCl M = Li, Na	$\text{UF}_6 + 2\text{MCl} \xrightarrow{\text{RT}} \text{MUF}_5 + \text{MF} + \frac{1}{2}\text{Cl}_2$ (excess) [138]	$\text{MoF}_6 + \text{MCl} \xrightarrow{\text{RT}} \text{Mo}_2\text{Cl}_3\text{F}_6 + \text{MF}$ (excess) [138]	$\text{WF}_6 + \text{MCl} \xrightarrow{\text{RT}} \text{No Reaction}$ [138]
M'Cl M' = K, Rb, Cs	$\text{UF}_6 + \text{M}'\text{Cl} \xrightarrow{\text{RT}} \text{No Reaction}$ (excess) [138]	$\text{MoF}_6 + \text{M}'\text{Cl} \xrightarrow{\text{RT}} \text{Mo}_2\text{Cl}_3\text{F}_6 + \text{M}'\text{F}$ (excess) [138]	$\text{WF}_6 + \text{M}'\text{Cl} \xrightarrow{\text{RT}} \text{No Reaction}$ (excess) [138]
BeCl <sub>2</sub>	$\text{UF}_6 + \text{BeCl}_2 \xrightarrow{\text{RT}} \text{UF}_4 + \text{BeF}_2 + \text{Cl}_2$ (excess) [138]	$\text{MoF}_6 + \text{BeCl}_2 \xrightarrow{\text{RT}} \text{Mo}_2\text{Cl}_3\text{F}_6 + \text{BeF}_2 + \text{Cl}_2$ (excess) [138]	$\text{WF}_6 + \text{BeCl}_2 \xrightarrow{\text{RT}} \text{WCl}_6 + \text{BeF}_2$ (excess) [138]
MgCl <sub>2</sub>	$\text{UF}_6 + \text{MgCl}_2 \xrightarrow{\text{RT}} \text{UF}_4 + \text{MgF}_2 + \text{Cl}_2$ (excess) [138]	$\text{MoF}_6 + \text{MgCl}_2 \xrightarrow{\text{RT}} \text{Mo}_2\text{Cl}_3\text{F}_6 + \text{MgF}_2$ (excess) [138]	$\text{WF}_6 + \text{MgCl}_2 \xrightarrow{\text{RT}} \text{No Reaction}$ (excess) [138]
M''Cl <sub>2</sub> M'' = Ca, Sr, Ba	$\text{UF}_6 + \text{M}''\text{Cl}_2 \xrightarrow{\text{RT}} \text{UF}_4 + \text{M}''\text{F}_2 + \text{Cl}_2$ (excess) [138]	$\text{MoF}_6 + \text{M}''\text{Cl}_2 \xrightarrow{\text{RT}} \text{Mo}_2\text{Cl}_3\text{F}_6 + \text{M}''\text{F}_2$ (excess) [138]	$\text{WF}_6 + \text{M}''\text{Cl}_2 \xrightarrow{\text{RT}} \text{No Reaction}$ (excess) [138]

of the tetrafluoride [138]. The overall formation of uranium tetrafluoride could arise from an initial metathetical reaction [138]



followed by the spontaneous reaction:-



If uranium hexafluoride is in stoichiometric excess, reaction [2] will always occur. However, if the chloride is in excess, the tetrafluoride will only be formed if reaction [1] is very slow in comparison with [2]. Uranium hexafluoride reacts with ionic chlorides much more slowly than with covalent chlorides [97,138].

When molybdenum hexafluoride reacts with ionic chlorides only  $\text{Mo}_3\text{Cl}_9(\text{MoF}_6)_3$  is produced regardless of the initial reactant stoichiometry [138]. Again it is assumed that molybdenum hexafluoride reacts slowly with ionic chlorides with the formation of molybdenum pentachloride and that the hexafluoride and pentachloride, which are present simultaneously, react directly to form  $\text{Mo}_3\text{Cl}_9(\text{MoF}_6)_3$  [132].

In the few cases in which a reaction occurs between tungsten hexafluoride and an ionic chloride, a halogen exchange occurs with the formation of tungsten hexachloride [138].

## 1.9 FLUORIDES [Table 1.7]

The reactions of the hexafluorides of uranium, molybdenum and tungsten with the trifluorides of group(V) trifluorides [Table 1.7] follow a simple pattern of oxidation of the trifluoride to the pentafluoride and reduction of the hexafluoride to a lower fluoride (oxidative fluorination; reaction type Ib1, Fig. 1.3). The particular lower metal fluoride formed depends upon their relative stabilities [97,98]. Reduction of uranium hexafluoride generally yields a mixture

TABLE 1.7

Reactions of UF<sub>6</sub>, MoF<sub>6</sub>, WF<sub>6</sub>, with 'Fluorides'

	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
CF <sub>2</sub>	UF <sub>6</sub> + 'CF <sub>2</sub> ' $\xrightarrow{RT}$ lower uranium fluorides [124]	MoF <sub>6</sub> + 'CF <sub>2</sub> ' $\xrightarrow{RT}$ lower molybdenum fluorides [124]	
AlF <sub>3</sub>	UF <sub>6</sub> + AlF <sub>3</sub> $\xrightarrow{80-200^\circ C}$ No Reaction small amount of uranium retained assumed to be due to impurities [97]		
PF <sub>3</sub>	UF <sub>6</sub> + PF <sub>3</sub> $\xrightarrow{RT}$ UF <sub>4</sub> + PF <sub>5</sub> (excess) [97] UF <sub>6</sub> + PF <sub>3</sub> $\xrightarrow{RT}$ UF <sub>5</sub> + PF <sub>5</sub> (excess) (or other intermediate fluorides such as U <sub>2</sub> F <sub>9</sub> , U <sub>n</sub> F <sub>17</sub> )	2MoF <sub>6</sub> + PF <sub>3</sub> $\xrightarrow{RT}$ 2MoF <sub>5</sub> + PF <sub>5</sub> [98]	WF <sub>6</sub> + PF <sub>3</sub> $\xrightarrow{RT}$ WF <sub>4</sub> + PF <sub>5</sub> [119]
SF <sub>4</sub>	UF <sub>6</sub> + SF <sub>4</sub> $\xrightarrow{500^\circ C}$ UF <sub>4</sub> + SF <sub>6</sub> [122,123]	MoF <sub>6</sub> + SF <sub>4</sub> $\xrightarrow{-40^\circ C}$ intensely yellow which decomposed at higher temps. [148]	
NiF <sub>2</sub>	UF <sub>6</sub> + NiF <sub>2</sub> $\rightarrow$ No Reaction [125,126]		
AsF <sub>3</sub>	UF <sub>6</sub> + AsF <sub>3</sub> $\rightarrow$ UF <sub>4</sub> + AsF <sub>5</sub> only a slight, very slow reaction [97]		
BrF <sub>3</sub>	UF <sub>6</sub> :BrF <sub>3</sub> - simple eutectic type system, exhibits a positive deviation from ideality [139]		

TABLE 1.7 (Continued) . . . .

	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
BrF <sub>5</sub>	UF <sub>6</sub> :BrF <sub>5</sub> - simple eutectic type system, exhibits a slight deviation from ideality; no azeotropes [139-141]		
SrF <sub>2</sub>	UF <sub>6</sub> + SrF <sub>2</sub> $\xrightarrow{80-200^\circ\text{C}}$ No Reaction small amount of uranium retained assumed to be due to impurities [127]		
MoF <sub>5</sub>	UF <sub>6</sub> + MoF <sub>5</sub> $\xrightarrow{\text{RT}}$ UF <sub>4</sub> + MoF <sub>6</sub> (excess) UF <sub>6</sub> + MoF <sub>5</sub> $\xrightarrow{\text{RT}}$ UF <sub>5</sub> + MoF <sub>6</sub> (excess) [97]		
SbF <sub>3</sub>	UF <sub>6</sub> + SbF <sub>3</sub> $\xrightarrow{\text{RT}}$ No Reaction [97]		
SbF <sub>5</sub>	UF <sub>6</sub> + 2SbF <sub>5</sub> $\xrightarrow{\text{Freon 114}}$ UF <sub>5</sub> ·2SbF <sub>5</sub> pale blue [99] $\xrightarrow{\text{thermal decomposition}}$ UF <sub>5</sub> SbF <sub>5</sub> + SbF <sub>5</sub>		

TABLE 1.7 (Continued) . . . .

	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
XeF <sub>2</sub>	UF <sub>6</sub> .XeF <sub>2</sub> system:- unlimited reciprocal soly. of the components in the liquid state. One dyctectic pt. corresponding to the formation of a congruently compound XeF <sub>2</sub> .UF <sub>6</sub> , with mpt. 120±5°C. [128,129]	MoF <sub>6</sub> .XeF <sub>2</sub> observed at 124°C from DTA studies. XeF <sub>2</sub> .4MoF <sub>6</sub> has been observed from thermal phase diagrams. [130]	WF <sub>6</sub> .XeF <sub>2</sub> observed at 125°C from DTA studies. XeF <sub>2</sub> .4WF <sub>6</sub> has been observed from thermal phase diagrams. [130]
XeF <sub>6</sub>	UF <sub>6</sub> + XeF <sub>6</sub> $\xrightarrow[131]{20-100^\circ\text{C}}$ No Reaction		
WF <sub>4</sub>	UF <sub>6</sub> + WF <sub>4</sub> $\xrightarrow[97]{\text{RT}}$ UF <sub>4</sub> + WF <sub>6</sub> (excess) UF <sub>6</sub> + WF <sub>4</sub> $\xrightarrow{\text{RT}}$ UF <sub>5</sub> + WF <sub>6</sub> (excess)		In the presence of WF <sub>6</sub> , WF <sub>4</sub> dissolves in MeCN to give upon concentration a bright green solid of composition:- [WF <sub>3</sub> <sup>+</sup> ][WF <sub>7</sub> <sup>-</sup> ] [120]
PbF <sub>2</sub>	UF <sub>6</sub> + PbF <sub>2</sub> $\xrightarrow[125]{800^\circ\text{C}}$ PbF <sub>4</sub> .UF <sub>6</sub> + PbF <sub>4</sub> + UF <sub>4</sub> (excess)		
UF <sub>4</sub>	UF <sub>6</sub> + UF <sub>4</sub> $\longrightarrow$ non-stoichiometric fluorides are formed at elevated temps. [100-103] 17 mmHg UF <sub>6</sub> + UF <sub>4</sub> $\xrightarrow{100^\circ\text{C}}$ β-UF <sub>5</sub> U <sub>4</sub> F <sub>17</sub> 120/140 mmHg UF <sub>6</sub> + UF <sub>4</sub> $\xrightarrow{200^\circ\text{C}}$ U <sub>2</sub> F <sub>9</sub> U <sub>4</sub> F <sub>17</sub> $\xrightarrow{300^\circ\text{C}}$ β-UF <sub>5</sub> α-UF <sub>5</sub> U <sub>2</sub> F <sub>9</sub> [104,105]		

of the tetra-, penta-, and intermediate fluorides. It is thought that uranium tetrafluoride is the initial product, which then reacts with excess of uranium hexafluoride to form either the pentafluoride or intermediate fluorides [97]. Molybdenum hexafluoride is usually reduced to the pentafluoride, since its tetrameric structure is particularly stable [142]. Due to the chemical and thermodynamic instability of tungsten pentafluoride, reduction of tungsten hexafluoride yields the tetrafluoride.

A pale blue 1:2 uranium pentafluoride - antimony pentafluoride adduct;  $UF_5 \cdot 2SbF_5$ , is formed from the interaction between stoichiometric quantities of uranium hexafluoride and antimony pentafluoride in Freon 114 at room temperature [99]. Thermal decomposition of the 2:1 adduct at 80°C under vacuum gives the 1:1 adduct;  $UF_5 \cdot SbF_5$  and antimony pentafluoride [99]. No reaction occurs between uranium hexafluoride and antimony trifluoride, whereas arsenic trifluoride is slowly oxidised to the pentafluoride (reaction type Ibl, Fig. 1.3) according to the equation:-



Unequivocal evidence that uranium hexafluoride is a stronger oxidant than molybdenum or tungsten hexafluorides is provided by the fact that uranium hexafluoride readily oxidises both tungsten tetrafluoride and molybdenum pentafluoride to the corresponding hexafluoride [97].

An early attempt to prepare uranium pentafluoride by the interaction of the tetrafluoride and hexafluoride resulted in the formation of a black product which was referred to as 'black  $UF_4$ ' [100]. Further investigations have revealed that, in addition to  $\alpha$ - and  $\beta$ - $UF_5$ , it is possible to prepare three intermediate fluorides by the controlled interaction of uranium tetra- and hexafluorides [101-105] [Fig. 1.4].

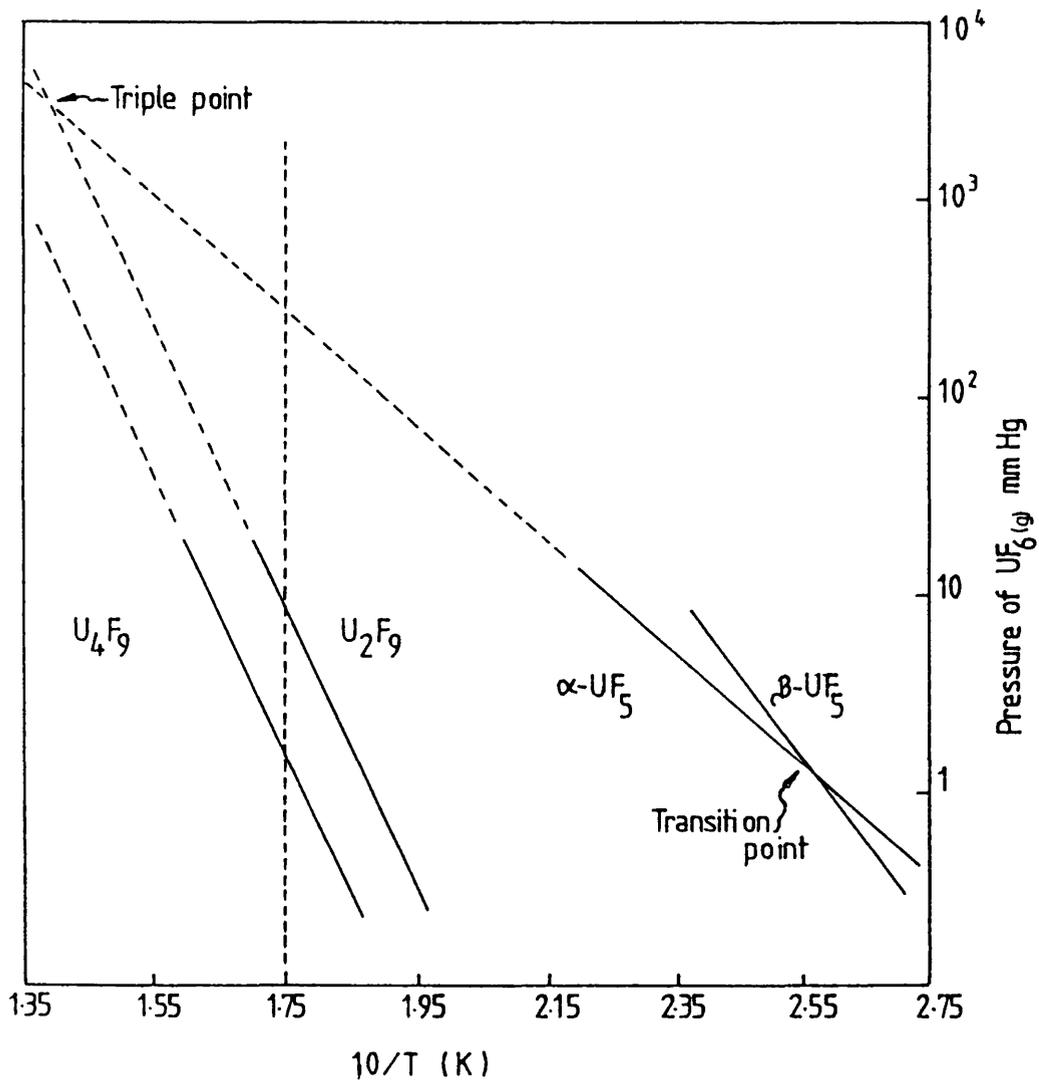


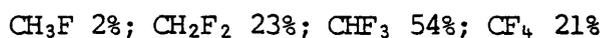
FIGURE 1.4

Equilibrium dissociation pressures of various uranium fluorides from  $\text{UF}_4$  to  $\text{UF}_5$  [105].

These intermediate fluorides are diuranium nonafluoride  $U_2F_9$  (the original 'black  $UF_4$ '),  $U_4F_{19}$  and  $U_5F_{22}$ . Like uranium pentafluoride, the intermediate fluorides disproportionate when heated.

#### 1.10 ORGANIC COMPOUNDS [Table 1.8]

Hydrocarbons ( $C_{1-12}$ ) and their chloride derivatives are fluorinated by uranium hexafluoride at temperatures between 100 and 600°C in the presence of sodium fluoride or calcium fluoride catalysts [145]. For example, the following fluorocarbons are obtained if a 9:1 molar ratio of uranium hexafluoride to methane is heated to 386°C in the presence of sodium fluoride pellets:-



High molecular hydrocarbons, e.g. paraffin oil, only react slowly with uranium hexafluoride with the formation of hydrogen fluoride and lower uranium fluorides [162]. There are no reports in the open literature of any analogous studies with molybdenum or tungsten hexafluorides.

Both uranium and tungsten carbides, MC (M = U, W) have been synthesised from the interactions of the respective hexafluoride with a mixture of hydrogen and methane at high temperatures [143,144]. Ditungsten carbide,  $W_2C$ , is obtained when aromatic hydrocarbons are used instead of methane [147]. Carbide formation is favoured by low pressures and high temperatures.

Tungsten hexafluoride forms a white crystalline compound,  $WF_6 \cdot C_6H_6$ , with benzene at dry ice temperatures [146]. Upon warming, the addition compound decomposes forming a red solution. Reduction to the tetrafluoride occurs when the hexafluoride-benzene mixture is heated for prolonged periods at 110°C [146].

At room temperature, the hexafluorides react vigorously with acetic

Reactions of UF<sub>6</sub>, MoF<sub>6</sub>, WF<sub>6</sub>, with Organic Compounds

	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluorides
CH <sub>4</sub> , H <sub>2</sub>	$\text{UF}_6 + \text{CH}_4 + 5\text{H}_2 \xrightarrow{200^\circ\text{C}} \text{UC} + 10\text{HF}$ <p>the reaction is favoured by decreases in pressure; increases in temp. [143]</p>		$\text{WF}_6 + 3\text{H}_2 + \text{CH}_4 \xrightarrow{800-900^\circ\text{C}} \text{WC} + 6\text{HF}$
C <sub>1-12</sub> hydrocarbons (aliphatic)	C <sub>1-12</sub> hydrocarbons, Cl- derivs. are fluorinated by UF <sub>6</sub> in the presence of NaF, CaF <sub>2</sub> catalysts at temps. between 100-600°C. [145]		
C <sub>6</sub> H <sub>6</sub>			$\text{C}_6\text{H}_6 + \text{WF}_6 \xrightarrow{-75^\circ\text{C}} \text{C}_6\text{H}_6 \cdot \text{WF}_6$ <p>white crystals, which decompose upon warming to give red solutions. [146]</p> $\text{C}_6\text{H}_6 + \text{WF}_6 \xrightarrow[3-9 \text{ days}]{110^\circ\text{C}} \text{WF}_4 \quad [146]$
Aromatic hydrocarbons			$\text{WF}_6 + \text{aromatic hydrocarbons} \xrightarrow{400-700^\circ\text{C}} \text{W}_2\text{C}$ <p>e.g. benzene, toluene, xylene [147]</p>
n-hexane; cyclohexane		charge transfer reactions were observed [149]	charge transfer reactions were observed [149]
MeOH	$\text{UF}_6 + \text{MeOH} \xrightarrow[-90^\circ\text{C}]{\text{CFCl}_3} \text{F}_3\text{UOMe}$ <p>[150]</p>		

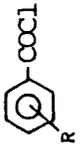
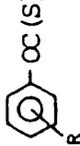
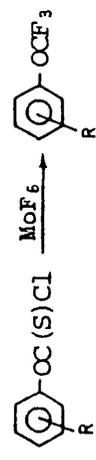
TABLE 1.8 (Continued) ....

	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
R <sub>2</sub> O (R = Me, Et)			$\text{WF}_6 + \text{Me}_2\text{O} \xrightarrow{100^\circ\text{C}} \text{WOF}_4 \cdot \text{OMe}_2$ colourless liquid [151]
Et <sub>2</sub> S			$\text{WF}_6 + \text{Et}_2\text{O} \xrightarrow{\text{RT}} \text{WOF}_4 \cdot \text{OEt}_2$ colourless liquid
Et <sub>2</sub> Se			$\text{WF}_6 + 2\text{Et}_2\text{S} \longrightarrow \text{WF}_6 \cdot 2\text{Et}_2\text{S}$ [151] yellow involatile liquid
MeNH <sub>2</sub>			$\text{WF}_6 + 2\text{Et}_2\text{Se} \longrightarrow \text{WF}_6 \cdot 2\text{Et}_2\text{Se}$ [151] orange involatile liquid
			$\text{WF}_6 + 3\text{MeNH}_2 \xrightarrow{-46^\circ\text{C}} (\text{MeNH}_2)_3\text{WF}_6$ [70] white hygroscopic solid
			$\text{WF}_6 + 2\text{MeNH}_2 \xrightarrow[\text{RT}]{\text{below}} \text{MeNH}_3^+ \cdot \text{WF}_5\text{Me}^- + \text{HF}$ [159]
EtNH <sub>2</sub>			$\text{WF}_6 + 2\text{EtNH}_2 \xrightarrow[\text{RT}]{\text{below}} \text{EtNH}_3^+ \cdot \text{WF}_5\text{NEt}^- + \text{HF}$ [159]
Bu <sup>t</sup> NH <sub>2</sub>			$\text{WF}_6 + 3\text{Bu}^t\text{NH}_2 \longrightarrow \text{WF}_6 \cdot 3\text{Bu}^t\text{NH}_2$ formulated as a 1:1 mixture of: - Bu <sup>t</sup> NH <sub>3</sub> <sup>+</sup> · WNBu <sup>t</sup> -; Bu <sup>t</sup> NH <sub>3</sub> <sup>+</sup> · F <sup>-</sup> [159]
			$\text{WF}_6 + 3 \text{C}_5\text{H}_5\text{N} \longrightarrow \text{WF}_6(\text{C}_5\text{H}_5\text{N})_3$ white hygroscopic solid; more stable than the MeNH <sub>2</sub> analogue [70]

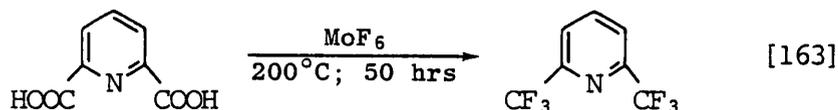
TABLE 1.8 (Continued) . . . .

	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
NMe <sub>3</sub>			$\text{WF}_6 + \text{NMe}_3 \xrightarrow{\text{CH}_2\text{Cl}_2} \text{WF}_6 \cdot \text{NMe}_3$ <p>[160] more stable than the phosphorus analogue</p>
PMe <sub>3</sub>			$\text{WF}_6 + \text{PMe}_3 \xrightarrow{\text{CH}_2\text{Cl}_2} \text{WF}_6 \cdot \text{PMe}_3$ <p>[160] orange solid; decomposes at 80°C in vacuo</p>
(TBA)I		$\text{MoF}_6 + (\text{TBA})\text{I} \xrightarrow{\text{SO}_2} (\text{TBA})\text{MoF}_6$ <p>[161] pale cream solid</p>	
CH <sub>3</sub> COOH	$\text{UF}_6 + \text{CH}_3\text{COOH} \xrightarrow{\text{RT}} \text{UO}_2\text{F}_2 + \text{HF} + \text{AcF}$ <p>vigorous heat evolution [152]</p>	$\text{MoF}_6 + \text{CH}_3\text{COOH} \xrightarrow{\text{RT}} \text{MoOF}_4 + \text{HF} + \text{AcF}$ <p>vigorous reaction [152]</p>	$\text{WF}_6 + \text{CH}_3\text{COOH} \xrightarrow{\text{RT}} \text{WO}_2\text{F}_2 + \text{HF} + \text{AcF}$ <p>[152]</p>
CF <sub>3</sub> COOH	<p>UF<sub>6</sub> dissolves in CF<sub>3</sub>COOH which upon standing yields:-  <math display="block">[\text{UF}_5\text{HF}] + \text{CF}_3\text{COF} + \text{CO}_2 + \text{COF}_2</math> green ppt. [152,153]</p>		
Alkali fluorides; CF <sub>3</sub> COOH	<p>UF<sub>6</sub> + CF<sub>3</sub>COOH in which alkali fluorides are dissolved in yields at RT.  <math display="block">\text{CF}_3\text{COOM} \cdot \text{ZUF}_5 + \text{CO}_2 + \text{HF} + \text{CF}_3\text{COF} + \text{COF}_2</math> M = alkali metal [152]</p>		
BrCH <sub>2</sub> COOH		$\text{MoF}_6 + \text{BrCH}_2\text{COOH} \xrightarrow{\text{RT}} \text{BrCH}_2\text{CF}_3 + \text{MoOF}_4 ?$ <p>[154]</p>	
RC <sub>6</sub> H <sub>4</sub> COCl		<p>MoF<sub>6</sub> is used as a selective fluorinating agent [155]</p> $\text{RC}_6\text{H}_4\text{OCCl} \xrightarrow[130-190^\circ\text{C}]{\text{MoF}_6} \text{RC}_6\text{H}_4\text{OCF}_3$ <p>R = H, o-, m-, p-Me, p-Cl, p-Br, m-CF<sub>3</sub></p>	

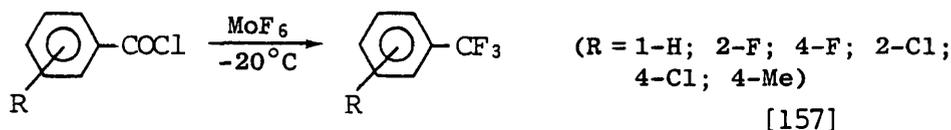
TABLE 1.8 (Continued) . . . .

	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
		<p>MoF<sub>6</sub> used as a selective fluorinating agent</p>  <p>R = 1-H; 2-F; 4-F; 2-Cl; 4-Cl; 4-Me [157]</p>	
		<p>MoF<sub>6</sub> used as a selective fluorinating agent</p>  <p>R = H, Me, Cl, CF<sub>3</sub>, Br [156]</p>	
<p>RSH (R = Et, Bu, Pb)</p>			<p> <math display="block">\text{WF}_6 + \text{RSH} \xrightarrow[\text{MeCN}]{\text{RT}} \text{WF}_5(\text{SR})</math> <math display="block">\text{WF}_5(\text{SR}) \xrightarrow{\text{RSH}} \text{trans WF}_4(\text{S})\text{MeCN}</math> <math display="block">\text{WF}_5(\text{S})(\text{SR})(\text{RSH}) \quad [158]</math> </p>

acid, with the formation of acetyl fluoride and the corresponding metal oxide fluoride [152]. Molybdenum hexafluoride has been used to convert aliphatic carboxylic acids to the respective trifluoromethyl derivative, [154,163] e.g.



and for the selective fluorination of substituted aromatic acetyl chlorides [156,157] e.g.



Uranium hexafluoride dissolves in trifluoroacetic acid which, upon standing, precipitates green crystals of composition  $\text{UF}_5\text{HF}$  [152,153]. The overall reaction gives  $\text{UF}_5\text{HF}$ ,  $\text{CF}_3\text{COF}$ ,  $\text{CO}_2$  and  $\text{COF}_2$  as products. Alkali metal fluorides dissolve in fluoroacetic acid which, with uranium hexafluoride, forms  $\text{CF}_3\text{COOM} \cdot 2\text{UF}_5$  ( $\text{M}$  = alkali metal),  $\text{CF}_3\text{COF}$ ,  $\text{COF}_2$ ,  $\text{CO}_2$  and  $\text{HF}$  as products [152].

In mild conditions, uranium hexafluoride can selectively exchange aldehyde hydrogens with fluorine, which cannot be carried out by any other fluorinating agent [10] e.g.



In 1957 Clark and Emeleus [70] obtained a white hygroscopic solid adduct of composition  $\text{WF}_6(\text{NC}_5\text{H}_5)_3$  from the reaction of tungsten hexafluoride with a large excess of pyridine at room temperature. Other workers [270] have synthesised both the 1:1  $\text{WF}_6(\text{NC}_5\text{H}_5)$  and the 1:2  $\text{WF}_6(\text{NC}_5\text{H}_5)_2$  adducts from interactions of molar ratios of the reactants

at room temperature. Tungsten hexafluoride undergoes imminolysis with primary amines  $\text{RNH}_2$  ( $\text{R} = \text{Me}, \text{Et}, \text{}^n\text{Bu}$ ) to form compounds of the type  $\text{RNH}_3^+ \text{WF}_5\text{NR}^-$  [159], according to the equation:-



With  $\text{}^t\text{BuNH}_2$ , tungsten hexafluoride forms a 1:1 adduct, which, from chemical analysis and spectroscopic studies, has been shown to be an equimolar mixture of  $\text{Bu}^t\text{NH}_3^+ \text{WF}_5\text{NBu}^t$  and  $\text{Bu}^t\text{-NH}_3^+ \text{F}^-$  [159].

The reactions of the hexafluorides with organic substances are summarised in Table 1.8.

#### 1.11 EXCHANGE REACTIONS (Reaction type Ia1) [Table 1.9]

Exchange of the fluorine atoms of the hexafluorides of uranium, molybdenum and tungsten by mono binding groups (e.g. Cl [164,165], -OMe [166-168]) have been extensively studied and take place mainly with nitrogen and silicon compounds.

It is worth noting the differing behaviour of the hexafluorides with  $\text{Me}_3\text{SiX}$  and related compounds which contain Si-X bonds [Table 1.9]. Uranium hexafluoride is reduced by  $\text{Me}_3\text{SiX}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) in Genetron at room temperature to either  $\beta\text{-UF}_5$  or  $\text{UF}_4$  depending upon the  $\text{UF}_6:\text{Me}_3\text{SiX}$  molar ratio [164] (reaction type Ia1, Fig. 1.3). A series of substituted tungsten(VI) fluorides,  $\text{WF}_{6-n}\text{X}_n$  ( $n = 1-6; \text{Cl}, \text{OR}$ ) have been prepared from such reactions in which the Si-X bonds are cleaved by tungsten hexafluoride [165,167-171].

The reactions of tungsten hexafluoride with alkoxy or phenoxy silanes occur smoothly at  $20^\circ\text{C}$  or below, with the cleavage of the Si-O bonds to form the corresponding fluorosilane. The other products are formulated as mixtures of fluoromethoxy or fluorophenoxy-tungsten(VI) compounds;  $\text{WF}_{6-n}\text{X}_n$  ( $\text{X} = \text{OMe}, n = 1-4; \text{X} = \text{OPh}, n = 1-2$ ). Except for

TABLE 1.9

Exchange reactions of UF<sub>6</sub>, MoF<sub>6</sub>, WF<sub>6</sub> (Trimethyl silyl compounds and derivatives)

	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
(Me <sub>3</sub> Si) <sub>2</sub> O			$\text{WF}_6 + (\text{Me}_3\text{Si})_2\text{O} \xrightarrow{\text{RT}} \text{WOF}_4 + 2\text{Me}_3\text{SiF}$ <p style="text-align: center;">very slow</p> $\text{WF}_6 + (\text{Me}_3\text{Si})_2\text{O} \xrightarrow[\text{RT}]{\text{MeCN}} \text{WF}_6\text{O}(\text{NMe}) + 2\text{Me}_3\text{SiF}$ <p style="text-align: center;">[168, 171]</p> $\text{WF}_6 + (\text{Me}_3\text{Si})_2\text{O} \xrightarrow[\text{pyrex}]{0^\circ\text{C}} \text{WO}_2\text{F}_2(?) + \text{Me}_3\text{SiF}$ <p style="text-align: center;">[183]</p>
Me <sub>3</sub> SiOMe	$\text{UF}_6 + n\text{Me}_3\text{SiOMe} \xrightarrow[\text{CH}_2\text{Cl}_2]{-78^\circ\text{C}} \text{U}(\text{OMe})_n\text{F}_{6-n} + n\text{Me}_3\text{SiF}$ <p style="text-align: center;">n = 1 to 6 [166]</p>		$\text{WF}_6 + \text{Me}_3\text{SiOMe} \xrightarrow[1-2 \text{ days}]{\text{RT}} \text{WF}_3\text{OMe} + \text{Me}_3\text{Si}$ <p style="text-align: center;">[168]</p> $\text{WF}_6 + 6\text{Me}_3\text{SiOMe} \xrightarrow[120^\circ\text{C}, \text{C}_6\text{F}_6]{120^\circ\text{C}} \text{W}(\text{OMe})_6 + 6\text{Me}_3\text{SiF}$
Me <sub>2</sub> Si(OMe) <sub>2</sub>		$\text{MoF}_6 + \text{Me}_2\text{Si}(\text{OMe})_2 \xrightarrow{\text{RT}} \text{MoF}(\text{OMe})_5 + \text{Me}_2\text{SiF}_2$ <p style="text-align: center;">[175]</p>	$\text{WF}_6 + \text{Me}_2\text{Si}(\text{OMe})_2 \xrightarrow[0^\circ\text{C}/2 \text{ hrs}]{0^\circ\text{C}} \text{molar ratios}$ <p>1:1 yields WF<sub>6</sub>(OMe)<sub>2</sub> + WF<sub>3</sub>(OMe)<sub>3</sub> + Me<sub>2</sub>SiF<sub>2</sub> in the ratio 8:1</p> <p>1:2.5 yields WF<sub>3</sub>OMe + WF<sub>4</sub>(OMe)<sub>2</sub> + Me<sub>2</sub>SiF<sub>2</sub> in the ratio 2:1 [168]</p>
MeSi(OMe) <sub>3</sub>	$\text{UF}_6 + 2\text{MeSi}(\text{OMe})_3 \xrightarrow[\text{CH}_2\text{Cl}_2]{-78^\circ\text{C}} \text{U}(\text{OMe})_6 + 2\text{MeSiF}_3$ <p style="text-align: center;">red platelets [166]</p>		$\text{WF}_6 + \text{MeSi}(\text{OMe})_3 \xrightarrow[0^\circ\text{C}]{0^\circ\text{C}} \text{molar ratio}$ <p>1:1 yields WF<sub>3</sub>(OMe)<sub>3</sub> + WF<sub>2</sub>(OMe)<sub>4</sub> + MeSiF<sub>3</sub></p> <p>1:2 yields WF<sub>2</sub>(OMe)<sub>4</sub> + MeSiF<sub>3</sub> [168]</p>
Si(OR) <sub>4</sub>	$\text{UF}_6 + \text{Si}(\text{OR})_4 \xrightarrow[100\%]{100\%} \text{U}(\text{OR})_6 + \text{SiF}_4$ <p style="text-align: center;">R = CH<sub>3</sub> [192] = CH<sub>2</sub>CF<sub>3</sub> [10]</p>	$\text{MoF}_6 + \text{Si}(\text{OMe})_4 \xrightarrow{\text{initially MoF}(\text{OMe})_5 \text{ is formed which is then converted to Mo}(\text{OMe})_6} \text{initially MoF}(\text{OMe})_5 \text{ is formed which is then converted to Mo}(\text{OMe})_6$ <p style="text-align: center;">[172]</p>	$\text{WF}_6 + \text{Si}(\text{OMe})_4 \xrightarrow[12 \text{ hrs}]{20^\circ\text{C}} \text{WF}_3\text{OMe} + \text{SiF}_4$ <p>6:1 molar ratio</p> $\text{WF}_6 + \text{Si}(\text{OMe})_4 \xrightarrow[2 \text{ hrs}]{20^\circ\text{C}} \text{cis-WF}_2(\text{OMe})_4 + \text{SiF}_4$ <p>1:1 molar ratio [170]</p>
Me <sub>2</sub> Si(OEt) <sub>2</sub>			$\text{WF}_6 + \text{Me}_2\text{Si}(\text{OEt})_2 \xrightarrow[2 \text{ hrs}]{-80^\circ\text{C}} \text{WF}_4(\text{OEt})_2 + \text{Me}_2\text{SiF}_2$ <p style="text-align: center;">[168]</p>

TABLE 1.9 (Continued) . . . .

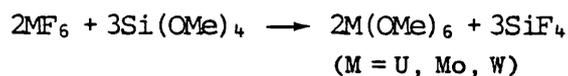
	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
$\text{Me}_3\text{SiOCH}_2\text{CF}_3$		$\text{MoF}_6 + n\text{Me}_3\text{SiOCH}_2\text{CF}_3 \longrightarrow (\text{CF}_3\text{CH}_2\text{O})_n\text{MoF}_{6-n}\text{Me}_3\text{SiF}$ [186] $n = 1-6$	
$\text{Me}_3\text{SiOPh}$			$\text{WF}_6 + \text{Me}_3\text{SiOPh}$ molar ratio 1:1 $\xrightarrow[0 \text{ hrs}]{20^\circ\text{C}}$ $\text{WF}_5\text{OPh} + \text{Me}_3\text{Si}$ [168] molar ratio 1:2 $\xrightarrow[6 \text{ hrs}]{20^\circ\text{C}}$ $\text{WF}_4(\text{OPh})_2 + \text{Me}_3\text{SiF}$ $\text{WF}_3(\text{OPh})_3 + \text{Me}_3\text{SiF}$ molar ratio 1:3 $\xrightarrow[2 \text{ hrs}]{20^\circ\text{C}}$ $\text{WF}_5\text{OPh} + \text{WF}_4(\text{OPh})_2 + \text{Me}_3\text{SiF}$
$\text{Me}_3\text{SiOC}_6\text{F}_6$			$\text{WF}_6 + \text{Me}_3\text{SiOC}_6\text{F}_6 \xrightarrow{0^\circ\text{C}}$ $\text{WF}_5\text{OC}_6\text{F}_6 + \text{Me}_3\text{SiF}$ (excess) [185] red liquid slightly volatile at RT
$\text{Me}_3\text{SiX}$ (X = Cl, Br)	$\text{UF}_6 + \text{Me}_3\text{SiX} \xrightarrow[\text{RT}]{\text{Genetron}}$ molar ratio 1:1 $\longrightarrow \beta\text{-UF}_5 + \text{Me}_3\text{SiF} + \frac{1}{2}\text{X}_2$ molar ratio 1:2 $\longrightarrow \text{UF}_4 + 2\text{Me}_3\text{SiF} + \text{X}_2$ [164]		$\text{WF}_6 + \text{Me}_3\text{SiCl} \xrightarrow{-30^\circ\text{C}}$ $\text{WF}_5\text{Cl}$ , (excess) cis, trans $\text{WF}_4\text{Cl}_2$ , in the presence of HCl [165] $\text{WCl}_3\text{F}_3 + \text{Me}_3\text{SiF}$ $\text{WF}_6 + \text{Me}_3\text{SiCl} \xrightarrow[-30^\circ\text{C}]{\text{Genetron}}$ $\text{WCl}_6 + \text{Me}_3\text{SiF}$ (excess) [165]
$\text{Me}_3\text{SiNCO}$			$\text{WF}_6 + \text{Me}_3\text{SiNCO} \xrightarrow[\text{RT}]{\text{Genetron}}$ $\text{WF}_5\text{NCO} + \text{Me}_3\text{SiF}$ (excess) [187] yellow solid
$\text{Me}_3\text{SiN}_3$			$\text{WF}_6 + \text{Me}_3\text{SiN}_3 \xrightarrow[\text{RT}]{\text{Genetron}}$ $\text{WF}_5\text{N}_3 + \text{Me}_3\text{SiF}$ (excess) yellow solid decomposes explosively at $63^\circ\text{C}$ [174]

TABLE 1.9 (Continued) ....

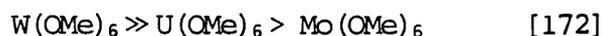
	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
$\text{Me}_3\text{SiNET}_2$			$\text{WF}_6 + 4\text{Me}_3\text{SiNET}_2 \xrightarrow{\text{RT}} \text{WF}_2(\text{NET}_2)_4 + 4\text{Me}_3\text{SiF}$ (large excess) dark brown involatile solid [185]
$(\text{Me}_3\text{Si})_2\text{NMe}$			$\text{WF}_6 + 2\text{Me}_3\text{SiNET}_2 \xrightarrow{\text{RT}} \text{WF}_4(\text{NET}_2)_2 + 2\text{Me}_3\text{SiF}$ red viscous liquid
$\text{Me}_2\text{SiNMePF}_2$			$\text{WF}_6 + (\text{Me}_3\text{Si})_2\text{NMe} \xrightarrow[1 \text{ wk}]{\text{RT}} \text{MeNWF}_4 + 2\text{Me}_3\text{SiF}$ yellow solid $\text{WF}_6 + (\text{Me}_3\text{Si})_2\text{NMe} \xrightarrow{\text{L}} \text{WF}_4(\text{NMe})\text{L} + 2\text{Me}_3\text{SiF}$ [188] L = MeCN yellow solid = py black solid
			$\text{WF}_6 + \text{Me}_2\text{SiNMePF}_2 \xrightarrow[1 \text{ wk}]{\text{RT}} \text{MeNWF}_4 + \text{PF}_3 + \text{Me}_2\text{SiF}_2$ [188] $\text{WF}_6 + \text{Me}_2\text{SiNMePF}_2 \xrightarrow{\text{MeCN}} \text{WF}_4\text{NMe}(\text{NCMe}) + \text{PF}_3 + \text{Me}_2\text{SiF}_2$

$WF_4(O\text{Me})_2$ , which is a liquid at  $20^\circ\text{C}$ , all the compounds are solids; the methoxy compounds being colourless, whereas the phenoxy compounds are red [168,171].

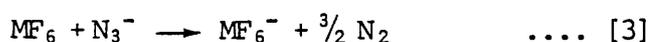
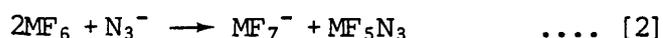
The reactions of the hexafluorides with silicon tetramethoxide,  $\text{Si}(\text{OMe})_4$  yield the corresponding metal hexamethoxides:-



It has been reported that initially  $\text{MoF}(\text{OMe})_5$  and  $\text{WF}(\text{OMe})_5$  are formed before being converted to the hexamethoxide [170,172]. Uranium hexamethoxide has also been obtained from the reactions of uranium hexafluoride with sodium methoxide in  $\text{CH}_2\text{Cl}_2$  [166] and with  $\text{MeSi}(\text{OMe})_3$  [166]. With methanol at  $-90^\circ\text{C}$ , uranium hexafluoride yields  $\text{UF}_5\text{OMe}$  [150]. A similar array of partially substituted molybdenum and tungsten fluoromethoxy compounds have been synthesised [Table 1.9]. In moist air the methoxides rapidly hydrolyse. The thermal stability of the metal hexamethoxides decrease in the series:-



The reactions of the hexafluorides of uranium, molybdenum and tungsten with azide ions may be described by the equations [1-3] [173]:-

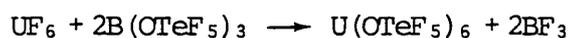


Reaction [1] is the predominant reaction for tungsten hexafluoride with tetramethyl or tetrabutylammonium azide in  $\text{SO}_2$  or in  $\text{CHCl}_3$  [173]. The reactions of uranium hexafluoride with azide ions may be described in terms of equation [3] in every case.

Somewhat analogous reactions are those of trimethylsilyl azide with the hexafluorides. The reaction with tungsten hexafluoride yields

WF<sub>5</sub>N<sub>3</sub> [174]; with uranium hexafluoride there is the evolution of nitrogen and the only observed fluorinated species from fluorine resonance spectroscopy is trimethylsilyl fluoride [173]. Similar results have been obtained for molybdenum hexafluoride with trimethylsilyl azide at room temperature [175]; however, at -70°C, a doublet and a quintet have been observed in the fluorine resonance spectra associated with MoF<sub>5</sub>N<sub>3</sub> and a pair of triplets from cis-MoF<sub>4</sub>(N<sub>3</sub>)<sub>2</sub> [175].

Studies have been made on the reactions of boron trispentafluoroxytellurate; B(OTeF<sub>5</sub>)<sub>3</sub> with all three hexafluorides [176-178]. Uranium hexafluoride reacts spontaneously, according to the equation [176]:-



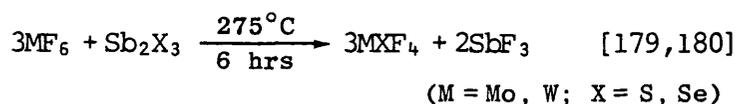
whereas molybdenum hexafluoride reacts more slowly and complex reaction schemes have been proposed [177], which include the formation of MoF<sub>n</sub>(OTeF<sub>5</sub>)<sub>6-n</sub> (n = 1-6), along with MoOF<sub>m</sub>(OTeF<sub>5</sub>)<sub>4-m</sub> (m = 1-4). The reaction with tungsten hexafluoride takes place above 120°C with the formation of WF<sub>5</sub>(OTeF<sub>5</sub>) and WF<sub>4</sub>(OTeF<sub>5</sub>)<sub>2</sub> [178].

The formation of H-F, B-F and Si-F bindings is the driving force of many of these exchange reactions. Although the hexafluoride and the hexachloride of tungsten have been long known, it was in the late sixties that chloride fluorides of tungsten(VI) were first isolated. The chloride pentafluoride, WF<sub>5</sub>Cl, has been synthesised in low yield by the action of titanium tetrachloride on tungsten hexafluoride [134] and the trichloride trifluoride, WCl<sub>3</sub>F<sub>3</sub>, is reported to result from the interaction of boron trichloride with the hexafluoride [119]. Tungsten chloride pentafluoride forms a yellow solid with a melting point of -33.7°C, a yellow liquid and a yellow vapour. The reaction of trimethylsilyl chloride with tungsten hexafluoride at -30°C in the presence of anhydrous hydrogen chloride is reported to successively

produce,  $WClF_5$ , cis-, trans- $WCl_2F_4$ ; mer-, fac- $WCl_3F_3$  and cis-, trans- $WCl_4F_2$  [165]. Tungsten dichloride tetrafluoride,  $WCl_2F_4$ , is a yellow solid which melts at approximately  $-30^\circ C$  to an orange-yellow liquid and is less volatile than  $WClF_5$ . It is unstable at room temperature; decomposing to  $WClF_5$  and other chloride fluorides [165]. In the absence of anhydrous hydrogen chloride, tungsten hexafluoride is converted by trimethylsilyl chloride into tungsten hexachloride [165].

Fluorine atoms in tungsten hexafluoride and, to a lesser extent, in molybdenum hexafluoride, can be replaced by nitrogen, sulphur and selenium groups with the formation of double bonds to the metal. With the exception of oxygen, which was discussed earlier, there are no reports of any exchange reactions of uranium hexafluoride involving the formation of double bonds.

Molybdenum and tungsten thio, seleno-tetrafluorides have been synthesised from the reactions of stoichiometric quantities of the respective hexafluoride with the appropriate antimony chalcogenide at  $275^\circ C$  in sealed reactors.



Uranium hexafluoride, however, is reduced by antimony sulphide under similar conditions to  $\beta\text{-UF}_5$  [181]. A study of the thermodynamic properties of uranium(VI) sulphur fluorides have shown that they are unstable at room temperature with respect to decomposition into lower fluorides and elemental sulphur [182].

Tables 1.9 and 1.10 show the other reported exchange reactions of uranium, molybdenum and tungsten hexafluorides. The most striking feature of these tables is the large number of reactions involving tungsten hexafluoride which have not been repeated for the other hexafluorides.

TABLE 1.10

Exchange reactions of  $\text{UF}_6$ ,  $\text{MoF}_6$ ,  $\text{WF}_6$ 

	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
$\text{B}(\text{OMe})_3$			$\text{WF}_6 + \text{B}(\text{OMe})_3$ 3:1 molar ratios $\xrightarrow[20 \text{ hrs}]{20^\circ \text{C}}$ $\text{WF}_5\text{OMe} + \text{MeF} + \text{BF}_3$ [170]
$\text{B}(\text{OTeF}_5)_3$	$\text{UF}_6 + 2\text{B}(\text{OTeF}_5)_3 \xrightarrow{\text{RT}} \text{U}(\text{OTeF}_5)_6 + 2\text{BF}_3$ yellow solid subliming at $60^\circ \text{C}$ in <i>vacuo</i> [176]	$\text{MoF}_6 + n\text{B}(\text{OTeF}_5)_3 \xrightarrow{\text{RT}} \text{MoF}_{6-n}(\text{OTeF}_5)_n + n\text{BF}_3$ rearrangements and internal fluorination of the products gives $\text{MoOF}_m(\text{OTeF}_5)_{4-m}$ ( $m = 1-4$ )	$\text{WF}_6 + n\text{B}(\text{OTeF}_5)_3 \xrightarrow[178]{120^\circ \text{C}}$ $\text{WF}_{6-n}(\text{OTeF}_5)_n + n\text{BF}_3$ both $\text{WF}_5(\text{OTeF}_5)$ and $\text{cis-WF}_4(\text{OTeF}_5)_2$ have been characterised and isolated
$(\text{SiF}_3)_2\text{O}$	$\text{UF}_6 + (\text{SiF}_3)_2\text{O} \xrightarrow{\text{RT}}$ uranium oxide fluorides + $\text{SiF}_4$ $\text{UF}_6 + (\text{SiF}_3)_2\text{O} \xrightarrow[\text{light}]{\text{UV}}$ $\beta\text{-UF}_5$ [193]		
$(\text{MeO})_3\text{PO}$			$\text{WF}_6 + (\text{MeO})_3\text{PO} \xrightarrow[170]{\text{RT}}$ $\text{WF}_5\text{OMe} + \text{POF}_3 + \text{MeF} + \text{WOF}_4\text{OP}(\text{OMe})_3$
$(\text{PhO})_3\text{PO}$			$\text{WF}_6 + (\text{PhO})_3\text{PO} \xrightarrow[170]{\text{RT}} \text{WF}_6[\text{OP}(\text{OPh})_3]_n$
$\text{ZnS}$			$\text{WF}_6 + \text{ZnS} \xrightarrow[189]{300^\circ \text{C}} \text{WSF}_4 + \text{ZnF}_2$ 10 hrs yellow
$\text{Sb}_2\text{S}_3$		$3\text{MoF}_6 + \text{Sb}_2\text{S}_3 \xrightarrow[180]{275^\circ \text{C}} 3\text{MoSF}_4 + 2\text{SbF}_3$ 6 hrs amber	$3\text{WF}_6 + \text{Sb}_2\text{S}_3 \xrightarrow[179]{300^\circ \text{C}} 3\text{WSF}_4 + 2\text{SbF}_3$ 3 hrs

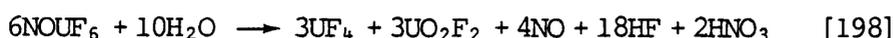
TABLE 1.10 (Continued) . . . .

	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
Sb <sub>2</sub> Se <sub>3</sub>			$3\text{WF}_6 + \text{Sb}_2\text{Se}_3 \xrightarrow{[190]} 3\text{WSeF}_4 + 2\text{SbF}_3$ <p style="text-align: center;">[190] amber</p> $\text{WF}_6 + \text{Sb}_2\text{Se}_3 \xrightarrow{\text{MeCN}} \text{WSeF}_4 \cdot \text{MeCN}$ <p style="text-align: center;">[191] evidence of <math>\text{WSeF}_5^-</math>, <math>\text{W}_2\text{SeF}_9^-</math> from <math>^{19}\text{F}</math> nmr</p>
CsN <sub>3</sub>	$\text{UF}_6 + \text{CsN}_3 \xrightarrow{\text{RT}} \text{CsUF}_6 + \frac{3}{2}\text{N}_2$ <p style="text-align: center;">[173]</p>	$\text{MoF}_6 + \text{CsN}_3 \xrightarrow{\text{RT}} \text{MoF}_5(\text{N}_3) + \text{CsF}$ <p style="text-align: center;">cis-MoF<sub>4</sub>(N<sub>3</sub>)<sub>2</sub> also observed [173]</p>	$2\text{WF}_6 + \text{CsN}_3 \xrightarrow{\text{SO}_2} \text{WF}_5\text{N}_3 + \text{CsWF}_7$ <p style="text-align: center;">[173]</p>

### 1.12 OXIDATION REACTIONS (Reaction type II) [Tables 1.12 and 1.13]

All the alkali metal hexafluoromolybdate(V) and tungstate(V) salts, except for lithium hexafluoromolybdate(V), have been synthesised from reactions of alkali metal iodides with the appropriate transition metal hexafluoride in liquid sulphur dioxide [194,195,197]. Iodine pentafluoride has been used as an alternative solvent for the preparation of the molybdenum salts [196]. The hexafluoromolybdate(V) salts are white in colour, whereas the corresponding tungstate(V) salts are slightly brown [195]. The salts are all thermally stable to 200°C in a vacuum and react violently with water to give blue solutions. There are no reports of the preparation of the analogous alkali metal hexafluorouranate(V) salts from uranium hexafluoride.

The difference in the reactivity of the hexafluorides is clearly shown in their behaviour towards nitrogen oxides, oxyhalides. The products of such reactions are shown in Table 1.12. NOUF<sub>6</sub> is a greenish-white solid which has a pseudo cubic unit cell;  $a_0 = 5.179 \text{ \AA}$  [86]. It decomposes above 200°C with the formation of gaseous NOF. Above 350°C a green melt is formed. Hydrolysis of NOUF<sub>6</sub> in air between 68 and 231°C obeys a parabolic rate law with an activation energy of 10.9 kcal/mol [204].



It is inert and insoluble towards carbon tetrachloride, Freon, liquid dinitrogen tetroxide and monochlorobenzene [86,198].

The molybdenum quinquevalent fluoro complex, NMoF<sub>6</sub>, is a rusty orange solid; it melts at approximately 190°C and has a pseudo cubic unit cell ( $a_0 = 5.08 \text{ \AA}$ ) [86]. IR spectra of these complexes are simple

TABLE 1.11

Lattice parameters of hexafluoromolybdates (V) and tungstates (V) [194]

Cation	Symmetry	Hexafluoromolybdate (V)	Hexafluorotungstate (V)
Li	Rhombohedral (LiSbF <sub>6</sub> -type)	a = 5.43 Å α = 57.1°	a = 5.45 Å α = 57.4°
Na	Cubic (NaSbF <sub>6</sub> -type)	a = 8.15 Å	a = 8.18 Å
K	Tetragonal (KNbF <sub>6</sub> -type)	a = 5.88 Å c = 9.98 Å	a = 5.85 Å c = 10.08 Å
Rb	Rhombohedral (KOsF <sub>6</sub> )	a = 5.11 Å α = 96.5°	a = 5.14 Å α = 97.6°
Cs	Rhombohedral (KOsF <sub>6</sub> )	a = 5.29 Å α = 96.0°	a = 5.31 Å α = 95.3°

TABLE 1.12

Reactions of UF<sub>6</sub>, MoF<sub>6</sub>, WF<sub>6</sub> with nitrogen oxides

	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
N <sub>2</sub> O	No Reaction [86,198]	No Reaction [86,198]	No Reaction [86,198]
NO	$\text{UF}_6(\text{g}) + \text{NO}(\text{g}) \xrightarrow{\text{RT}} \text{NOUF}_6(\text{s})$ [86,198,199] greenish-white m.pt. 340°C; non-volatile	$\text{MoF}_6(\text{g}) + \text{NO}(\text{g}) \xrightarrow{\text{RT}} \text{NOMoF}_6$ [86,198] orange-yellow non-volatile	No Reaction [86,198]
NO <sub>2</sub>	$\text{UF}_6(\text{g}) + \text{NO}_2(\text{g}) \xrightarrow{\text{RT}} \text{NO}_2\text{UF}_6(\text{s})$ [200,201] yellow-white non-volatile	No Reaction [200,201]	No Reaction [200,201]
N <sub>2</sub> O <sub>4</sub>	$\text{UF}_6(\text{g}) + \text{N}_2\text{O}_4 \xrightarrow{\text{RT}} \text{NOU}_6$ [203]	$\text{MoF}_6(\text{g}) + \text{N}_2\text{O}_4 \xrightarrow{\text{RT}} \text{NOMoOF}_5$ (g or l) [203]	$\text{WF}_6(\text{g}) + \text{N}_2\text{O}_4 \xrightarrow{\text{RT}} \text{NOWOF}_5$ (g or l) [203]
NOCl	$\text{UF}_6(\text{g}) + \text{NOCl}(\text{g}) \xrightarrow{\text{RT}} \text{NOUF}_6(\text{s}) + \frac{1}{2}\text{Cl}_2$ [201,202]	$\text{MoF}_6(\text{g}) + \text{NOCl}(\text{g}) \xrightarrow{\text{RT}} \text{NOMoF}_6(\text{s}) + \frac{1}{2}\text{Cl}_2(\text{g})$ [201,202]	No Reaction [201,202]

TABLE 1.13

Transition Metal Hexafluorurates (V), Molybdates (V), Tungstates (V)

Hexafluoruranates (V) [208]	Hexafluoromolybdates (V) [205,207]	Hexafluorotungstates (V) [205,207]
Tl[UF <sub>6</sub> ] <sub>3</sub> .5MeCN green	Ag[MoF <sub>6</sub> ] <sub>2</sub> .4MeCN white Tl <sup>I</sup> Tl <sup>III</sup> [MoF <sub>6</sub> ] <sub>4</sub> .2MeCN yellow	Ag[WF <sub>6</sub> ] <sub>2</sub> .2MeCN white Tl[WF <sub>6</sub> ] white
Cd[UF <sub>6</sub> ] <sub>2</sub> .5MeCN green Hg[UF <sub>6</sub> ] <sub>2</sub> .6MeCN	Zn[MoF <sub>6</sub> ] <sub>2</sub> .5MeCN white Cd[MoF <sub>6</sub> ] <sub>2</sub> .5MeCN white Hg[MoF <sub>6</sub> ] <sub>2</sub> .4MeCN cream	Pb[WF <sub>6</sub> ] <sub>2</sub> .2MeCN cream Zn[WF <sub>6</sub> ] <sub>2</sub> .6MeCN cream Cd[WF <sub>6</sub> ] <sub>2</sub> .5MeCN cream
Cu[UF <sub>6</sub> ] <sub>2</sub> .5MeCN green	Co[MoF <sub>6</sub> ] <sub>2</sub> .5MeCN pink Cu[MoF <sub>6</sub> ] <sub>2</sub> .5MeCN blue Cu[MoF <sub>6</sub> ] <sub>2</sub> .4MeCN yellow	Mn[WF <sub>6</sub> ] <sub>2</sub> .4MeCN white Co[WF <sub>6</sub> ] <sub>2</sub> .5MeCN salmon Ni[WF <sub>6</sub> ] <sub>2</sub> .6MeCN blue/pink Cu[WF <sub>6</sub> ] <sub>2</sub> .4MeCN yellow

showing only two bands; one at approximately  $2300\text{ cm}^{-1}$  and the other at  $525\text{ cm}^{-1}$  ( $\text{NOUF}_6$ ),  $625\text{ cm}^{-1}$  ( $\text{NOMoF}_6$ ), which are attributable to  $\text{NO}^+$  and  $\text{MF}_6^-$  ( $\text{M} = \text{U}, \text{Mo}$ ) ions respectively. Uranium hexafluoride reacts spontaneously with nitrogen dioxide at room temperature forming a yellow/white solid of composition  $\text{NO}_2\text{UF}_6$  [200,201], in contrast to molybdenum and tungsten hexafluorides which do not react [200].

The metals Ag, Tl, Pb, Zn, Cd, Hg, Mn, Co, Ni and Cu are oxidised by molybdenum and tungsten hexafluorides in acetonitrile at ambient temperatures [206,207]. The products are solvated metal cations; the counter anions being hexafluoro-molybdate(V) or -tungstate(V). Molybdenum hexafluoride oxidises Ag and Tl to Ag(I) and Tl(III) respectively, whereas Ag(I) and Tl(I) are formed with tungsten hexafluoride; thus molybdenum hexafluoride is the stronger oxidising agent [206]. Uranium hexafluoride also oxidises metals, Cu, Cd and Tl in acetonitrile to give solutions of Cu(II), Cd(II) and thallium(III) hexafluorouranates(V), from which the salts are obtained as solvates [208]. A comprehensive summary of the metal hexafluorouranate(V), molybdate(V), tungstate(V) salts characterised from such reactions is given in Table 1.13.

### 1.13 FLUOROADDITION REACTIONS (Reaction type III) [Table 1.14]

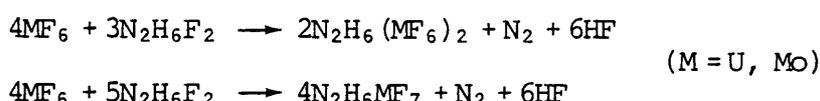
Ammonium heptafluorouranate(VI),  $\text{NH}_4\text{UF}_7$ , is formed when uranium hexafluoride is condensed onto a suspension of ammonium fluoride in tetrachloroethane [209] or by adding ammonium fluoride to a solution of uranium hexafluoride in chlorine trifluoride [209,210]. This complex decomposes to a mixture of  $\alpha$ - and  $\beta$ - $\text{UF}_5$  at  $170^\circ\text{C}$  in vacuo and to the tetrafluoride at  $450^\circ\text{C}$  [210]. The salts  $\text{NH}_4\text{MoF}_7$ ,  $\text{NH}_4\text{MoF}_6$  and  $\text{NH}_4\text{MoF}_5$  have all been separated and characterised from mixtures of

Fluoroaddition reactions of UF<sub>6</sub>, MoF<sub>6</sub>, WF<sub>6</sub>

	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
NH <sub>4</sub> F	<p>UF<sub>6</sub> + NH<sub>4</sub>F</p> <p>↓ ClF<sub>3</sub> or tetrachloroethane</p> <p>NH<sub>4</sub>UF<sub>7</sub> [209-212]</p> <p>170°C in vacuo → UF<sub>4</sub></p> <p>450°C → UF<sub>4</sub></p> <p>α-, β-UF<sub>5</sub> [209,210]</p>	<p>NH<sub>4</sub>F + saturated soln. of MoF<sub>6</sub>/HF at 0°C</p> <p>when 21.9% of phase is NH<sub>4</sub>F.2MoF<sub>6</sub> [213,214]</p> <p>NH<sub>4</sub>MoF<sub>6</sub></p> <p>MoF<sub>6</sub> + NH<sub>4</sub>F (in fused MoF<sub>6</sub>) [213]</p> <p>25-70°C</p> <p>NH<sub>4</sub>MoF<sub>7</sub>, NH<sub>4</sub>MoF<sub>8</sub>, NH<sub>4</sub>MoF<sub>9</sub> have all been isolated and characterised</p>	
N <sub>2</sub> H <sub>6</sub> F <sub>2</sub>	<p>UF<sub>6</sub> + N<sub>2</sub>H<sub>6</sub>F<sub>2</sub> <math>\xrightarrow[\text{HF}]{\text{RT}}</math> N<sub>2</sub>H<sub>6</sub>(UF<sub>6</sub>)<sub>2</sub> (excess)</p> <p>UF<sub>6</sub> + N<sub>2</sub>H<sub>6</sub>F<sub>2</sub> <math>\xrightarrow[\text{HF}]{\text{RT}}</math> N<sub>2</sub>H<sub>6</sub>UF<sub>7</sub> yellow [215-218]</p> <p>4UF<sub>6</sub> + 5N<sub>2</sub>H<sub>6</sub>F<sub>2</sub> <math>\xrightarrow[\text{HF}]{\text{RT}}</math> 4N<sub>2</sub>H<sub>6</sub>UF<sub>7</sub> + N<sub>2</sub> + 6HF [215-218]</p> <p>N<sub>2</sub>H<sub>6</sub>F<sub>2</sub>(g) + UF<sub>6</sub>(g) → UF<sub>4</sub></p>	<p>MoF<sub>6</sub> + N<sub>2</sub>H<sub>6</sub>F<sub>2</sub> <math>\xrightarrow[\text{HF}]{\text{RT}}</math> N<sub>2</sub>H<sub>6</sub>(MoF<sub>6</sub>)<sub>2</sub> (excess)</p> <p>MoF<sub>6</sub> + N<sub>2</sub>H<sub>6</sub>F<sub>2</sub> (excess) <math>\xrightarrow[\text{HF}]{\text{RT}}</math> N<sub>2</sub>H<sub>6</sub>MoF<sub>6</sub> [217]</p>	
NO <sub>2</sub> F	<p>UF<sub>6</sub>(g) + NOF<sub>2</sub>(g) <math>\xrightarrow[\text{NOUF}_8]{\text{RT}}</math> NOUF<sub>8</sub> [202,219]</p>	<p>MoF<sub>6</sub>(g) + NOF<sub>2</sub>(g) <math>\xrightarrow[\text{NOMoF}_8(s)]{\text{RT}}</math> NOMoF<sub>8</sub>(s) [202,219]</p>	<p>WF<sub>6</sub>(g) + NOF<sub>2</sub>(g) <math>\xrightarrow[\text{NOWF}_8(s)]{\text{RT}}</math> NOWF<sub>8</sub>(s) [202,219]</p>
NOF	<p>UF<sub>6</sub>(g) + NOF(g) <math>\xrightarrow[\text{NOUF}_7]{\text{RT}}</math> NOUF<sub>7</sub> [202,219]</p>	<p>MoF<sub>6</sub>(g) + NOF(g) <math>\xrightarrow[\text{NOMoF}_7]{\text{RT}}</math> NOMoF<sub>7</sub> [202,219]</p>	<p>WF<sub>6</sub>(g) + NOF(g) <math>\xrightarrow[\text{NOWF}_7]{\text{RT}}</math> NOWF<sub>7</sub> [202,219]</p>
NF <sub>3</sub> .HF <sub>2</sub>	<p>UF<sub>6</sub> + NF<sub>3</sub>.HF<sub>2</sub> <math>\xrightarrow[\text{NF}_4\text{UF}_7]{\text{HF/RT}}</math> NF<sub>4</sub>UF<sub>7</sub> yellow [220]</p> <p>UF<sub>6</sub> + NF<sub>3</sub> + F<sub>2</sub></p>		<p>WF<sub>6</sub> + NF<sub>3</sub>.HF<sub>2</sub> <math>\xrightarrow[\text{WF}_6\text{WF}_7]{\text{HF/RT}}</math> WF<sub>6</sub>WF<sub>7</sub> white [220]</p> <p>WF<sub>6</sub> + NF<sub>3</sub> + F<sub>2</sub> <math>\xrightarrow{\Delta}</math> WF<sub>6</sub>WF<sub>7</sub> white</p>
AgF	<p>UF<sub>6</sub> + 2AgF <math>\xrightarrow[\text{Ag}_2\text{UF}_6]{\text{HF/RT}}</math> Ag<sub>2</sub>UF<sub>6</sub> (dissolved in HF) white [121]</p>		

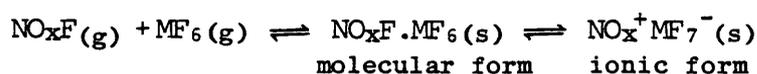
molybdenum hexafluoride and ammonium fluoride in fused molybdenum hexafluoride at temperatures between 25-70°C [213]. The actual product obtained depends upon the amount of ammonium fluoride present.

Both uranium and molybdenum hexafluorides undergo fluoroaddition reactions with hydrazinium difluoride in anhydrous hydrogen fluoride at room temperature; the product formed depends upon the reactant stoichiometry [215-218].



Hydrazinium heptafluorouranate(VI),  $\text{N}_2\text{H}_5\text{UF}_7$ , is formed from interactions between uranium hexafluoride and hydrazinium bifluoride at 0°C in either anhydrous hydrogen fluoride or carbon tetrachloride and is independent of reactant stoichiometry [215]. Reduction to uranium tetrafluoride occurs when the reactants are mixed in the gaseous phase. The tetrafluoride is also the ultimate product from the thermal decomposition of both hydrazinium heptafluorouranate(VI) and hydrazinium bishexafluorouranate(V) [215].

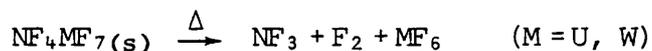
Fluoroaddition reactions also occur between nitryl and nitrosyl fluorides and the hexafluorides at room temperature to form compounds of the type  $\text{NO}_x\text{F}.\text{MF}_6$  ( $x = 1, 2$ ;  $\text{M} = \text{U}, \text{Mo}, \text{W}$ ) [202,219]. Spectroscopic data of the 1:1 addition compounds indicate that the following equilibrium exists:-



The salts are highly hygroscopic and are soluble in anhydrous hydrogen fluoride.

Perfluoroammonium heptafluorouranate(VI) and tungstate(VI) have been prepared from the interaction of  $\text{NF}_4.\text{HF}_2$  with the appropriate

hexafluoride at room temperature in anhydrous hydrogen fluoride [220]. The salts are stable in a dynamic vacuum at 125°C, but decompose at higher temperatures.



Uranium, molybdenum and tungsten hexafluorides undergo fluoro-addition reactions with alkali and alkaline earth metal fluorides. Alkali metal heptafluorouranates(VI) are produced from reactions between the fluorides in inert solvents [251]. Thermal decomposition of the heptafluorouranates(VI) in vacuo yields the appropriate octafluorouranate(VI) [251]. The heterogenous interactions between solid metal fluorides and the gaseous hexafluorides are discussed extensively in the next section.

#### 1.14 SORPTION [Table 1.15]

The sorption of uranium hexafluoride on alkali metal fluorides and the reactions of uranium hexafluoride with these compounds were studied with some vigour between 1950-1965, since it was hoped that uranium hexafluoride might be purified by a series of selective sorptions and desorptions on various Group I and II metal fluorides. Comparative studies were also made on the hexafluorides of molybdenum and tungsten - two compounds likely to be present in impure uranium hexafluoride.

Ruff and Heinzelmann in 1911 [2] were the first to observe that uranium hexafluoride was adsorbed on sodium fluoride. However, they did not establish whether a chemical reaction took place. The observed sorption was sufficient in itself to be the basis of many technological studies. A typical report is that by Cathers et al. [221] who condensed uranium hexafluoride onto sodium fluoride and allowed the mixture to



TABLE 1.15 (Continued) .....

	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
RbF	<p><math>UF_6(g) + RbF \xrightarrow[244,245]{100-200^\circ C} UF_6 \cdot 2RbF</math> sorption</p> <p><math>Liq. UF_6 + RbF \xrightarrow[251]{65-100^\circ C} UF_6 \cdot 2RbF</math> <math>\xrightarrow[251]{150^\circ C \text{ in vacuo}}</math> <math>Rb_2UF_6</math> [251]</p>	<p><math>MoF_6(g) + RbF \xrightarrow[244,245]{100-200^\circ C} MoF_6 \cdot 2RbF</math> white sorption</p> <p><math>MoF_6 + RbF \xrightarrow[256]{IF_3/RT} MoF_6 \cdot RbF</math> white <math>a = 10.25 \text{ \AA}</math></p>	<p><math>WF_6(g) + RbF \xrightarrow[244,245,237]{100-200^\circ C} WF_6 \cdot 2RbF</math> white sorption</p>
CsF	<p><math>UF_6(g) + CsF \xrightarrow[257]{180^\circ C} CsUF_7</math> cubic <math>a = 5.51 \text{ \AA}</math></p> <p><math>UF_6 + CsF \xrightarrow[251]{65^\circ C} Liq. UF_6 + CsF</math> [251,258]</p> <p><math>UF_6 + CsF \xrightarrow[259]{L} L = C_7F_{16}</math> [259]</p> <p><math>UF_6 + CsF \xrightarrow[260]{L} = ClF_3</math> [260]</p> <p><math>\sim 200^\circ C \text{ in vacuo} \rightarrow Cs_2UF_6</math> [251]</p> <p>orthorhombic <math>a = 6.480 \text{ \AA}</math>  <math>b = 14.036 \text{ \AA}</math>  <math>c = 9.271 \text{ \AA}</math></p>	<p><math>MoF_6 + CsF \xrightarrow[225,256]{100-200^\circ C} MoF_6 \cdot 2CsF</math> white sorption</p>	<p><math>WF_6 + CsF \xrightarrow[225,256]{100-200^\circ C} WF_6 \cdot 2CsF</math> white sorption</p>
MgF <sub>2</sub>	<p><math>UF_6(g) + MgF_2 \xrightarrow[254,246,262]{100-150^\circ C \text{ flow system}} \text{No Reaction}</math></p> <p>physical sorption observed at 20°C [261]</p>	<p><math>MoF_6(g) + MgF_2 \xrightarrow[246]{100-150^\circ C \text{ flow system}} \text{sorption}</math> [246]</p>	<p><math>WF_6(g) + MgF_2 \xrightarrow[246]{100-150^\circ C \text{ flow system}} \text{same sorption}</math> [246]</p>
CaF <sub>2</sub>	<p><math>UF_6(g) + CaF_2 \xrightarrow[125,254]{} \text{No Reaction}</math></p>		<p><math>WF_6(g) + CaF_2 \xrightarrow[262]{60-300^\circ C} \text{No Reaction}</math> [262]</p> <p>2 atm. constant pressure</p>
AlF <sub>3</sub>	<p><math>UF_6(g) + AlF_3 \xrightarrow[227]{80-200^\circ C} \text{No Reaction}</math></p> <p>the small amount of uranium retained was assumed to be due to impurities [227]</p>		

TABLE 1.15 (Continued) . . . .

	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
BaF <sub>2</sub>	$\text{UF}_6(\text{g}) + \text{BaF}_2 \xrightarrow{150^\circ\text{C}} \text{UF}_6 \cdot x\text{BaF}_2$ [229] At > 220°C side reactions result in the reduction of UF <sub>6</sub> to UF <sub>4</sub>		$\text{WF}_6(\text{g}) + \text{BaF}_2 \xrightarrow{60-150^\circ\text{C}} \text{No Reaction}$ [262]
Na <sub>2</sub> CO <sub>3</sub>	$\text{UF}_6(\text{g}) + \text{Na}_2\text{CO}_3 \xrightarrow[263]{150-200^\circ\text{C}} \text{some sorption observed}$		
CaCO <sub>3</sub>	CaCO <sub>3</sub> removes gaseous fluorides more reactive than UF <sub>6</sub> by sorption [264] Ethanolamine can sorb up to 40% wt. UF <sub>6</sub> [265]		

stand at 110°C for several minutes. After removing the excess uranium hexafluoride, they determined that three moles of sodium fluoride adsorbed about one mole of uranium hexafluoride and so it became the convention to call the complex  $\text{Na}_3\text{UF}_6$  or  $3\text{NaF}\cdot\text{UF}_6$ . This conclusion was confirmed by other workers [222]. There are numerous reports in the literature describing the properties of this 'compound'. The rates of sorption, desorption of this complex were also studied along with many other of its physical and chemical properties.

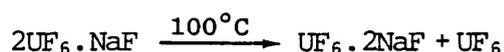
A study of the exchange of fluorine atoms between uranium hexafluoride and some inorganic fluorides including sodium fluoride was initiated in the early sixties in the hope of learning more about the nature of such complexes [223]. Rapid exchange between fluorine atoms is good evidence for the introduction of fluorine atoms into the nearest neighbour coordination sphere of the uranium atom, whilst absence of such exchange can be taken as evidence that uranium hexafluoride is incorporated mechanically into the metal fluoride. It was shown that at temperatures above 350°C, there was no fluorine atom exchange, but at lower temperatures where sodium fluoride strongly sorbs uranium hexafluoride there is considerable exchange. This was taken as evidence that a real compound is formed, rather than just physical adsorption. The amount of fluorine exchange was measured and both Katz [224] and Sheft et al. [223] concluded that the complex formed is, in fact,  $\text{UF}_6\cdot 2\text{NaF}$ , not  $\text{UF}_6\cdot 3\text{NaF}$ .

It has now been clearly established that above about 80°C, uranium hexafluoride sorbs on sodium fluoride to form  $\text{UF}_6\cdot 2\text{NaF}$  [225-227]; between 180-260°C, the 1:3 adduct,  $\text{UF}_6\cdot 3\text{NaF}$  is also formed [226-228]. As the temperature is raised there is further evidence for a non-stoichiometric material of approximate composition  $\text{UF}_6\cdot 2.5\text{NaF}$  [226].

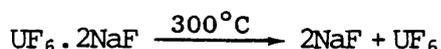
Desorption begins above 300°C with uranium hexafluoride being liberated [228]; at temperatures between 200–300°C some reduction to uranium(V) has been detected [228,229].

The yellow complex,  $\text{UF}_6 \cdot 2\text{NaF}$  is highly hygroscopic and it has been shown from single crystal studies to possess a body centred tetragonal unit cell,  $a = 5.27 \text{ \AA}$ ,  $c = 11.20 \text{ \AA}$ , with a calculated X-ray density of  $4.68 \text{ g cm}^{-3}$  [230].

Both  $\text{UF}_6 \cdot \text{NaF}$  and  $\text{UF}_6 \cdot 2\text{NaF}$  are reported to be formed if sodium fluoride is suspended in an inert solvent,  $\text{C}_7\text{F}_{16}$  [230]. The observation of two compounds has also been noted when gaseous uranium hexafluoride and sodium fluoride react in a nickel vessel at 100°C [230]. One of these was stable at room temperature, but evolved uranium hexafluoride at temperatures above 100°C to form a second compound, which gave off uranium hexafluoride rapidly at temperatures above 300°C, i.e.



Total decomposition to the original components occurs above 300°C:-



A large number of reports have been published [226,231-237] on the kinetics of the uranium hexafluoride - sodium fluoride reaction system. Early reports were inconsistent and have produced unsatisfactory results [235], but further work seems to have established the following points. Both adsorption and chemisorption are spontaneous at low temperatures, but at temperatures above 170°C sorption ceases [226], and there is also evidence for a dual mechanism [233]. Massoth et al. [234] investigated the kinetics of gaseous uranium hexafluoride with sodium fluoride powder, crushed pellets and pellets in the 24–68°C temperature range. They state that the reaction of uranium hexafluoride

with sodium fluoride powder follows the parabolic rate law, while the reaction with crushed pellets follows the logarithmic rate law initially, and the parabolic rate law in later stages. They also observed that the reaction with pellets obeys logarithmic kinetics to about 0.4 mole fraction converted after which no reaction appears to take place. The reactions between uranium hexafluoride and sodium fluoride powder and crushed pellets go to completion, whereas the reactions with pellets are generally slower and less complete.

The maximum sorption of uranium hexafluoride on sodium fluoride pellets occurs at 100°C; it is proportional to uranium hexafluoride concentration in the gaseous phase and is inversely proportional to the temperature [232,237]. In the initial stages of the reaction, it has been proposed that the diffusion of uranium hexafluoride into the interior of the pellets is the rate determining step and that kinetically the parabolic rate law is obeyed [233,234].

The continuous operation of a uranium hexafluoride - sodium fluoride cyclic sorption-desorption system has also been investigated [231,232, 235]. It has been found that the loading factor of sodium fluoride pellets is dependent upon their porosity and that it is at a maximum for the first sorption cycle [232,234]. On subsequent cycles, there is a gradual decrease in the sorption capacity of sodium fluoride which appears to stabilise after about 5 cycles at 40 wt. % uranium [232,234]. Desorption at 400°C is very fast with 95-98% sorbed uranium being recovered within five minutes, with the desorption process being virtually complete within ten minutes.

Three patents [238-240] all use sodium fluoride traps at 100° or 200°C to recover uranium hexafluoride gas streams containing fission product fluorides.

Ruff and Eisner [69] reported that the hexafluorides of molybdenum and tungsten combine with alkali metal fluorides, but gave no details and described no compounds. However, the majority of other early workers [241-243] failed to sorb large quantities of molybdenum or tungsten hexafluorides on sodium fluoride. This is somewhat surprising considering the ease of preparation of  $\text{MoF}_6 \cdot 2\text{KF}$ ,  $\text{MoF}_6 \cdot 2\text{RbF}$ ,  $\text{MoF}_6 \cdot 2\text{CsF}$ ,  $\text{WF}_6 \cdot 2\text{KF}$ ,  $\text{WF}_6 \cdot 2\text{RbF}$ ,  $\text{WF}_6 \cdot 2\text{CsF}$  by reactions of the gaseous hexafluorides directly with solid alkali metal fluorides.

Katz [224,225] prepared  $\text{UF}_6 \cdot 2\text{NaF}$ ,  $\text{WF}_6 \cdot 2\text{NaF}$  and  $\text{MoF}_6 \cdot 2\text{NaF}$  by the sorption of the metal hexafluorides upon sodium fluoride prepared from the decomposition of  $\text{NaF} \cdot 4\text{HF}$  at  $100^\circ\text{C}$ . The successful preparation of the molybdenum and tungsten complexes appears to depend upon the pre-treatment of sodium fluoride causing the formation of more holes and active nucleation sites, i.e. a higher surface area. The reaction of uranium hexafluoride with the pretreated sodium fluoride goes to completion whereas molybdenum and tungsten hexafluorides react much more slowly and do not proceed to completion [224,225].

The vapour (dissociation) pressures as a function of temperature over these complexes are given by [224]:-

$\text{UF}_6$  over  $\text{UF}_6 \cdot 2\text{NaF}$

$$\log P_{\text{mm}} (\text{UF}_6) = 9.25 \pm 0.02 - (4.18 \times 10^3)/T(\text{K})$$

$\text{MoF}_6$  over  $\text{MoF}_6 \cdot 2\text{NaF}$

$$\log P_{\text{mm}} (\text{MoF}_6) = 8.27 \pm 0.07 - (2.87 \times 10^3)/T(\text{K})$$

$\text{WF}_6$  over  $\text{WF}_6 \cdot 2\text{NaF}$

$$\log P_{\text{mm}} (\text{WF}_6) = 8.80 \pm 0.01 - (3.99 \times 10^3)/T(\text{K})$$

Molybdenum hexafluoride was found to sorb much more slowly than either uranium or tungsten hexafluorides, with the optimum reaction rate occurring at  $160-185^\circ\text{C}$ . The uranium complex is yellow while the

molybdenum and tungsten complexes are white.

It has been stated [244,245] that it is possible to achieve an efficient separation of uranium and molybdenum hexafluorides by joint sorption on sodium fluoride at 100°C followed by the selective desorption of molybdenum hexafluoride at 150°C and that uranium losses in this process are small. The possibility of separating uranium and molybdenum hexafluorides by desorption at 150°C appears to be confirmed from the vapour pressure equations above. At this temperature, the vapour pressures of molybdenum and uranium hexafluorides over their respective complexes with sodium fluoride are 31 torr and 0.235 torr respectively; the ratio of  $p(\text{MoF}_6)/p(\text{UF}_6)$  decreases with increasing temperature.

Golliher's patent [246] refers to the removal of molybdenum hexafluoride from uranium hexafluoride containing vanadium pentafluoride as a co-contaminant. Only very low concentrations of molybdenum hexafluoride were present in the inlet gas of this large scale system (~240,000 kg  $\text{UF}_6$  passed through the system). Due to the low concentration of the contaminant, ~0.2 ppm in a large throughput, calculation of decontamination factors and recovery percentages was not possible.

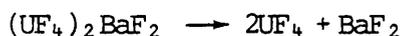
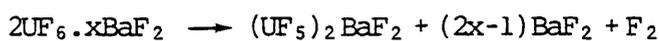
The rate of sorption of metal hexafluorides on solid metal fluorides is highly dependent upon the following:-

- (a) sorbent pretreatment
- (b) temperature
- (c) pressure
- (d) the method by which the hexafluoride is introduced (i.e. flow or static systems)

which may go some way to explain discrepancies in the results and conclusions published by different workers.

An example of the confusion which exists in the literature is the

interaction between uranium hexafluoride and barium fluoride. Most workers have noted no reaction between these fluorides, but Kormek et al. [247] claim that uranium hexafluoride is sorbed by barium fluoride at temperatures up to 157°C to form a complex of nominal formula  $UF_6 \cdot xBaF_2$  and that at higher temperatures the following reactions occur:-



Such a reaction sequence seems most unlikely considering the chemistry of the other metal fluoride-uranium hexafluoride complexes. A possible explanation is that the observed reduction is due to interactions between uranium hexafluoride and the experimental apparatus.

Another confusing observation is that when uranium hexafluoride is sorbed by  $BiF_3$ ,  $FeF_3$ ,  $AlF_3$ ,  $PbF_4$ ,  $ThF_4$  and  $TiF_4$  some reduction occurs with the formation of lower uranium fluorides such as  $UF_4$  and  $U_4F_{17}$  [125]. Although uranium hexafluoride is reduced, none of the compounds listed above can be oxidised except bismuth trifluoride and this only by the strongest fluorinating agents such as chlorine trifluoride. It seems most unlikely that free fluorine would be evolved so, possibly, these results indicate the same reaction had occurred between uranium hexafluoride and the apparatus used or with impurities present in the reactants. The remaining published reactions of the hexafluorides are summarised in Table 1.16.

TABLE 1.16

Miscellaneous reactions of UF<sub>6</sub>, MoF<sub>6</sub>, WF<sub>6</sub>

	Uranium Hexafluoride	Molybdenum Hexafluoride	Tungsten Hexafluoride
Hg(CN) <sub>2</sub>	$\text{UF}_6 + \text{Hg}(\text{CN})_2 \xrightarrow[24 \text{ hrs}]{\text{RT}} \text{No reaction}$ <p>[36]</p>		
H <sub>2</sub> SO <sub>4</sub>	$\text{UF}_6 + \text{H}_2\text{SO}_4 \xrightarrow{\text{RT}} \text{yellow ppt. of U(VI) sulphate containing } \sim 1\% \text{ U(V)}$ <p>[267]</p> <p>1 part UF<sub>6</sub> + 2 parts 70% H<sub>2</sub>SO<sub>4</sub> <math>\xrightarrow{\text{RT}}</math> UO<sub>2</sub>SO<sub>4</sub> [268]</p>		
DMSO			$\text{WF}_6 + \text{DMSO} \xrightarrow{\text{RT}} \text{yellow viscous liquid containing at least 2 species}$ <p>[269]</p>



# CHAPTER 2

Interactions between nitrogen oxides  
and the hexafluorides of uranium,  
molybdenum and tungsten

## 2.1 INTRODUCTION

Initial studies on the interactions between the hexafluorides of uranium, molybdenum, and tungsten with nitrogen oxides and oxide halides were made in the mid-sixties [Tables 1.12 and 1.14]. Due to the differences in the chemical behaviour of the hexafluorides towards these reactants, the possibility of separating molybdenum and tungsten hexafluorides from uranium hexafluoride on the basis of this chemistry seemed worth investigating.

## PRESENT STUDY

### 2.2 MF<sub>6</sub> (M = U, Mo, W) WITH NITROUS OXIDE

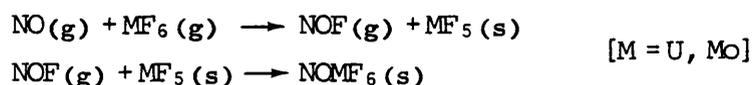
An equimolar gaseous mixture of nitrous oxide, N<sub>2</sub>O, and the appropriate hexafluoride was held at a total pressure of approximately 400 mmHg in a sealed prefluorinated nickel or stainless steel reactor at room temperature or 300°C. The contact times varied from 4-16 hours. No solid products were observed. The initial pressure in the reactor did not change in any of the systems, indicating no reaction. Also the IR spectra of nitrous oxide mixed with the individual hexafluorides remained unaltered.

### 2.3 MF<sub>6</sub> (M = U, Mo, W) WITH NITRIC OXIDE

An excess of nitric oxide purified by low temperature distillation was condensed into a prefluorinated nickel reactor at -196°C along with the desired hexafluoride. The reaction mixtures were allowed to warm to room temperature and left for 2-4 hours prior to being evacuated until a constant vapour pressure was obtained. Solid products obtained were analysed by vibrational spectroscopy and X-ray powder photography.

Mass balance and vapour pressure measurements indicated that the hexafluorides of uranium and molybdenum combine in a 1:1 molecular ratio with nitric oxide to yield the salts, NOUF<sub>6</sub> and NOMoF<sub>6</sub> respectively, whereas no reaction was observed for tungsten hexafluoride.

The reactions were repeated in a 10 cm path length IR gas cell fitted with silver chloride windows, so that they could be followed spectroscopically. Rapid reactions were indicated by the instantaneous disappearance of the bands associated with the reactants. Previous workers [86,198-201] proposed the following reaction scheme:-



Since, in the present study, no IR bands associated with nitrosyl fluoride were observed, it appears that nitric oxide reacts directly with uranium and molybdenum hexafluorides without proceeding via an intermediate. The reaction seems to be a simple electron exchange.

### 2.3.1 Vibrational Spectroscopy [Tables 2.1 and 2.2]

The solid products were characterised mainly using vibrational spectroscopy. Sharp bands observed in the IR spectra of both nitrosyl hexafluorouranate(V) and molybdate(V) at approximately 2330 cm<sup>-1</sup> belong to the absorption of the nitrosyl ion, NO<sup>+</sup>. The large shift from 1876 cm<sup>-1</sup> for the neutral molecule to 2332 cm<sup>-1</sup> for NOMoF<sub>6</sub> and to 2330 cm<sup>-1</sup> for NOUF<sub>6</sub> can be explained on the basis of completely ionised NO<sup>+</sup> groups in the solids. This is in agreement with published data [271-273], the shift being consistent with that expected for the removal of one electron from the antibonding orbital of the nitric oxide. Removal of such an electron would result in a decreased internuclear distance, which increases the bond strength and, hence, would cause a shift in

the direction observed. In addition to the nitrosyl ion adsorption band, the only other IR bands for these salts fall in the 650-500  $\text{cm}^{-1}$  region. Broad, intense, unresolved bands were observed in this region for both  $\text{NOUF}_6$  and  $\text{NOMoF}_6$ . In both cases, these frequencies are characteristic of the  $\nu_3$  vibration of the metal hexafluoroanions.

The Raman spectra of  $\text{NOUF}_6$  and  $\text{NOMoF}_6$  are shown in Figs. 2.1 and 2.2 respectively. In both spectra the three expected Raman-active vibrations resulting from the octahedral symmetry of the hexafluoroanions are observed. Some splitting was observed in the degenerate vibrations of  $[\text{UF}_6]^-$  whereas the  $\nu_2$  vibration for  $[\text{MoF}_6]^-$  is rather broad, but still clearly observable. The reduction of the oxidation state of the central atom to the pentavalent state results in the shifting of both  $\nu_1$  and  $\nu_2$  to lower frequencies [Table 2.2]. This is to be expected since, in the higher oxidation state, the ligands are closer to the central metal atom resulting in a larger polarisation, which thus increases the covalent character of the bonds. Therefore, upon reduction, since  $\nu \propto (f/\mu)^{1/2}$  (where  $f$  is the force constant and  $\mu$  is the reduced mass) both parameters change in such a manner that  $\nu$  increases, i.e. the distance between the central metal atom and the ligands decreases resulting in higher force constants. This shift to lower frequencies is also observed for  $\nu_3$  in the IR.

### 2.3.2 Nitrosyl Hexafluorouranate(V) and Molybdate(V)

Nitrosyl hexafluorouranate(V) is a yellowish-green non-volatile solid. When heated it appears to decompose gradually above 200°C with the evolution of an unidentified colourless gas. Melting occurs at approximately 340°C with the formation of a green melt. X-ray diffraction data for the compound were indexed on the basis of a cubic

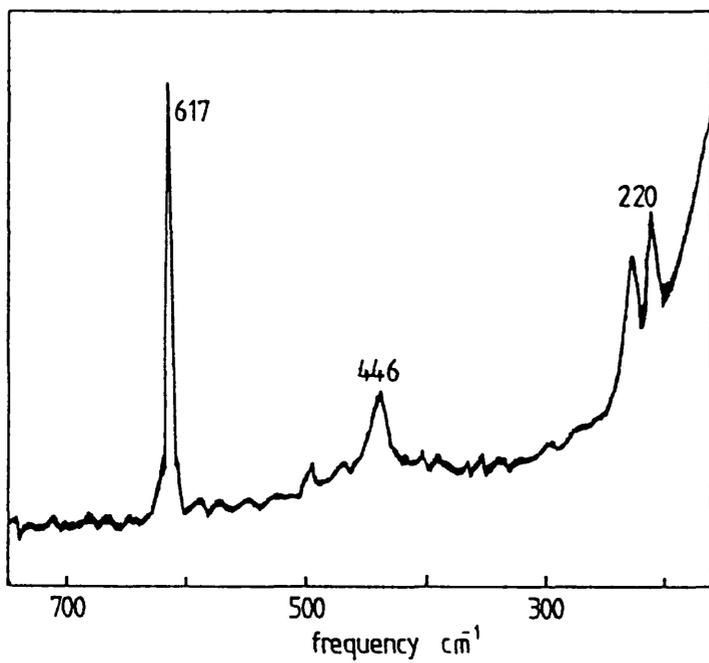


FIGURE 2.1

The Raman spectrum (800-150 cm<sup>-1</sup>) of NOUF<sub>6</sub>.

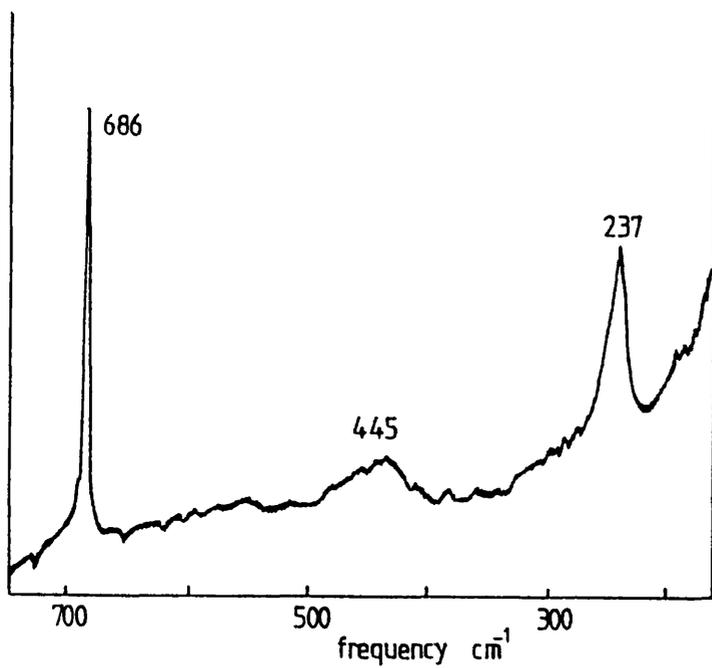


FIGURE 2.2

The Raman spectrum (800-150 cm<sup>-1</sup>) of NOMoF<sub>6</sub>.

unit cell with  $a_0 = 5.18 \text{ \AA}$ .

Neutron diffraction studies at room temperature and 4.2 K [274,275] have established that nitrosyl hexafluorouranate(V) has a cubic structure with eight formula units for each singular cell. It was found that  $a_0 = 10.464 \pm 0.001 \text{ \AA}$  [274] at room temperature and  $a_0 = 10.336 \pm 0.001 \text{ \AA}$  [275] at 4.2 K. Details of structural defects in nitrosyl hexafluorouranate(V) at 4.2 K have also been published [276].

The salt is highly hygroscopic, but can be stored indefinitely in dry nitrogen and is inert to and insoluble in carbon tetrachloride.

The analogous molybdenum salt is a rusty-orange, non-volatile solid which is insoluble in carbon tetrachloride and turns purple upon exposure to the atmosphere. X-ray diffraction data for nitrosyl hexafluoromolybdate(V) were indexed on the basis of a cubic unit cell with  $a_0 = 5.08 \text{ \AA}$ . It melted at approximately  $190^\circ\text{C}$  to give a blue liquid.

Aqueous solutions of both nitrosyl hexafluorouranate(V) and molybdate(V) contained nitrite ions but tests for nitrate were negative. This result is to be expected for the hydrolytic behaviour of a solid containing  $\text{NO}^+$  ions [281].

TABLE 2.1

Vibrational data of nitrosyl hexafluorouranate(V)  
and molybdate(V)

$\text{NOUF}_6$		$\text{NOMoF}_6$		Assignment
IR	Raman	IR	Raman	
2330 m		2332 m		$\nu(\text{NO}^+)$
	617		686	$\nu_1(\text{MF}_6^-)$
525 s,br		623 s,br		$\nu_3(\text{MF}_6^-)$
	446		445	$\nu_2(\text{MF}_6^-)$
	220		237	$\nu_5(\text{MF}_6^-)$

TABLE 2.2

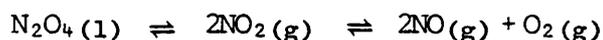
Vibrational data of hexafluoroanions compared with those of the corresponding metal hexafluoride

	$\nu_1$ (A <sub>1g</sub> ) $\nu_{\text{sym}}$ (MF)	$\nu_2$ (E <sub>g</sub> ) $\nu$ (MF <sub>2</sub> )	$\nu_3$ (F <sub>1u</sub> ) $\nu_{\text{assym}}$ (MF <sub>2</sub> )	$\nu_4$ (F <sub>1u</sub> ) $\delta$ (MF <sub>2</sub> )	$\nu_5$ (F <sub>2g</sub> ) $\delta$ (MF <sub>2</sub> )	$\nu_6$ (F <sub>2u</sub> ) $\delta$ (MF <sub>2</sub> )	Ref.
UF <sub>6</sub>	667	535	626	186	202	(144)	[277-279]
UF <sub>6</sub> <sup>-</sup>	617	446	525	-	220	-	
MoF <sub>6</sub>	741	643	741	264	306	(190)	[280]
MoF <sub>6</sub> <sup>-</sup>	686	445	623	-	237	-	

## 2.4 MF<sub>6</sub> (M = U, Mo, W) WITH NITROGEN DIOXIDE/DINITROGEN TETROXIDE

### 2.4.1 Introduction

Nitrogen dioxide is involved in a complex equilibrium with other nitrogen oxides:-



It is unlikely that nitrogen dioxide can be obtained pure, since the temperature of dissociation of dinitrogen tetroxide to nitrogen dioxide also coincides with the onset of the thermal decomposition of nitrogen dioxide which becomes significant above 150°C and complete above 600°C. Nitrogen dioxide and dinitrogen tetroxide exist in a complex, strongly temperature dependent equilibrium in both solution and the gas phase. Pure liquid contains very little nitrogen dioxide. Magnetic susceptibility measurements suggest that the liquid, which is pale yellow in colour contains only 0.7% nitrogen dioxide [282]. The solid is assumed to contain only dinitrogen tetroxide. At the normal boiling point (21.15°C at 760 mmHg) the vapour is brown containing only 0.1% nitrogen dioxide. As the temperature is raised, the proportion of nitrogen dioxide increases and the vapour darkens. At 150°C, when only nitrogen dioxide is present, the vapour is black.

The major problem when studying reactions involving NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> mixtures is to decide which one of the components in the equilibrium mixture is reacting. This can be simplified to some extent by varying the reaction conditions.

### 2.4.2 MF<sub>6</sub> (M = U, Mo, W) with Dinitrogen Tetroxide

Equimolar quantities (~4m moles) of dinitrogen tetroxide and the desired hexafluoride were condensed into a nickel reactor at -196°C. The reaction mixtures were allowed to warm, but were kept below 20°C

to ensure that liquid dinitrogen tetroxide was present. After several hours the residual pressure of the systems were measured and indicated that, in all three cases, a reaction had taken place.

#### UF<sub>6</sub> with N<sub>2</sub>O<sub>4</sub>

Vibrational spectroscopy and X-ray powder diffraction studies showed that uranium hexafluoride forms the same compound with dinitrogen tetroxide as it does with nitric oxide, NOUF<sub>6</sub>.

#### MoF<sub>6</sub>, WF<sub>6</sub> with N<sub>2</sub>O<sub>4</sub>

In both reactions, white non-volatile solids were isolated which were identified by vibrational spectroscopy and X-ray powder diffraction studies to be nitrosyl pentafluoroxymolybdate(VI); NOMoOF<sub>5</sub> and nitrosyl pentafluoroxytungstate(VI); NOWOF<sub>5</sub>.

The vibrational spectra of the solids, which are shown in Table 2.3 and Figs. 2.3 and 2.4, can be assigned on the basis of the presence of MOF<sub>5</sub><sup>-</sup> salts. It is worth noting the respective position of the axial (M-F) vibration and that due to the in-phase symmetric (M-F) stretching of the anion in both salts. In line with the more ionic character of the axial M-F bond, the former appears at a lower frequency than the other does. This has also been noted by other workers [283,284]. The metal-oxygen stretching frequencies of molybdenum and tungsten oxide tetrafluorides occur at 1064 and 1045 cm<sup>-1</sup> [285] respectively compared with 990 and 1002 cm<sup>-1</sup> for the MOF<sub>5</sub><sup>-</sup> salts, which again is in line with the change in ionic character.

The X-ray powder diffraction patterns of both nitrosyl pentafluoroxymolybdate(VI) and tungstate(VI) are identical to those previously reported [286]; Table 2.4. Both diffraction patterns were indexed on the basis of tetragonal unit cells.

TABLE 2.3

Vibrational data of nitrosyl pentafluoroxymolybdate (VI) and tungstate (VI)

NO <sub>2</sub> MoOF <sub>5</sub>		NO <sub>2</sub> WOF <sub>5</sub>		Assignment
IR	Raman	IR	Raman	
440 s	158 w		162 w	$\nu_9$ (e), $\delta$ (MOF <sub>4</sub> ) or $\nu_{10}$ (e), $\delta$ (FMF <sub>4</sub> ) $\nu_3$ (a <sub>1</sub> ), $\nu$ (axial MF) $\nu_5$ (b <sub>1</sub> ), $\nu$ (sym. out-of-phase MF <sub>4</sub> ) $\nu_8$ (e), $\nu$ (assym. in plane MF <sub>4</sub> ) $\nu_2$ (a <sub>1</sub> ), $\nu$ (sym. in plane MF <sub>4</sub> ) $\nu_1$ (a <sub>1</sub> ), $\nu$ (MO) $\nu$ (NO <sup>+</sup> )
555 sh	320 m		326 m	
650 vs, br		445 m	594 w	
990 s	667 s	610 vs	682 m	
2320 m	987 s	685 sh	1002 vs	
		1000 s		
		2315 m		

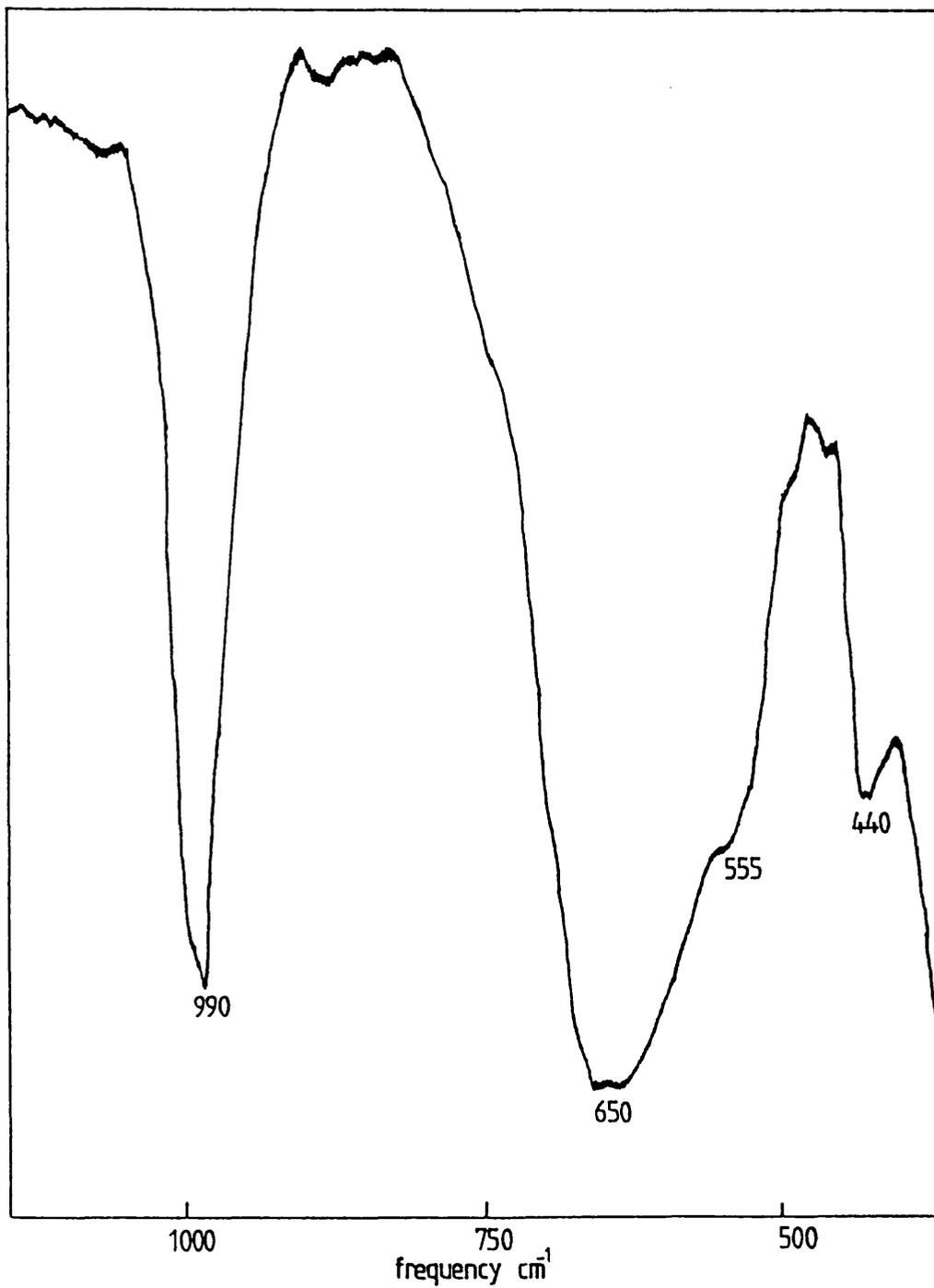


FIGURE 2.3

The infrared spectrum (1200-350 cm<sup>-1</sup>) of NOMoOF<sub>5</sub>.

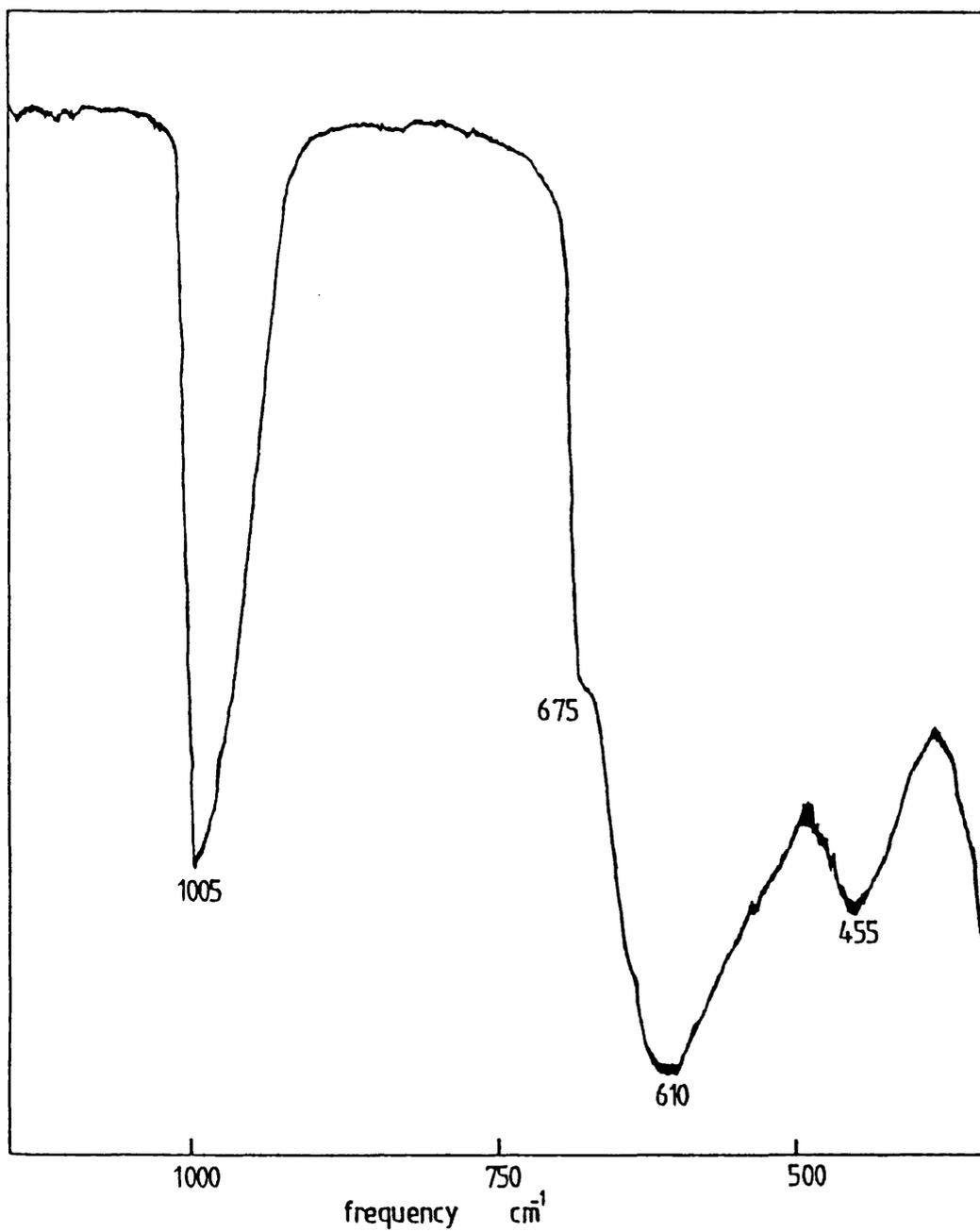


FIGURE 2.4

The Infrared spectrum ( $1200\text{-}350\text{ cm}^{-1}$ ) of  $\text{NO}_2\text{OF}_5$ .

TABLE 2.4

X-ray powder diffraction data for nitrosyl pentafluoroxymolybdate(VI) and tungstate(VI)

NOMoOF <sub>5</sub>					NOWOF <sub>5</sub>				
hkl	d, Å	[286] Intensity	Present Study d, Å	Present Study Intensity	hkl	d, Å	[286] Intensity	Present Study d, Å	Present Study Intensity
100	5.20	s	5.198	s	100	5.18	s	5.175	s
002	4.87	m	4.869	ms	002	4.87	ms	4.901	s
101	4.56	s	4.562	s	101	4.57	s	4.581	s
110	3.67	m	3.670	m	110	3.67	m	3.715	m
102	3.56	s	5.555	s	102	3.56	s	3.555	s
111	3.43	m	3.434	m	111	3.41	m	3.409	m
112	2.93	mw	2.923	w	112	2.94	m	2.935	m
103	2.751	w			103	2.766	mw	2.800	w
200	2.596	vw			200	2.590	w,br		
201	2.508	vwv			201	2.499	mw	2.501	w
004	2.436	vw			004	2.450	w		
113					113				
210	2.321	vw			210	2.296	vwv		
211	2.257	m	2.261	m	211	2.244	m	2.245	m
104	2.207	vwv			104	2.218	w		
212	2.094	m	2.100	m	212	2.100	m	2.099	m
114	2.027	ms	2.032	s	114	2.034	s,br	2.044	s
203									
218	1.886	m	1.879	mm	213	1.886	ms	1.880	m
220	1.833	mw	1.838	w	105	1.835	w		
221	1.804	vwv			220				
204	1.779	vwv			204	1.783	w,br		
115	1.719	w			115	1.726	vw		
222					300				
301	1.704	vw			222	1.704	vw		
214	1.681	w			301				
310	1.642	vw			214	1.685	vw		
006	1.620	w			310	1.634	vw		
311					006				
312	1.555	mw,br	1.538	w,br	311	1.614	w,br		
205							223	1.589	w
303	1.528	vw			205	1.564	m	1.558	m
215	1.491	vw,br			312	1.550	w		
116					303	1.527	m	1.529	m
313	1.465	mw	1.472	w	116	1.496	m	1.479	m
224									
Tetragonal: a = 5.191 Å c = 9.731 Å					Tetragonal: a = 5.178 Å c = 9.807 Å				

### 2.4.3 MF<sub>6</sub> (M=U, Mo, W) with Nitrogen Dioxide

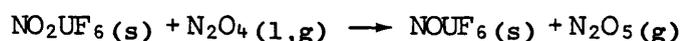
The interactions between nitrogen dioxide and the hexafluorides of uranium, molybdenum, and tungsten were studied at low partial pressures to decrease the amount of dinitrogen tetroxide present. At 100 mmHg pressure, dinitrogen tetroxide is only present in about 15% concentration [287]. The desired hexafluoride was introduced into one compartment of the apparatus shown in Fig. 2.5 and nitrogen dioxide to the other at an equal pressure and, upon equilibrating, the valves between them were opened. The gases were allowed to mix by diffusion at room temperature for several hours.

#### UF<sub>6</sub> with NO<sub>2</sub>

Gaseous uranium hexafluoride and nitrogen dioxide were found to react spontaneously at room temperature with the formation of a yellowish-white non-volatile solid, which was shown by vibrational spectroscopy, chemical analysis and mass balance to be nitrylium hexafluorouranate(V); NO<sub>2</sub>UF<sub>6</sub>.

The IR and Raman spectra of nitrylium hexafluorouranate(V) are shown in Table 2.5 and clearly show the presence of both NO<sub>2</sub><sup>+</sup> and UF<sub>6</sub><sup>-</sup> ions. Attempts to obtain a measureable X-ray powder diffraction pattern of the salt have so far been unsuccessful. To date there appears to be no structural data on nitrylium hexafluorouranate(V).

It has been suggested that the formation of nitrylium hexafluorouranate(V) proceeds via nitryl fluoride and uranium pentafluoride, but no evidence for this was obtained in this study. Nitrylium hexafluorouranate(V) is converted to the nitrosyl salt by liquid or gaseous dinitrogen tetroxide at room temperature [201], according to the following equation:-



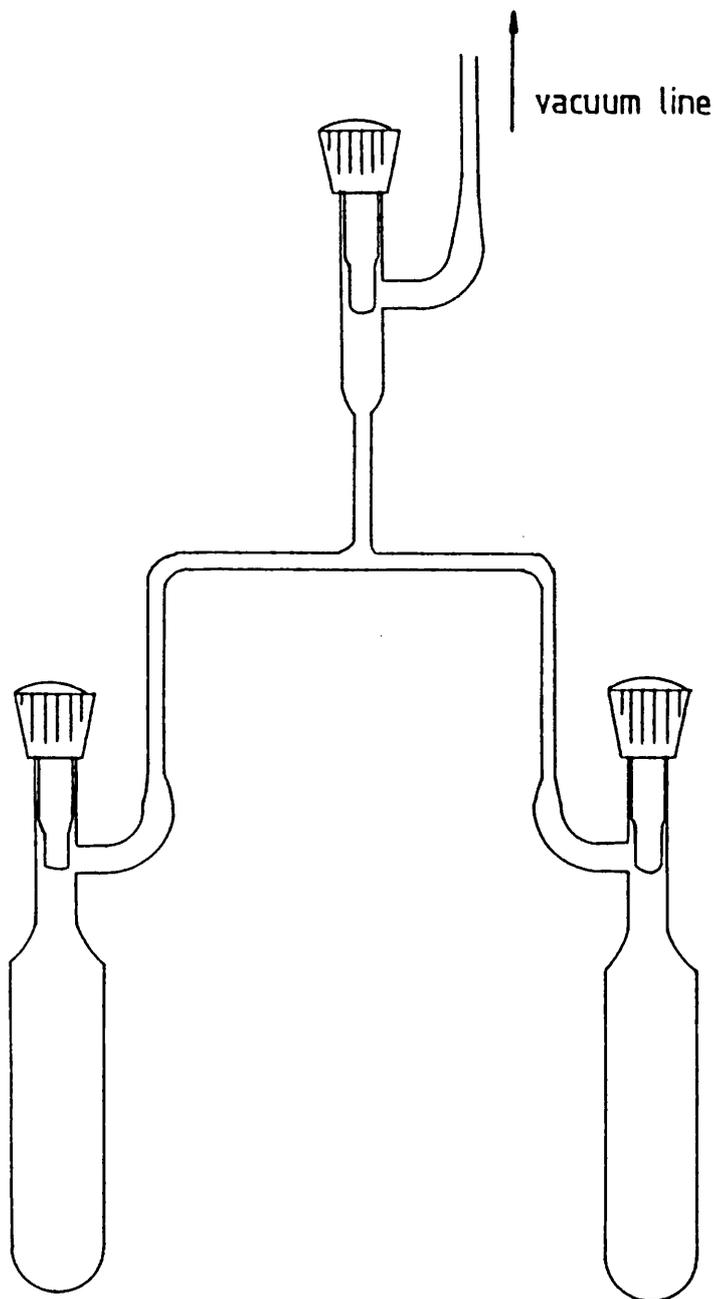


FIGURE 2.5

Apparatus used for the investigation of the interactions between  $\text{MF}_6$  and  $\text{NO}_2$ .

TABLE 2.5

Vibrational data of nitrylium hexafluorouranate(V)

<u>NO<sub>2</sub>UF<sub>6</sub></u>		<u>Assignment</u>
<u>IR</u>	<u>Raman</u>	
2375 m		$\nu$ (NO <sub>2</sub> <sup>+</sup> )
	618	$\nu_1$ (UF <sub>6</sub> <sup>-</sup> )
520 s,br		$\nu_3$ (UF <sub>6</sub> <sup>-</sup> )
	445	$\nu_2$ (UF <sub>6</sub> <sup>-</sup> )
	220	$\nu_5$ (UF <sub>6</sub> <sup>-</sup> )

Elemental analysis for NO<sub>2</sub>UF<sub>6</sub>; found (calculated):-

N,3.52(3.52); O,8.05(8.04); U,59.85(59.81); F,28.58(28.64)

MoF<sub>6</sub>, WF<sub>6</sub> with NO<sub>2</sub>

At low partial pressures (below 100 mmHg) no reactions were observed between nitrogen dioxide and the hexafluorides of molybdenum and tungsten which was confirmed by there being no measureable pressure change in the systems, and the IR of the volatiles containing only the initial components.

When the reactions were carried out at higher partial pressures, fine white films were deposited on the walls of the apparatus. Infra-red spectra of these solids showed them to be NOMoF<sub>5</sub> and NOWoF<sub>5</sub> resulting from interactions between dinitrogen tetroxide and the hexafluorides of molybdenum and tungsten respectively.

Since tungsten hexafluoride does not react with nitric oxide, its inertness towards nitrogen dioxide was anticipated.

2.4.4 An equimolar mixture of UF<sub>6</sub>, MoF<sub>6</sub>, WF<sub>6</sub> with nitrogen dioxide

An equimolar mixture of the three hexafluorides was allowed to react with nitrogen dioxide. It was found that at low partial pressures of nitrogen dioxide, the hexafluorides of molybdenum and tungsten can be effectively removed from a mixture containing uranium hexafluoride via the formation of nitrylium hexafluorouranate(V). This separation was less effective at higher partial pressures of nitrogen dioxide due to the formation of NOUF<sub>6</sub>, NOWoF<sub>5</sub>, and NOMoOF<sub>5</sub> from interactions of

the hexafluorides with dinitrogen tetroxide.

## 2.5 MF<sub>6</sub> (M=U, Mo, W) WITH NITROSYL BROMIDE

The reactions between nitryl fluoride, nitrosyl fluoride, and nitrosyl chloride and the hexafluorides of uranium, molybdenum, and tungsten have all been characterised; Tables 1.12 and 1.14. Thermodynamically, nitrosyl bromide is the least stable of the nitrosyl halides; it undergoes irreversible decomposition at room temperature to nitric oxide and bromine to the extent of 7% [288]. Nitrosyl bromide was prepared by the method cited in Inorganic Synthesis [288], purified by low temperature distillation and regularly checked by IR spectroscopy.

Equimolar quantities of nitrosyl bromide and the desired hexafluoride were condensed into a prefluorinated sealed nickel reactor at -196°C and allowed to warm to room temperature. Both uranium and molybdenum hexafluorides yielded non-volatile solids which were identified as nitrosyl hexafluorouranate(V) and nitrosyl hexafluoromolybdate(V) respectively from vibrational spectroscopy and X-ray powder diffraction, whereas no reaction occurred between nitrosyl bromide and tungsten hexafluoride.

The reactions were also followed spectroscopically to ensure that the salts were formed from interactions between the hexafluorides and nitrosyl bromide, and not from nitric oxide. A decrease in the intensity of the absorption bands of nitrosyl bromide was observed only when either uranium or molybdenum hexafluorides were present.

## 2.6 DISCUSSION

Salts containing nitrosonium and nitronium ions undergo hydrolytic

reactions leading to the formation of nitrite or nitrate ions respectively [281,289,290]. Qualitative tests [291] of this kind on the solids formed from the reactions of the hexafluorides with nitric oxide and nitrogen dioxide indicate that they should be formulated as nitrosyl hexafluorouranate(V), nitrosyl hexafluoromolybdate(V) and nitrylium hexafluorouranate(V). Further evidence that the compounds are ionic is provided by IR spectroscopy and the fact that they are insoluble in carbon tetrachloride.

The X-ray powder diffraction patterns of the nitrosyl salts were indexed on the basis of cubic symmetry, which is in agreement with the conclusions of previous workers [86]. Even though the structures of these salts have not been fully elucidated due to the lack of single crystal data, it has been clearly demonstrated that the gross geometrical arrangement in each involves an  $\text{NO}^+$  ion in the centre of a cube with  $\text{MF}_6^-$  ions at the corners [292]. Attempts to study the structure of nitrylium hexafluorouranate(V) were unsuccessful.

This study clearly suggests that a simple electron transfer mechanism plays a dominant rôle in the formation of the salts. Thus the reactions of the hexafluorides with nitrous oxide, nitric oxide and nitrogen dioxide can be used to assess their relative oxidising powers [thermochemical cycle, Fig. 2.6].

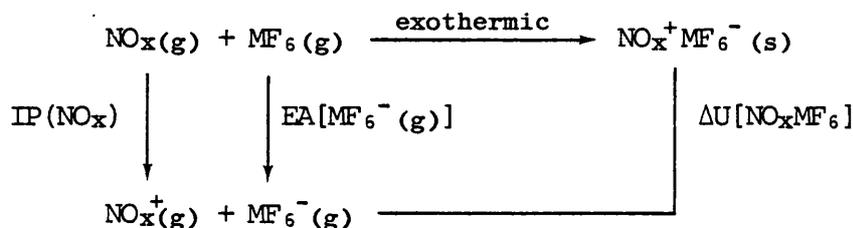


FIGURE 2.6

The Born-Haber cycle used for the reactions,  
 $\text{NO}_x(\text{g}) + \text{MF}_6(\text{g}) \rightarrow \text{NO}_x^+[\text{MF}_6^-](\text{s})$  (kcal/mol).

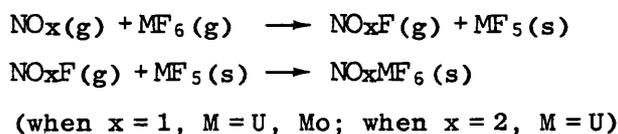
i.e.  $EA[MF_6(g)] + IP(NO_x) + \Delta U[NO_xMF_6] < 0$   
for a spontaneous reaction to occur.

Since the hexafluoroanions are large in size, the lattice energy of the salts,  $\Delta U[NO_xMF_6]$  does not vary by much more than 1-2 kcal/mol for a common cation, and the oxidising ability of the hexafluorides is determined by their electron affinities,  $EA[MF_6(g)]$ . The first ionisation potentials,  $IP(NO_x)$  of nitrous oxide, nitric oxide and nitrogen dioxide are 12.9, 9.5 and 11.0 eV respectively [304]. Thus, from the chemical behaviour of uranium, molybdenum, and tungsten hexafluorides towards these reactants, the electron affinities of the hexafluorides can be arranged in the following series:-



Many workers [293-303] have determined the electron affinities of these hexafluorides experimentally, but there is some disagreement about their precise values [Table 2.6]. Most of the data, however, indicate that the order of electron affinities is the same as predicted from this study.

However, it has been suggested that the reactions of the hexafluorides with nitric oxide and nitrogen dioxide proceeds via an intermediate [86,200,201]:-



If this mechanism occurs, then the oxidising ability of the hexafluorides is determined by the strength of the  $F_5M-F$  bond (i.e. the first bond dissociation energy) which, from the data given in Chapter 5, increase in the series:-



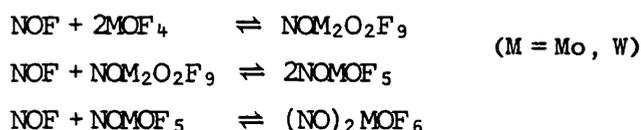
TABLE 2.6

Electron affinities of UF<sub>6</sub>, MoF<sub>6</sub> and WF<sub>6</sub> (kcal/mol)

UF <sub>6</sub>	MoF <sub>6</sub>	WF <sub>6</sub>	Technique	Reference
>118	83±5		Effusion mass spectroscopy	[293]
>99	>118	>118	Molecular beam reaction with alkali metals	[294]
	>103	>113		[295]
		84		[296]
112±10			Ion cyclotron resonance spectroscopy	[297]
		81±5		[298]
		<88	Reaction with graphite	[299]
133	132	103	Absorption spectra of XeMF <sub>6</sub> complexes (M = U, Mo, W)	[300]
113±5			Ion molecular equilibrium	[301]
126±7				[302]
129±4				[303]

The inability of tungsten hexafluoride to oxidise either nitric oxide or nitrogen dioxide is thus related to either the strength of the F<sub>5</sub>W-F bond or its low electron affinity relative to those of the hexafluorides of uranium and molybdenum. Since tungsten hexafluoride is not reduced by nitric oxide, reduction by nitrosyl bromide would not be expected. Formation of a 1:1 addition complex between tungsten hexafluoride and nitrosyl bromide might be suspected but does not occur.

Ionic complexes containing pentafluoroxymolybdate(VI) and pentafluoroxytungstate(VI) anions have been reported through reactions between organic bases [160,171,305], dinitrogen tetroxide [203], or alkali fluorides in the presence of moisture or sulphur dioxide [196,306] and the corresponding hexafluoride. The nitrosyl salts have also been prepared from interactions between nitrosyl fluoride and the corresponding oxytetrafluoride [284]:-



The above equilibria are temperature and pressure dependent. A sufficient pressure of nitrosyl fluoride is necessary to transform MOF<sub>4</sub> into pure (NO)<sub>2</sub>MOF<sub>6</sub>, while a temperature higher than 70° (M=Mo) or 150°C (M=W) and pumping are necessary to decompose the NOM<sub>2</sub>O<sub>2</sub>F<sub>9</sub> adducts to MOF<sub>4</sub> [284]. There are very few reports of complexes containing pentafluoroxoyuranate(VI) anions [307], presumably due to the thermal instability of uranium oxytetrafluoride [81,82].

Initially it was thought that the formation of such anions from the interactions of molybdenum and tungsten hexafluorides with dinitrogen tetroxide was due to the presence of moisture. The present reinvestiga-

tion of these systems showed this is not the case, by employing stringently dry conditions. However, it is still difficult to envisage a mechanism by which the nitrosyl pentafluoroxymolybdate(VI) and tungstate(VI) salts are formed. Presumably, nitrosyl pentafluoroxyuranate(VI) is formed initially from interactions between uranium hexafluoride and dinitrogen tetroxide, but due to its known thermal instability [284,307], nitrosyl hexafluorouranate(V) is the observed product.

This work has shown that nitrogen dioxide will selectively remove uranium hexafluoride from a mixture of the three hexafluorides, via the formation of nitrylium hexafluorouranate(V). An efficient separation only occurred at low partial pressures of nitrogen dioxide. Ideally, we require a reagent which will form non-volatile solids with both molybdenum and tungsten hexafluorides, whilst not reacting with uranium hexafluoride. However, since uranium hexafluoride is a more powerful fluorinating and oxidising agent than either molybdenum or tungsten hexafluorides, it seems most unlikely that such a reagent will be found.



# CHAPTER 3

Oxidation of metals by uranium  
hexafluoride in acetonitrile

### 3.1 INTRODUCTION

Few studies of the chemical behaviour of uranium hexafluoride have been made in solution. The inert solvents Genetron [164],  $C_7F_{16}$  [230] and tetrachloroethane [260] have been employed and chlorine trifluoride has also been used [93,94,209], although in this latter solvent there is a strong possibility of the formation of ionised adducts of the type  $(ClF_2)_n(UF_{6+n})$ . The advantages of studying the chemical behaviour of uranium hexafluoride in solution are:-

- ( i ) reaction rates are generally vastly increased and less vigorous conditions can be used;
- ( ii ) 'complexing' solvents can often initiate and stabilise the formation of new adducts [62,63];
- (iii) solution reactions are easy to follow by various physical techniques.

One of the most popular solvents for uranium hexafluoride appears to be acetonitrile. Uranium hexafluoride dissolves in acetonitrile to give a clear yellow solution which, although stable for short periods (~18hr), gradually darkens as attack of  $UF_6$  on the solvent initiates polymerisation of the acetonitrile. It has been postulated [14,309] that the polymerisation of the solvent involves the reduction of U(VI) to U(V) either via the solvent or dissolved water or oxygen. Since other workers [308] found that  $UF_6$  was only stable in acetonitrile for approximately two hours, the solvent they used may have been insufficiently dried.

### 3.2 COMPLEXES OF ACETONITRILE

Nitriles, particularly acetonitrile have been shown to be versatile in the field of inorganic chemistry. They form a large number of complexes with a range of metal halides, and are also widely used as

solvents for preparative work and for the measurement of physical properties of compounds. As a preparative medium acetonitrile can greatly increase the rates of many inorganic reactions.

In general terms, metal halides form four types of complexes with acetonitrile:-

- ( i ) Adducts involving Sc, Ti, V and Cr sub groups which tend to be non-ionic, e.g.  $\text{MoF}_5 \cdot 2\text{MeCN}$  [312].
- ( ii ) The remaining transition metal halides, which form ionic complexes, e.g.  $\text{FeCl}_3 \cdot 2\text{MeCN}$  which has been shown to contain both Fe(III) and Fe(II) complex ions and can be written as  $[\text{Fe}(\text{MeCN})_6]^{2+} \cdot 2[\text{FeCl}_4]^-$  [313].
- (iii) Lanthanide/actinide halides, in general, form neutral, monomeric adducts, e.g.  $\text{LaCl}_3 \cdot n\text{MeCN}$  ( $n = 4, 5$ ) [314].
- ( iv ) Ternary complexes, which involve either a combination of metal halides or a metal with a metal halide, e.g. tin(IV) chloride with the dichlorides of Be, Mg, Co, Sr, Ba, Mn, Fe, Co, Ni, Cu, Zn in acetonitrile, form a range of complexes of general formula  $\text{M}(\text{MeCN})_n(\text{anion})_p$  where the anions formed were  $[\text{SnCl}_6]^-$  and  $[\text{SnCl}_5(\text{MeCN})]^-$  and  $n = 2-8$  inclusive [315].

### 3.3 TERNARY ACETONITRILE ADDUCTS FORMED BY $\text{UF}_6$ , $\text{MoF}_6$ AND $\text{WF}_6$ (Table 1.13)

Prescott et al. [206,207] reported the oxidation of metals; Ag, Tl, Pb, Zn, Hg, Mn, Co, Ni and Cu by tungsten and molybdenum hexafluorides in acetonitrile solution. The acetonitrile complexes formed contained solvated metal cations and hexafluoromolybdate(V) and hexafluoro-tungstate(V) anions. The hexafluoromolybdate adducts produced can be represented by the general formula  $\text{M}[\text{MoF}_6]_m \cdot n\text{MeCN}$ , where M represents the metal,  $m = 2$  or  $3$  (which is dependent upon M) and  $n = 4, 5$  or  $6$ ,

e.g.  $\text{Ag}[\text{MoF}_6]_2 \cdot 4\text{MeCN}$ ,  $\text{Tl}[\text{MoF}_6]_3 \cdot 6\text{MeCN}$ . Similarly, the hexafluoro-tungstate complexes can be regarded as having the general formula  $\text{M}[\text{WF}_6]_x \cdot y\text{MeCN}$  (where  $x = 1$  or  $2$ ;  $y = 2, 3, 4, 5, 6$ ), e.g.  $\text{Ni}[\text{WF}_6]_2 \cdot 6\text{MeCN}$ ,  $\text{Mn}[\text{WF}_6]_2 \cdot 4\text{MeCN}$ . The solid air-sensitive ternary adducts were characterised by vibrational spectroscopy and chemical analysis. This work was extended when the ternary adduct  $\text{CuF}_2 \cdot 2\text{WF}_6 \cdot 5\text{MeCN}$  was isolated from the reaction of copper(II) fluoride with tungsten hexafluoride in acetonitrile [205].

Similarly, the metals Cu, Tl and Cd are oxidised by  $\text{UF}_6$  in acetonitrile [208]. The products isolated again can be represented by a general formula,  $\text{M}[\text{UF}_6]_a \cdot b\text{MeCN}$ , (where  $a = 2$  or  $3$  depending upon the oxidation of the metal M) and  $b$  is predominantly 5, but 6 in the case of  $\text{Hg}[\text{UF}_6]_2 \cdot 6\text{MeCN}$ . Furthermore, the reaction of copper(II) fluoride with uranium hexafluoride gave the salt,  $\text{Cu}[\text{UF}_7]_2 \cdot 5\text{MeCN}$  [208].

## PRESENT STUDY

### 3.4 URANIUM HEXAFLUORIDE WITH TRANSITION METALS IN ACETONITRILE

Metal powders; Cu, Zn, Mo, W were first cleaned using dilute acid and dried in an oven prior to being introduced into prefluorinated FEP reaction tubes in an inert atmosphere. Powders were used instead of metal wire or plates due to their higher surface area. A mixture of uranium hexafluoride and dried acetonitrile was distilled onto the metal powders which had been degassed for at least thirty minutes.

#### 3.4.1 Uranium hexafluoride with copper and zinc in acetonitrile

Preparation of the adducts;  $\text{Cu}[\text{UF}_6]_2 \cdot 5\text{MeCN}$ ;  $\text{Cu}[\text{UF}_6]_2 \cdot 6\text{MeCN}$ ;

$\text{Zn}[\text{UF}_6]_2 \cdot 4\text{MeCN}$ ;  $\text{Zn}[\text{UF}_6]_2 \cdot 5\text{MeCN}$

Reactions occurred at ambient temperatures and were complete within

2-4 hours. The excess of acetonitrile was removed by vacuum distillation leaving behind pale blue (Cu-UF<sub>6</sub>-MeCN) and pale green (Zn-UF<sub>6</sub>-MeCN) highly air-sensitive solids.

When non-dried acetonitrile was used both (Cu-UF<sub>6</sub>-MeCN) and (Zn-UF<sub>6</sub>-MeCN) systems yielded green air-sensitive solids. It was thought that transition metal uranium oxide fluoride acetonitrile adducts would be obtained similar to those reported for molybdenum by Prescott et al. [207]. However, analysis of these solids showed that only the hexafluorouranate(V) anion was present with no indication of any oxide fluoride formation. This was further confirmed by the observation of green solutions which are indicative of the hexafluorouranate anion [208,310,311].

The differing stoichiometries of the hexafluorouranate(V) acetonitrile adducts containing the same transition metal were determined by colour, IR spectroscopy (Table 3.1) and chemical analysis (Table 3.3).

#### 3.4.2 Vibrational spectroscopy

Raman spectra could not be obtained for any of the ternary adducts at room temperature, probably because of their poor crystallinity.

Infrared data for the four acetonitrile adducts are shown in Table 3.1. The spectra are all similar and the positions of the ligand bands are as expected for co-ordinated acetonitrile. Table 3.2 compares data for Cu[UF<sub>6</sub>]<sub>2</sub>.5CH<sub>3</sub>CN with those of pure acetonitrile and other ternary adducts showing the shift ranges for all the modes of vibration of acetonitrile co-ordinated via nitrogen in similar compounds. The shift to higher frequency for the -C≡N stretching mode is a strong indication of co-ordinated acetonitrile and all the adducts prepared exhibit this phenomenon. It should be noted that

TABLE 3.1

Infrared data ( $\text{cm}^{-1}$ ) for the ternary adducts

$\text{Cu}[\text{UF}_6]_2 \cdot 5\text{MeCN}$	$\text{Cu}[\text{UF}_6]_2 \cdot 6\text{MeCN}$	$\text{Zn}[\text{UF}_6]_2 \cdot 4\text{MeCN}$	$\text{Zn}[\text{UF}_6]_2 \cdot 5\text{MeCN}$	Assignment
2945 w	3020 m-	2935 w	3020 m-	C-H str. ( $\nu_5$ )
	2980 m		2970 w+	C-H str. ( $\nu_1$ )
	2345 s-		2340 m+	
2320 m	2320 m	2310 m-	2320 m-	C≡N str. ( $\nu_2$ )
2300 w-	2300 w+	2300 w-	2300 w-	
1410 m	1425 bm-	1415 m-	1420 m	CH <sub>3</sub> def. ( $\nu_6$ )
1370 m+	1380 m	1360 m-	1375 m	CH <sub>3</sub> def. ( $\nu_3$ )
1035 m-	1042 m-	1035 m-	1040 m-	CH <sub>3</sub> rock ( $\nu_7$ )
948 m+ (d)	955 m 940 sh, w+	948 m (d)	945 m (d)	C-C str. ( $\nu_4$ )
	750 bw+	744 bm	740 bm-	overtone ( $2\nu_8$ )
525 s+	525 s+	525 s+	525 s+	U-F str. ( $\nu_3$ )
470 w-	470 w	460 s	470 w	
450 w+				
400 w-	400 w-	400 w-	400 w-	C-CN def. ( $\nu_8$ )

TABLE 3.2

Infrared data ( $\text{cm}^{-1}$ ) for compounds with co-ordinated acetonitrile

<u>Vibrational mode</u>	<u>MeCN(1) [316, 317]</u>	<u><math>\text{UF}_5 \cdot 2\text{SbF}_5 \cdot 5\text{CH}_3\text{CN}</math> [318]</u>	<u><math>\text{Cu}[\text{UF}_6]_2 \cdot 5\text{CH}_3\text{CN}</math></u>	<u>Shift range for co-ordinated MeCN in ternary adducts [316, 317]</u>
C≡N str. ( $\nu_2$ )	2257	2310	2320	2321-2266
CH <sub>3</sub> def. ( $\nu_3$ )	1376	1370	1370	1374-1360
C-C str. ( $\nu_4$ )	920	942	948	980-924
comb. ( $\nu_3 + \nu_4$ )	2297	2335		2335-2300
CH <sub>3</sub> rock ( $\nu_7$ )	1040	1035	1035	1038-1025
comb. ( $2\nu_4 + \nu_8$ )	2208	2282		2278-2216
overtone ( $2\nu_8$ )	750	795		825-750
C-CN def. ( $\nu_8$ )	380	400	400	420-380

TABLE 3.3  
 Elemental Analysis of the MF<sub>5</sub>.2L Adducts Found (calc.).

	F	H	N	C	S
UF <sub>5</sub> .2L	19.49 (19.57)	1.64 (1.65)	11.57 (11.55)	4.97 (4.95)	13.22 (13.22)
MoF <sub>5</sub> .2L	27.72 (27.68)	2.36 (2.35)	16.40 (16.33)	7.08 (7.00)	18.72 (18.69)
WF <sub>5</sub> .2L	21.95 (22.04)	1.87 (1.87)	12.94 (13.00)	5.62 (5.57)	14.92 (14.87)

the shifts in the vibrational modes associated with the methyl group are very much smaller than those associated with the cyanide group. Since acetonitrile acts as a rod-like molecule in complexes, the chemical environments experienced by the methyl groups in solution and as a ligand are very similar.

In all the infrared spectra of dry ternary adducts the most striking feature is the strong unresolved band centred at  $525\text{ cm}^{-1}$  which is indicative of the  $\nu_3$  vibration of the  $[\text{UF}_6]^-$  ion [86,216]. The strong, sharp absorption at  $460\text{ cm}^{-1}$  for  $\text{Zn}[\text{UF}_6]_2 \cdot 4\text{MeCN}$  and similar weaker bands observed around this frequency for the other three ternary adducts are, at the moment, unassigned. The position of this band was found to be highly reproducible but its relative strength varied dramatically.

The band associated with the C-C stretching mode for all four ternary adducts is a doublet with a very small splitting constant (approximately  $1\text{-}2\text{ cm}^{-1}$ ). Similar splittings have been observed previously for uranium(V) adducts [308,319] and in a variety of adducts involving acetonitrile [318,320,321] where the C-C str. band is split due to  $\text{CH}_3\text{CN}$  ligands unequally bound to the  $\text{Cu}^{2+}$  ion as a result of Jahn-Teller deformation. Whether the observed band splitting is due to this or to symmetry effects, as observed for  $\text{SnCl}_4 \cdot 2\text{MeCN}$  [314] is unknown, but the former seems most likely.

The relative intensity of the C-C str. with respect to the intensity of the  $\text{CH}_3$  rock is also of interest. In free acetonitrile the  $\text{CH}_3$  rocking mode yields a band of much greater intensity than the band due to C-C str. whereas for the adducts  $\text{Cu}[\text{UF}_6]_2 \cdot n\text{MeCN}$  and  $\text{Zn}[\text{UF}_6]_2 \cdot n\text{MeCN}$  the intensities are reversed. These intensity changes generally occur where the dipole is significantly altered with respect to the free

ligand allowing increased or decreased interaction with the infrared radiation.

### 3.4.3 Electron spin resonance spectroscopy

There are numerous reports of e.s.r. measurements on  $5f^1$  ions ( $\text{Pa}^{4+}$ ,  $\text{U}^{5+}$ ,  $\text{Np}^{6+}$ ) [319,322,323]. The spectra of the uranium(V) adducts were recorded as solutions in acetonitrile in 4 mm O.D. tubing at 77 K. Strong, broad unsymmetrical signals were obtained. No hyperfine coupling was observed for any of the species. An average  $\underline{g}$ -value of 0.69 was obtained for all four adducts. Table 3.4 shows  $\langle \underline{g} \rangle$  average values obtained for other uranium(V) species.

The  $\langle \underline{g} \rangle$  average value of  $\text{UF}_5$  is higher at 0.83, but as  $\text{UF}_5$  is a bridged polymer, it will have a differing  $\underline{g}$ -value from any related monomeric species because of spin-spin interactions.

The absence of fine structure is due to the fact that the  $f$ -orbitals are not involved in the bonding to the fluorides, therefore the fluorides do not share any of the spin-density of the unpaired electron to create hyperfine splitting patterns. This is typical for uranium(V) systems and a broad asymmetrical signal is observed, the line shape being in agreement with the axial symmetry of the  $\underline{g}$ -tensor.

Copper(II) ion is a  $d^9$  ion and, consequently, Jahn-Teller distorted to give six co-ordinate species of  $D_{4h}$  symmetry, where the ligands along the  $z$  axis are further away from the metal than the ligands along the  $x$  and  $y$  axes. The change in symmetry from  $O_h$  to  $D_{4h}$  on the basis of the crystal field theory is shown in Figure 3.1.

Comparison of  $\Delta \underline{g}_{//}$  and  $\Delta \underline{g}_{\perp}$  values obtained both experimentally and theoretically can be used to determine the configuration of the ion. To obtain the magnitude of the shifts of  $\underline{g}_{//}$  and  $\underline{g}_{\perp}$  from  $\underline{g}_0$  (free

TABLE 3.4

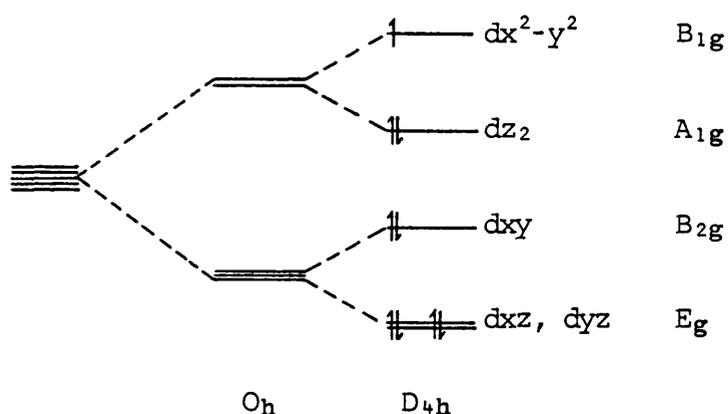
Average  $\underline{g}$ -values of uranium(V) species studied  
by e.s.r. spectroscopy

Compound	$\langle \underline{g} \rangle$ aver.	Ref.
Cu[UF <sub>6</sub> ].5MeCN	0.69	This work
UF <sub>5</sub>	0.83	[324]
UCl <sub>5</sub> .TCAC	1.1	[322]
UCl <sub>5</sub> .PCl <sub>5</sub>	1.1	[322]
UCl <sub>5</sub> .SOCl <sub>2</sub>	1.1	[322]
MUF <sub>6</sub> (M = Li, Na, Cs)	0.7	[325]

TABLE 3.5

Average  $\underline{g}$ -values of copper(II) species studied  
by e.s.r. spectroscopy

Compound	Solvent	$\langle \underline{g} \rangle$ aver.	Ref.
Cu[UF <sub>6</sub> ] <sub>2</sub> .5MeCN	MeCN	2.25	This work
CuCl <sub>2</sub> (anhyd.)	MeCN	2.19	This work
CuCl <sub>2</sub>	pyridine (60%) chloroform (40%)	2.13	[326]
CuCl <sub>2</sub>	NH <sub>3</sub> (0.5 N) in methanol	2.13	[326]
CuCl <sub>2</sub>	CH <sub>3</sub> NH <sub>2</sub> (14%) methanol (86%)	2.13	[326]



**FIGURE 3.1**

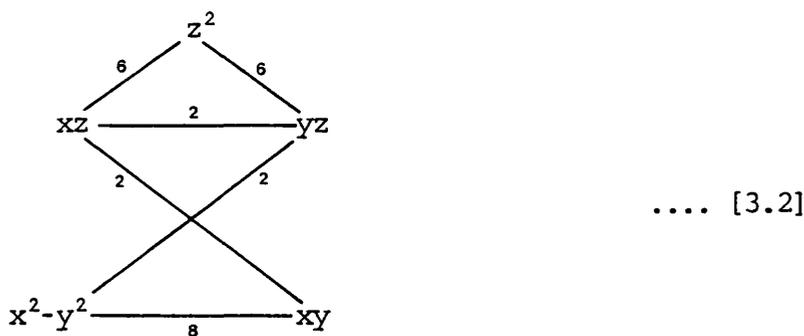
Molecular orbital energy levels of  $MF_6$  depicting the lowering of symmetry from  $O_h$  to  $D_{4h}$ .

electron), we must first examine the efficiency of the transformations, which is given by:-

$$\Delta g = \pm \frac{n\lambda}{\Delta} \quad \dots [3.1]$$

where  $n$  is the measure of the efficiency of the coupling of orbitals relative to one another;  $\lambda$  is the spin orbital coupling constant;  $\Delta$  is the energy between the transforming orbitals.

The value of  $n$  may be obtained by using [3.2].



Thus for a  $d^9$  ion:-

$$\Delta g_{\parallel} = \frac{8\lambda}{\Delta E(x^2-y^2 \leftrightarrow xy)} \quad \dots [3.3]$$

$$\Delta g_{\perp} = \frac{2\lambda}{\Delta E(x^2-y^2 \leftrightarrow xz, yz)} \quad \dots [3.4]$$

Theoretically the ratio of  $\Delta g_{\parallel} : \Delta g_{\perp}$  is 4:1. Experimentally the following shifts from  $g_0$  were obtained:  $\Delta g_{\parallel} = 470$  G,  $\Delta g_{\perp} = 120$  G, which leads to a  $\Delta g_{\parallel} : \Delta g_{\perp}$  ratio of 3.9:1. This thus confirms the presence of Cu(II) ions which is further enhanced by a comparison of  $\langle g \rangle$  average values obtained here with previous work on copper(II) systems [Table 3.5].

The e.s.r. spectra shown in Figure 3.2 show the effect of dilution on the resolution of the copper(II) signal. Both naturally occurring isotopes of copper ( $\text{Cu}^{63}$ -69.09%/ $\text{Cu}^{65}$ -31.91%) have spins of  $3/2$ . Figure 3.2 shows the development of the four allowed transitions for  $A_{\parallel}$  (where A is the hyperfine splitting constant). The reason why  $A_{\perp}$  peaks are not seen is because there is greater spin electron density associated with the xy plane where the ligands are closest to the metal. Fine structure for co-ordinated nitrogen remains hidden.

In solution the copper(II) ion would appear to be octahedrally co-ordinated to acetonitrile, but exists completely separate from hexa-fluorouranate(V) species with little or no interaction. This is indicated by the similarity of the e.s.r. spectra of  $\text{Cu}[\text{CuF}_6]_2 \cdot 5\text{MeCN}$  and anhydrous  $\text{CuCl}_2$  in acetonitrile.

#### 3.4.4 Nuclear magnetic resonance spectroscopy

Proton n.m.r. spectra of  $\text{Cu}[\text{UF}_6]_2 \cdot 5\text{MeCN}$  in acetonitrile were measured. Since co-ordinated acetonitrile will have a different chemical environment to free acetonitrile, a shift in the methyl protons should be observed. However, due to the presence of paramagnetic species, a broad signal was observed, which made detection of co-ordinated methyl protons impossible.

Attempts to record  $^{19}\text{F}$  nmr spectra of the adducts failed, since the expected fluorine signals were off the range of the spectrometer.

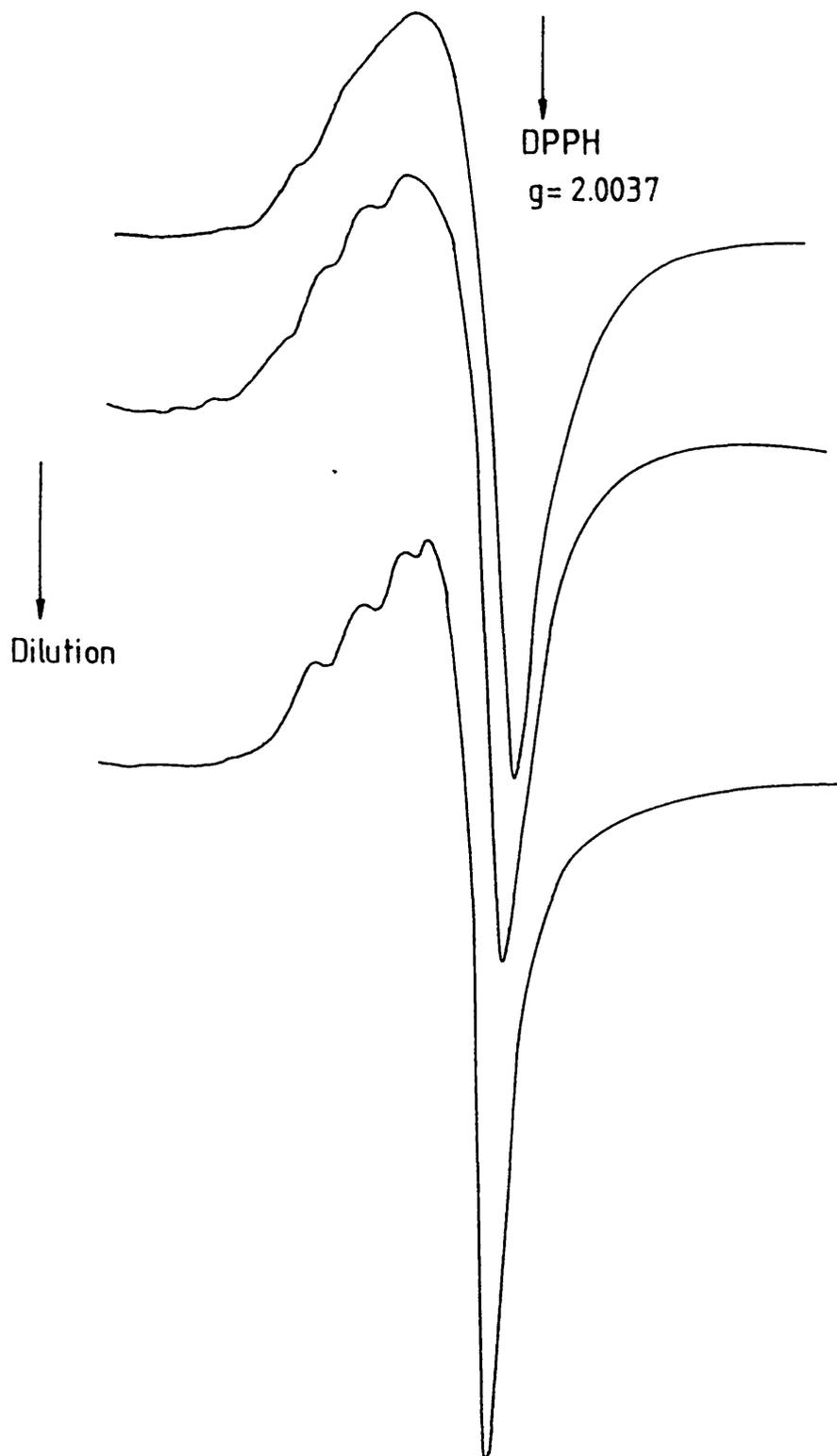


FIGURE 3.2

ESR spectra of  $\text{Cu}[\text{UF}_6]_2 \cdot 6\text{MeCN}$ , showing the effect of dilution on the signal associated with the  $\text{Cu}(\text{II})$  ion.

### 3.4.5 Discussion

Infrared and e.s.r. spectroscopy showed the presence of the hexafluorouranate(V) anion in all of the adducts. In solution, six acetonitriles are octahedrally co-ordinated to the Cu(II) ion whose presence was observed from e.s.r. spectroscopy, and it appears that the ions exist as separate entities.

Why the 'dryness' of acetonitrile should determine the composition of the adducts is somewhat puzzling. If 'non-dried' acetonitrile was used then one would expect oxide fluoride formation, however, no evidence for this was observed.

Very little is known on the structure of such adducts and it will probably remain this way until single crystals can be obtained.

### 3.5 URANIUM HEXAFLUORIDE WITH MOLYBDENUM AND TUNGSTEN IN ACETONITRILE

A mixture of uranium hexafluoride and dry acetonitrile was condensed onto the metal powders which had been degassed for at least thirty minutes. Green solutions were obtained at room temperature for both (Mo-UF<sub>6</sub>-MeCN) and (W-UF<sub>6</sub>-MeCN) systems, but no solids were isolated. The reactions were repeated and left overnight, but polymerisation of the solvent occurred. It can be concluded from the observation of green solutions that some reaction takes place.

### 3.6 URANIUM HEXAFLUORIDE WITH COPPER IN GENETRON

A mixture of uranium hexafluoride and Genetron was distilled onto a known quantity of degassed copper powder in a prefluorinated FEP tube. No reaction was observed even after several days when the solvent was removed by vacuum distillation, leaving behind the unreacted copper powder.



# CHAPTER 4

Attempted preparation of  
uranium thiofluoride

#### 4.1 INTRODUCTION

Much of the work on the synthesis of transition metal chalcogenide fluorides, and on the reactions of the hexafluorides of uranium, molybdenum, and tungsten with sulphur containing reagents has been performed in this laboratory [49,179-181,189] and by Russian workers [62,63,158] who in many cases have based their characterisation of the appropriate system by  $^{19}\text{F}$  nmr spectroscopy alone. The majority of the studies have been concentrated on tungsten hexafluoride and to a lesser extent on uranium hexafluoride, and molybdenum hexafluoride.

The methods used for the preparation of transition metal thiohalides are summarised in Table 4.1. Molybdenum and tungsten thiotetrafluorides have both been synthesised and characterised [179,180]. Attempts to prepare uranium thiofluorides have so far been unsuccessful (Fig. 4.1) and so the possibility of the separation of molybdenum, tungsten, and uranium hexafluorides on the basis of this chemistry seemed worth investigating. However, not all of the known methods for the preparation of transition metal thiohalides given in Table 4.1 have been applied to uranium hexafluoride. The aim of the work discussed in this Chapter is to fill these gaps and to find new methods for the synthesis of tungsten thiotetrafluoride from tungsten hexafluoride which may, in turn, lead to the successful synthesis of uranium thiofluorides.

In the following Chapter, the thermodynamic stabilities of uranium(VI), molybdenum(VI) and tungsten(VI) substituted fluorides, e.g.  $\text{MCl}_n\text{F}_{6-n}$ ;  $\text{MO}_n\text{F}_{6-2n}$ ;  $\text{MS}_n\text{F}_{6-2n}$  ( $\text{M}=\text{U}, \text{Mo}, \text{W}$ ;  $n=1$  or  $2$ ) with respect to decomposition and disproportionation are also discussed. Uranium thiofluorides are predicted to be thermodynamically unstable with respect to decomposition into elemental sulphur and lower uranium

TABLE 4.1

Established methods for the synthesis of metal thiohalides

Method	Examples	References
Metal Halide/Sulphur	$\text{MoCl}_5 + \text{S} \xrightarrow[3 \text{ weeks}]{140^\circ\text{C}} \text{MoSCl}_3$	[327]
	$\text{WCl}_5 + \text{S} \rightarrow \text{WSCl}_3$	[327]
	$\text{WF}_6 + \text{S} \rightarrow \text{WSF}_4$	[49]
Metal Halide/ $\text{H}_2\text{S}$	$\text{MoCl}_4 + \text{H}_2\text{S} \xrightarrow{\text{H}_2\text{S}} \text{MoS}_2\text{Cl}_2$	[327]
	$\text{WF}_6 + \text{H}_2\text{S} \xrightarrow{\text{MeCN}} \text{WSF}_4 \cdot \text{MeCN}$	[63]
Metal Halide/Metal Sulphide	$\text{Cr}_2\text{S}_3 + \text{CrBr}_3 \xrightarrow[870^\circ\text{C}]{\text{sealed ampoule}} \text{CrSBr}$	[328]
	$\text{Y}_2\text{S}_3 + \text{YF}_3 \xrightarrow{900-1200^\circ\text{C}} \text{YSF}$	[329]
Metal Halide/ $\text{Sb}_2\text{S}_3$	$\text{WF}_6 + \text{Sb}_2\text{S}_3 \xrightarrow{300^\circ\text{C}} \text{WSF}_4$	[179]
	$\text{MoF}_6 + \text{Sb}_2\text{S}_3 \xrightarrow{300^\circ\text{C}} \text{MoSF}_4$	[180]
	$\text{TaCl}_5 + \text{Sb}_2\text{S}_3 \xrightarrow{120^\circ\text{C}} \text{TaSCl}_3$	[330]
Metal Halide/ $\text{B}_2\text{S}_3$	$\text{MoCl}_5 + \text{B}_2\text{S}_3 \xrightarrow{190^\circ\text{C}} \text{MoSCl}_3$	[331]
	$\text{TaCl}_5 + \text{B}_2\text{S}_3 \xrightarrow{80^\circ\text{C}} \text{TaSCl}_3$	[331]
Metal Halide/ $\text{RSSiMe}_3$	$\text{MoCl}_5 + \text{RSSiMe}_3 \xrightarrow{\text{R.T.}} \text{MoSCl}_3$	[332]
	$\text{WCl}_5 + \text{RSSiMe}_3 \xrightarrow{\text{R.T.}} \text{WSCl}_3$	[332]

Continued .....

TABLE 4.1 (Continued) .....

Method	Examples	References
Metal Halide/ZnS	$\text{WF}_6 + \text{ZnS} \xrightarrow[10 \text{ hrs.}]{300^\circ\text{C}} \text{WSF}_4$	[189]
Metal Halide/Sulphur Halide	$\text{MoCl}_5 + \text{S}_2\text{Cl}_2 \xrightarrow{250^\circ\text{C}} \text{MoSCl}_2$	[333]

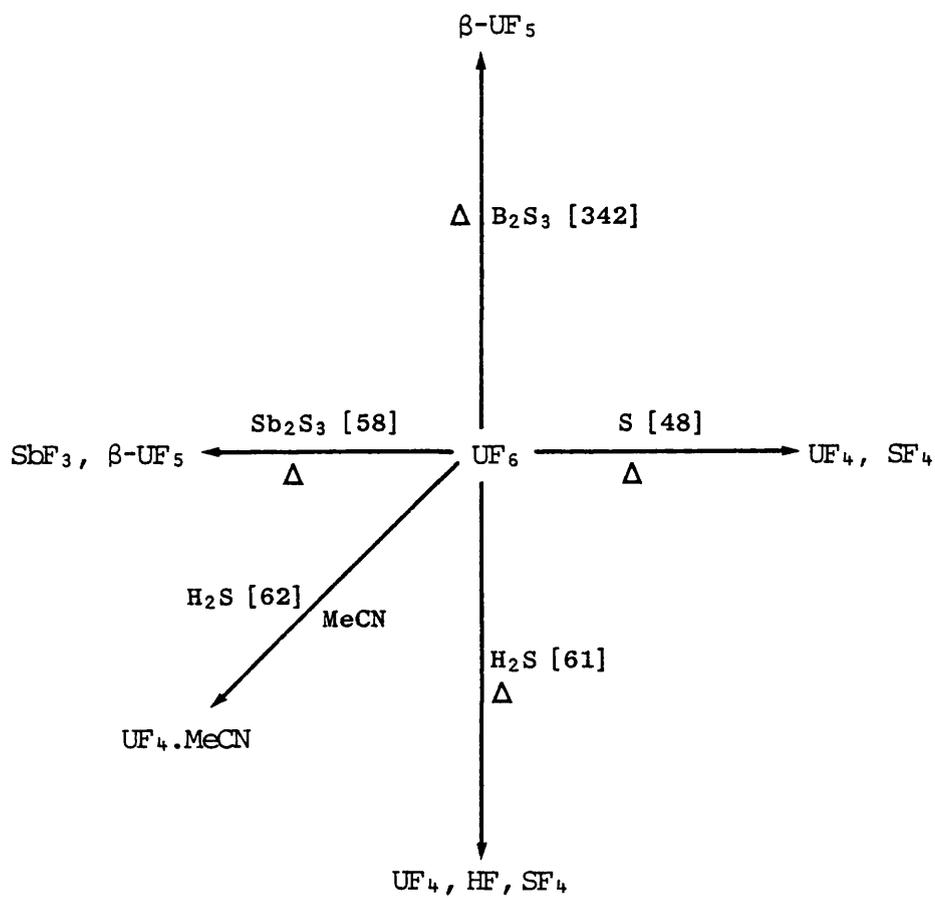


FIGURE 4.1

Previously attempted methods for the synthesis of uranium thiofluorides.

fluorides at room temperature. The production of uranium tetra-, pentafluorides and elemental sulphur or sulphur fluorides from many of the attempted preparations of uranium thiofluorides discussed in this Chapter and in experiments by other workers [48,61,62,181] appears to confirm their predicted instability at room temperature.

#### 4.1.1 Tungsten Thiofluorides

The first reported observation of tungsten-sulphur-fluorine species;  $WSF_4^+$ ,  $WSF_3^+$ ,  $WSF_2^+$  and  $WS_2F_2^+$  was by Hildenbrand [8] from a mass spectroscopic study of the interaction between tungsten hexafluoride, sulphur hexafluoride and tungsten in an effusion cell at 1000-2200 K. In 1973 Buslaev et al. [334] observed tungsten thiotetrafluoride,  $WSF_4$  in solution at room temperature from a  $^{19}F$  nmr study of the reaction between  $WSCl_4$  and HF in acetonitrile. The  $WSF_4$   $^{19}F$  nmr spectrum has also been obtained from the reactions of tungsten hexafluoride in acetonitrile with many inorganic sulphides including  $Na_2S$ ,  $K_2S$ ,  $Bu_2S$ ,  $Ph_2S$  and  $(NH_2)_2CS$  [71]. Some solution phase reactions of tungsten thiotetrafluoride in acetonitrile have also been studied [335-337]; for instance it has been shown that butylamine will react with the thiotetrafluoride in solution to produce  $WSF_4.MeCN$ ,  $[WSF_5]^-$  and  $[W(NBu)F_5]^-$  [335].

Tungsten thiotetrafluoride was first prepared as an uncomplexed solid by Atherton and Holloway [179] from the reaction of tungsten hexafluoride with antimony sulphide ( $3WF_6 + Sb_2S_3 \rightarrow 3WSF_4 + 2SbF_3$ ) in an autoclave at 300°C. Yellow crystals of tungsten thiotetrafluoride melt at approximately 90°C, on exposure to the atmosphere, HF and  $H_2S$  are rapidly evolved [179]. The main features of the IR spectrum of the solid include strong peaks at 699, 673 and 643  $cm^{-1}$  assigned to

terminal  $\nu(\text{W-F})_{\text{str.}}$ , an intense band at  $577 \text{ cm}^{-1}$  attributable to  $\nu(\text{W=S})_{\text{str.}}$  and broad bands at  $534$  and  $514 \text{ cm}^{-1}$  characteristic of (W-F-W) bridge vibrations [179]. Tungsten thiotetrafluoride has also been isolated as one of the products from the interaction of sulphur hexafluoride with a tungsten filament at temperatures above  $500^\circ\text{C}$ ; the other product being tungsten tetrafluoride [338].

#### 4.1.2 Molybdenum Thiofluorides

Thiofluorides of molybdenum have been isolated in which the metal is in an oxidation state of V or VI. Molybdenum thiotrifluoride;  $\text{MoSF}_3$  was the first reported chalcogenide fluoride of molybdenum. It has been prepared from the reaction of metallic molybdenum with sulphur hexafluoride in a quartz reactor in the presence of a filament at  $600\text{--}800^\circ\text{C}$  [339]. Molybdenum thiotrifluoride is also the product of the reaction between molybdenum and sulphur hexafluoride in the presence of a white-hot filament [340]. Solid molybdenum thiotetrafluoride is orange with a melting point of  $85.6^\circ\text{C}$ . It has been characterised by X-ray powder diffraction, chemical analysis and IR spectroscopy,  $\nu(\text{Mo=S})$  being observed at  $584 \text{ cm}^{-1}$  and bands attributable to terminal  $\nu(\text{Mo-F})$  at  $690$ ,  $670$  and  $633 \text{ cm}^{-1}$  and to  $\nu(\text{Mo-F-Mo})$  bridging modes at  $500$  and  $480 \text{ cm}^{-1}$  [340,341].

Molybdenum thiotetrafluoride;  $\text{MoSF}_4$  was first isolated from the reaction of molybdenum hexafluoride with antimony sulphide at  $300^\circ\text{C}$  in an autoclave [180]. X-ray powder diffraction studies have shown that molybdenum thiotetrafluoride and the analogous tungsten compound have different structures [180]. The IR spectrum of the solid shows a band at  $594 \text{ cm}^{-1}$  assignable to  $\nu(\text{Mo=S})$ , along with strong absorption bands in the regions characteristic of both terminal and bridging molybdenum-fluorine stretching modes [180].

### 4.1.3 Attempted Preparations of Uranium Thiofluorides

In the quest for uranium thiotetrafluoride, many of the attempted preparations have been made by direct analogy with the established methods for the synthesis of uranium oxytetrafluoride from the hexafluoride (Fig. 4.1). For instance, boron oxide with uranium hexafluoride yields uranium oxytetrafluoride [96] whereas the sulphide analogue, B<sub>2</sub>S<sub>3</sub>, reduces the hexafluoride to the pentafluoride [342].

## PRESENT STUDY

### 4.2 METAL HEXAFLUORIDES WITH ELEMENTAL SULPHUR

The reaction between uranium hexafluoride and elemental sulphur was first reported by Aubert et al. [48] in 1968. They reported that the reaction between gaseous uranium hexafluoride and sulphur vapour takes place in flow systems at temperatures above 130°C or when uranium hexafluoride is bubbled through liquid sulphur at 150°C. The products of the reaction vary with conditions, but uranium tetrafluoride and sulphur tetrafluoride are the major products under most conditions. The reaction:-



is unaffected by the presence of a carrier gas such as nitrogen.

Interactions between elemental sulphur and the hexafluorides of molybdenum and tungsten appear to have received relatively little attention, which is somewhat surprising considering the large number of transition metal thiohalides which have been synthesised from reactions between elemental sulphur and metal halides; Table 4.1.

#### 4.2.1 Uranium Hexafluoride with Elemental Sulphur

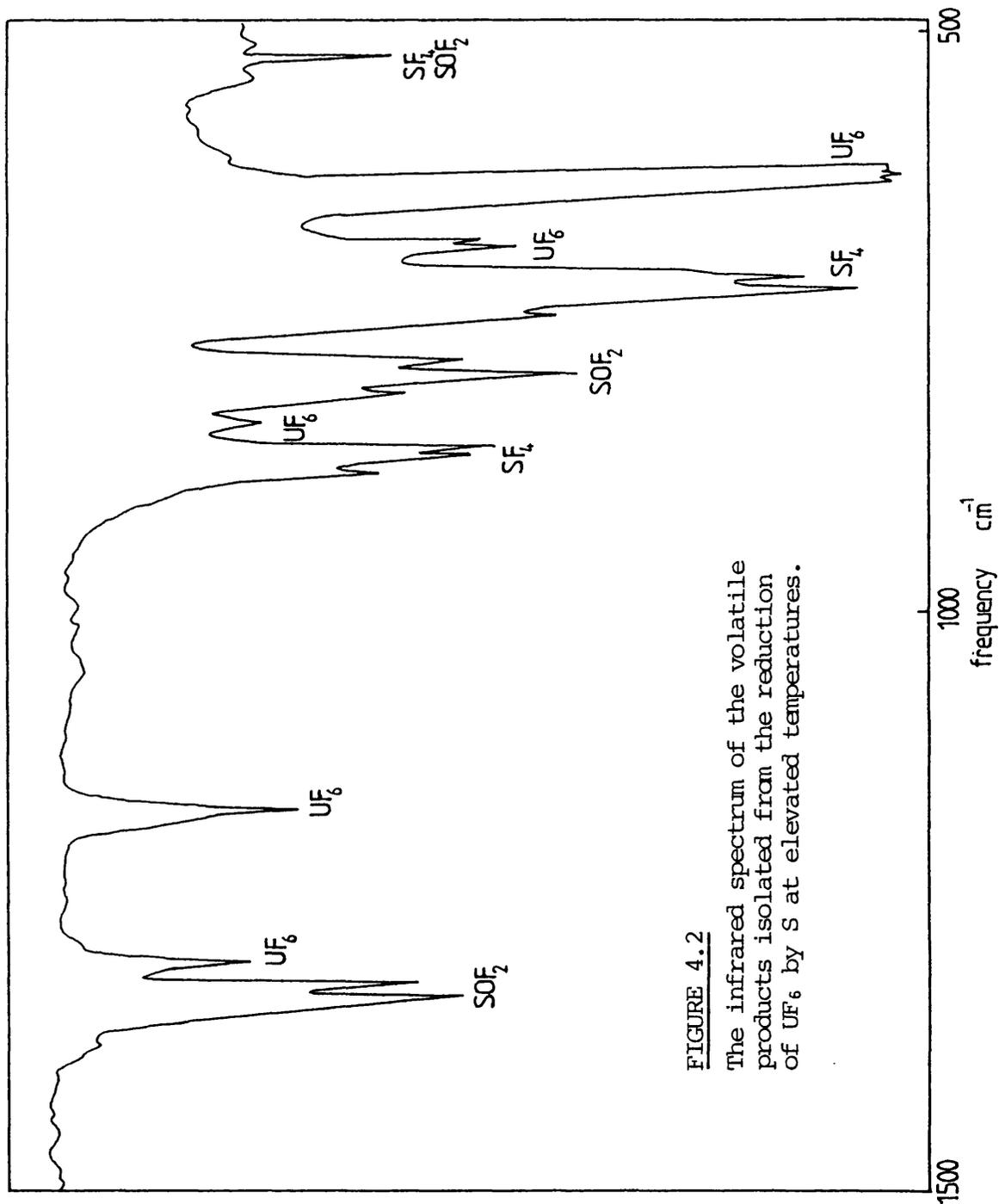
Elemental sulphur which had been dried in an oven overnight was introduced into a prefluorinated stainless steel reactor sealed with

a gold gasket. The reactor was then re-evacuated and the volatile impurities in the sulphur were removed by exposure under high vacuum at 60°C for three hours. A three-fold excess of uranium hexafluoride was condensed into the reactor and the mixture was heated to 140°C for 4½ hours by means of a thermostatically controlled furnace. Upon cooling, the volatile products were expanded into a 10 cm path-length IR gas cell. Typically, a pressure of 10 mmHg was admitted and the IR spectrum was immediately recorded (Fig. 4.2). The green solid product was removed from the reactor in an inert atmosphere after the volatiles had been removed. Its X-ray powder diffraction pattern showed it to be uranium tetrafluoride by comparison with that of a pure sample.

The gas-phase IR spectrum of the volatiles showed that some uranium hexafluoride remained by virtue of the  $\nu_3$  band at  $625\text{ cm}^{-1}$  [343]. Sulphur tetrafluoride was the only binary fluoride of sulphur formed, Table 4.2. Vibrational spectroscopy also showed that substantial quantities of an oxyfluoride,  $\text{SOF}_2$  were formed during the reaction. The results agree with previous studies [48,342], but the observation of thionyl fluoride in the volatiles is presumably due to the difficulty in drying elemental sulphur.

#### 4.2.2 Uranium Hexafluoride with Elemental Sulphur in Genetron

The reaction between uranium hexafluoride and elemental sulphur was repeated in a prefluorinated FEP tube, using Genetron as a solvent. An excess of uranium hexafluoride was condensed onto a mixture of elemental sulphur in Genetron at -196°C and the system was allowed to warm to room temperature. No reaction was observed to take place even after 36 hours when the volatiles were removed by vacuum distillation leaving behind the unreacted sulphur.



**FIGURE 4.2**

The infrared spectrum of the volatile products isolated from the reduction of  $\text{UF}_6$  by S at elevated temperatures.

TABLE 4.2

Infrared stretching frequencies ( $\text{cm}^{-1}$ ) of the volatile products formed during the static reduction of  $\text{UF}_6$  by sulphur

Observed	$\text{UF}_6$ [343]	$\text{SF}_4$ [344-346]	$\text{SOF}_2$ [347,348]	$\text{SO}_2\text{F}_2$ [349]
1340				1502 $\nu_6$ ; $\nu$ as (SO)
1335			1333 $\nu_1$ ; $\nu$ (SO)	
1290	1291 comb. ( $\nu_1+\nu_3$ )			1269 $\nu_1$ ; $\nu$ sym (SO)
1160	1157 comb. ( $\nu_2+\nu_3$ )	889 $\nu_1$ ; $\nu$ sym (eq)		
900				
890				
875		867 $\nu_6$ ; $\nu$ as (ax)		
865				848 $\nu_2$ ; $\nu$ sym (SF)
830	828 comb. ( $\nu_3+\nu_5$ )			
820				
805			808 $\nu_2$ ; $\nu$ sym (SF <sub>2</sub> )	
795				
755				
740			748 $\nu_5$ ; $\nu$ as (SF <sub>2</sub> )	
725		728 $\nu_8$ ; $\nu$ as (eq)		
675	678 doublet			
670	671 comb. ( $\nu_2+\nu_6$ )			
624	625 $\nu_3$			553 $\nu_7$ ; $\delta$ (SOF) 544 $\nu_3$ ; $\delta$ (SF <sub>2</sub> )
540				
525		532 $\nu_7$	530 $\nu_3$ ; $\delta$ (SOF)	
510				

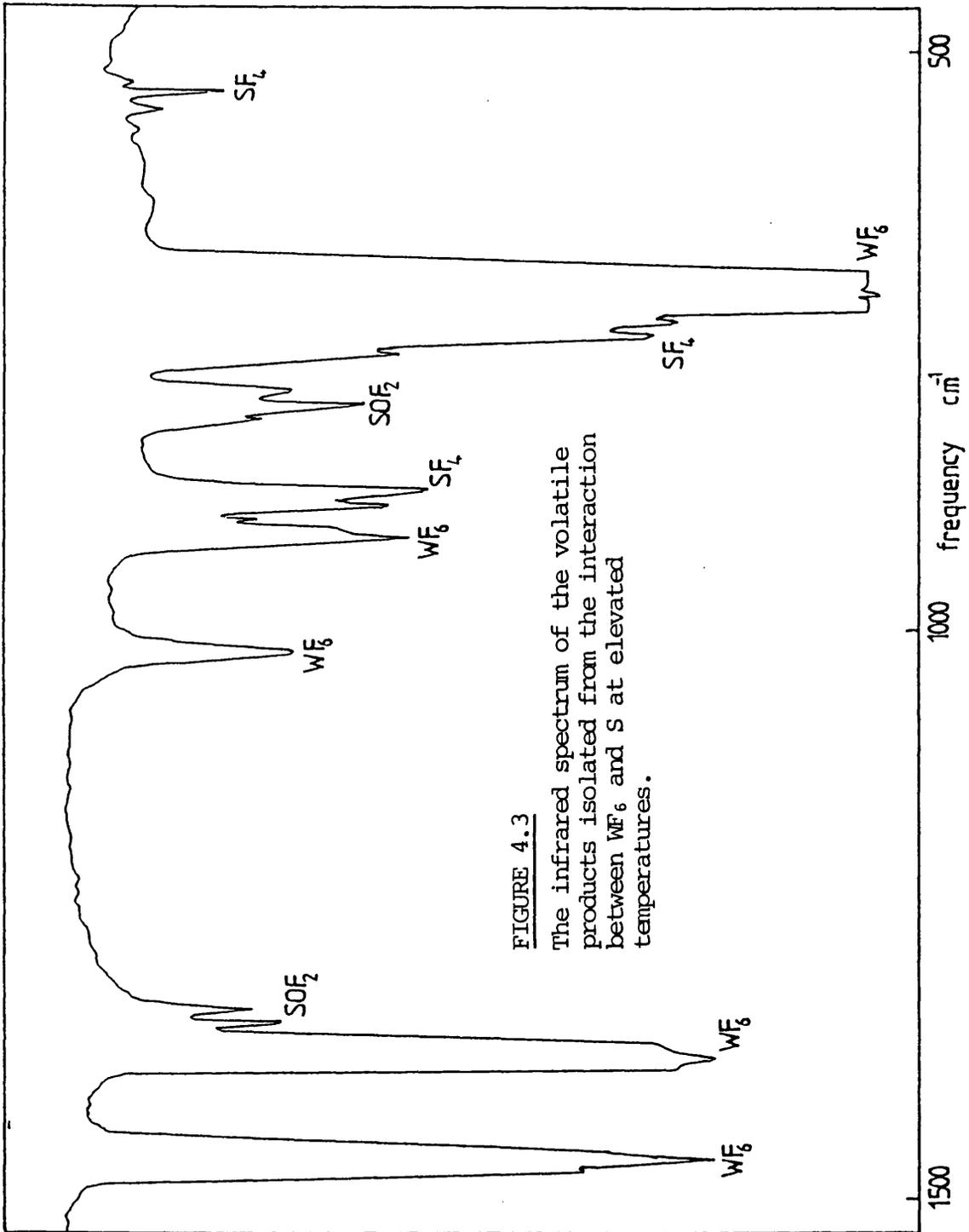
### 4.2.3 Tungsten Hexafluoride with Elemental Sulphur

The interactions between tungsten hexafluoride and elemental sulphur were studied in prefluorinated sealed stainless steel reactors containing nickel buckets. Various reactant stoichiometries and temperatures were investigated:-

<u>WF<sub>6</sub>:S Ratio</u>	<u>Temp. °C</u>	<u>Duration of Reaction (hrs)</u>
1:1	160	48
10.1:1	120	72
24.4:1	90	71

After cooling, and evacuating, the reactors were found to contain small quantities of a pale yellow solid on the sides of the reactor along with a pool of yellow liquid lying on top of the unreacted elemental sulphur in the nickel bucket. Mass spectra of the solid material showed it to be elemental sulphur, while the IR spectra of the vapour over the yellow liquid showed only absorption bands attributable to tungsten hexafluoride. Thus under the conditions outlined above, no significant reaction was observed to take place between tungsten hexafluoride and elemental sulphur.

In a final attempt, a 2:3 molar ratio of tungsten hexafluoride to elemental sulphur was heated to 300°C for two days in a sealed reactor, since Holloway et al. [49] reported to yield tungsten thiotetrafluoride by employing a similar procedure. After cooling, gas-phase IR spectra of the volatiles (Fig. 4.3) clearly showed the presence of both sulphur tetrafluoride and thionyl fluoride as well as unreacted tungsten hexafluoride. Upon opening the reactor in an inert atmosphere, a brownish-yellow crystalline material was observed at the top of the reactor, with the unreacted elemental sulphur remaining in the bucket. The IR spectrum of the brownish-yellow product, Table 4.3, showed it to be tungsten thiotetrafluoride [179], with only a small band at 1050 cm<sup>-1</sup>



**FIGURE 4.3**

The infrared spectrum of the volatile products isolated from the interaction between  $\text{WF}_6$  and S at elevated temperatures.

TABLE 4.3

The infrared spectrum ( $\text{cm}^{-1}$ ) of  $\text{WSF}_4$  prepared from the reaction between  $\text{WF}_6$  and S at elevated temperatures

<u>WSF<sub>4</sub></u>	<u>Assignment</u>
720sh	} $\nu(\text{W-F})$ terminal
700s	
690sh	
670s	
655sh	
645vs	
625sh	
575m	$\nu(\text{W-S})$
560sh	} $\nu(\text{W-F-W})$ bridging
535s	
515s	

TABLE 4.4

Indexed X-ray powder diffraction pattern for  $\text{WSF}_4$

<u>hkl</u>	<u><math>\sin^2\theta</math></u>	<u>d-values</u>	<u>I/I<sub>0</sub></u>
201	0.01623	6.052	35
110	0.02277	5.109	40
210	0.02833	4.580	35
400	0.03479	4.133	100
211	0.03597	4.065	90
012	0.04778	3.527	20
402	0.06228	3.089	45
510	0.07062	2.901	55
221	0.09524	2.498	15
014	0.12965	2.141	15
802	0.16256	1.912	65
030	0.1796	1.819	20
910	0.19012	1.768	15

due to the presence of tungsten oxytetrafluoride [350], which is the expected initial hydrolysis product [335]. The X-ray powder diffraction pattern, Table 4.4, confirmed that the solid product was tungsten thiotetrafluoride, the data being indexed on the basis of the results obtained from the single crystal X-ray structure determination [351].

Thus the reaction between tungsten hexafluoride and elemental sulphur is highly dependent upon the reactant stoichiometry, temperature, and the contact time.

#### 4.2.4 Molybdenum Hexafluoride with Elemental Sulphur

Various stoichiometric ratios of molybdenum hexafluoride to elemental sulphur were heated to temperatures of between 110 and 300°C for up to 70 hours in sealed prefluorinated stainless steel reactors:-

<u>MoF<sub>6</sub>:S Ratio</u>	<u>Temp. °C</u>	<u>Duration of Reaction (hrs)</u>
1:1	210	42
2:3	300	24
11.3:1	120	70
23.7:1	70	68

After cooling, the residual pressures of the systems were measured and indicated that no reactions had taken place. Also the IR of the volatiles remained unaltered. Upon evacuating and opening the reactors in an inert atmosphere, the sides were found to be encrusted with a yellow solid which was identified as elemental sulphur by mass spectroscopy. Thus under the conditions outlined above no significant reaction was observed to take place between molybdenum hexafluoride and elemental sulphur.

Considering that both uranium hexafluoride and tungsten hexafluoride react with elemental sulphur at elevated temperatures, it is surprising that no reaction was observed with molybdenum hexafluoride.

### 4.3 METAL HEXAFLUORIDES WITH METAL SULPHIDES

#### 4.3.1 Tungsten Hexafluoride with Tungsten(IV) Sulphide

Varying stoichiometric ratios of tungsten(IV) sulphide, which had been dried under dynamic vacuum at 100°C for 3 hours, and tungsten hexafluoride were heated to 300°C for up to 10 hours in sealed stainless steel reactors. After cooling, the residual pressures of the systems were measured and indicated that no reactions had taken place, which was confirmed by no measurable weight change in tungsten(IV) sulphide, with the IR spectra of the volatiles remaining unaltered.

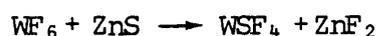
#### 4.3.2 Tungsten Hexafluoride with Tungsten(IV) Sulphide in Genetron

The reaction between tungsten hexafluoride and tungsten(IV) sulphide was repeated in a prefluorinated FEP tube using Genetron as a solvent. An excess of tungsten hexafluoride was condensed onto a known quantity of tungsten(IV) sulphide in Genetron at -196°C and the mixture was allowed to warm to room temperature. No observable reaction occurred even after several days. Infrared spectra of the volatiles revealed the presence of tungsten hexafluoride and Genetron which, with no measurable weight change in tungsten(IV) sulphide, confirmed that no reaction had taken place.

#### 4.3.3 Uranium Hexafluoride with Zinc Sulphide

##### Introduction

Tungsten thiotetrafluoride has recently been prepared from the interaction between tungsten hexafluoride and zinc sulphide in an autoclave at elevated temperatures, according to the following equation [189]:-



It was hoped that the analogous reaction with uranium hexafluoride

would lead to the first successful synthesis of uranium thiotetrafluoride.

#### Present Study

Zinc sulphide which had been dried at 80°C for several hours under dynamic vacuum was introduced into a prefluorinated stainless steel reactor. An equimolar quantity of uranium hexafluoride was condensed onto the zinc sulphide and the system was heated to 300°C for 4 hours. When heating was terminated and the volatiles transferred into a seasoned FEP tube, the reactor was opened in a dry box, revealing a non-volatile white solid with traces of a green solid also present. The white/green solid gave a complex X-ray diffraction pattern with many overlapping lines suggesting it to be a mixture. If, however, the green solid was carefully separated out and its X-ray powder diffraction pattern recorded, two lines coincident with the two strongest lines of a reference diffraction pattern, Table 4.5, were observed suggesting the presence of uranium tetrafluoride. The remaining solid product was identified by X-ray powder diffraction studies to be a mixture of zinc fluoride and unreacted zinc sulphide by comparison with those of pure samples.

Infrared spectra of the volatile products showed that all of the uranium hexafluoride had been reduced, since the strongest IR band of uranium hexafluoride at 624  $\text{cm}^{-1}$  was not present. The spectra also showed that sulphur tetrafluoride was not the only binary fluoride of sulphur formed, since bands in the region of 725  $\text{cm}^{-1}$  suggested the presence of FSSF and/or SSF<sub>2</sub>; Table 4.6. In addition to these binary fluorides, it was noted that thionyl fluoride was also produced in the reaction.

Variation of the molar ratio of the reactants established that the

TABLE 4.5

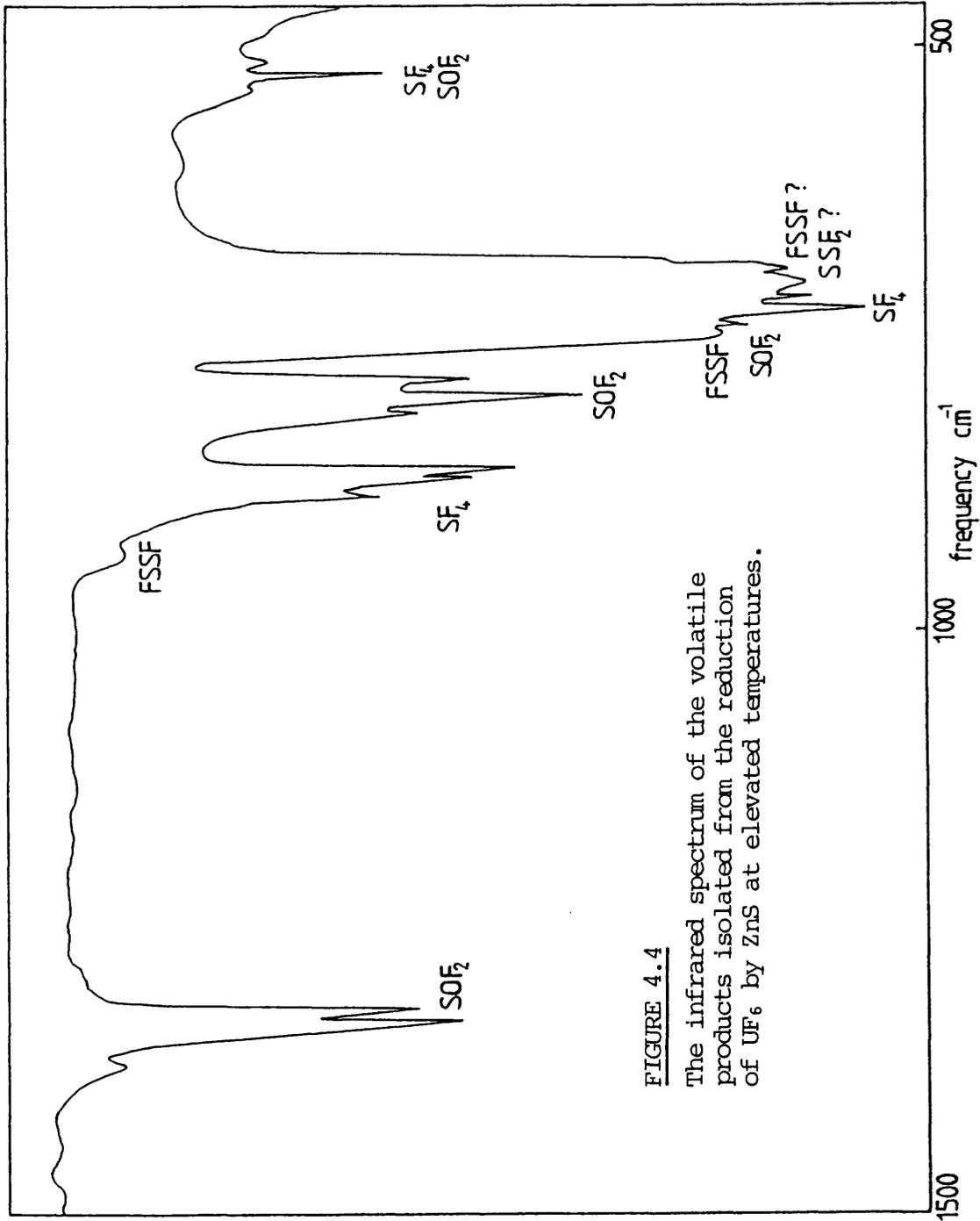
Indexed X-ray diffraction pattern for UF<sub>4</sub>

<u>hkl</u>	<u>sin<sup>2</sup>θ</u>	<u>d-values</u>	<u>I/I<sub>0</sub></u>
111	0.03418	4.1685	70
221	0.03887	3.9086	40
220	0.04388	3.6793	80
130	0.04796	3.5187	10
222	0.05298	3.3486	5
310	0.05610	3.2547	50
040	0.08182	2.6954	10
150	0.13476	2.0981	5
023	0.13869	2.070	10
510, 204	0.14564	2.0205	100
531	0.1501	1.9898	30
151	0.15629	1.9492	5
440	0.17364	1.8506	50
350	0.1775	1.8298	5
060	0.1834	1.8001	5
600	0.2009	1.7234	15
004	0.2081	1.6894	15
402, 351	0.2237	1.6299	40
620	0.2265	1.6193	35
531	0.2539	1.523	15
550	0.2713	1.4808	25
640	0.2827	1.449	10
044	0.2906	1.4307	5

TABLE 4.6 [Fig. 4.4]

Infrared stretching frequencies ( $\text{cm}^{-1}$ ) of the volatile products formed during the reaction between  $\text{UF}_6$  and zinc sulphide at elevated temperatures

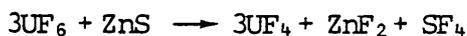
Observed	$\text{SF}_4$ [344-346]	$\text{SSF}_2$ [352,353]	FSSF [352,353]	$\text{SOF}_2$ [347,348]
1385			1389	}1333
1340				
1330				
940			941	
900	}889 }867			
890				
875				
825				808
810				
795				
790				
760		760		
750				
730				
720	728	718	717	
700		692		
695				
685				
540	}532		615	}530
530				
525				



**FIGURE 4.4**

The infrared spectrum of the volatile products isolated from the reduction of UF6 by ZnS at elevated temperatures.

following reaction takes place between uranium hexafluoride and zinc sulphide at elevated temperatures:-



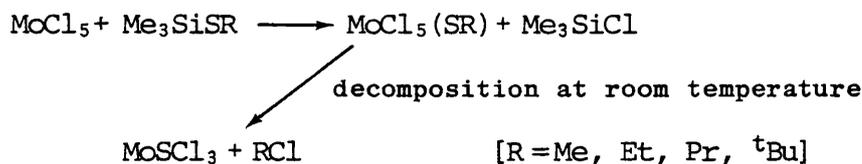
The nature of the volatiles were found to be dependent upon the uranium hexafluoride/zinc sulphide stoichiometric ratio. About 100% sulphur tetrafluoride formation occurs when the  $\text{UF}_6/\text{ZnS}$  ratio is greater than 3, but when the ratio was less than 3 there is some  $\text{S}_2\text{F}_2$  formation.

#### 4.4 REACTIONS OF URANIUM AND TUNGSTEN HEXAFLUORIDES WITH TRIMETHYLSILYL SPECIES

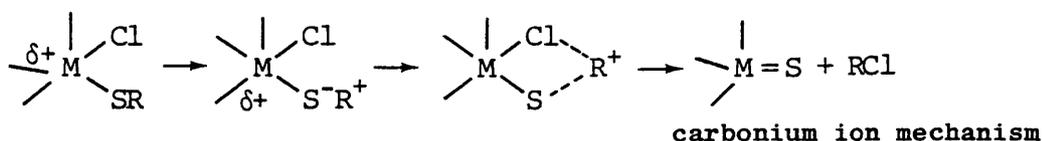
##### 4.4.1 Reactions between Uranium Hexafluoride and Trimethylsilyl Methyl Sulphide

###### Introduction

Trimethylsilyl methyl sulphide has been used for the synthesis of transition metal thiohalides from direct reactions with metal halides at room temperature [332].



The following mechanism has been proposed for the decomposition of  $\text{MoCl}_5(\text{SR})$  [332].



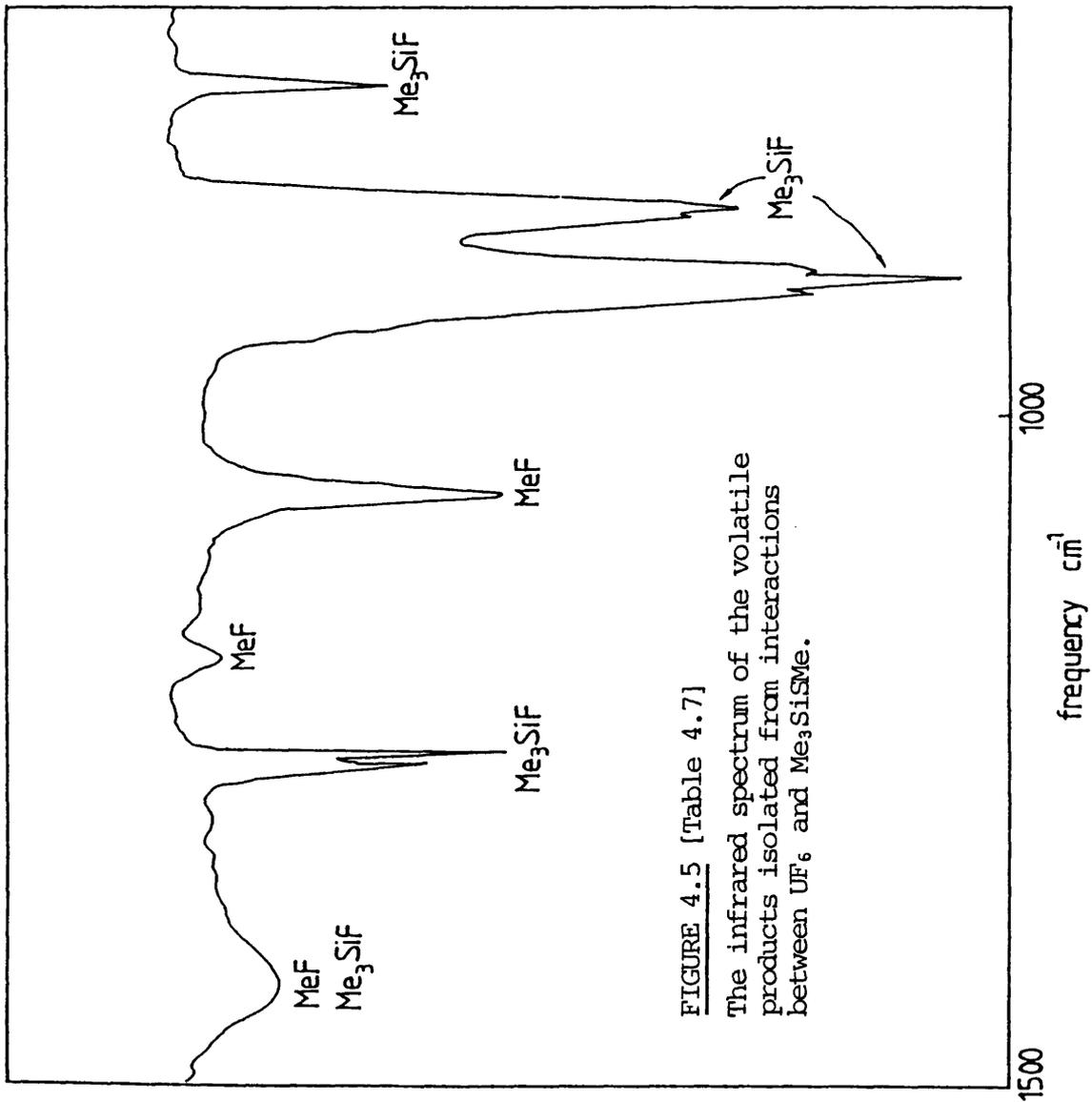
Interactions between uranium hexafluoride and trimethylsilyl methyl sulphide were studied in the hope of producing uranium thiofluorides.

## PRESENT STUDY

### Summary

Reactions involving 1:1 molar ratios of uranium hexafluoride to trimethylsilyl methyl sulphide yielded uranium tetrafluoride and elemental sulphur. With a 2:1 molar excess of uranium hexafluoride, the products obtained are uranium pentafluoride and elemental sulphur. The volatile products, trimethylsilyl fluoride and methyl fluoride, were independent of the reactant stoichiometry.

The reactions between uranium hexafluoride and trimethylsilyl methyl sulphide were studied in prefluorinated FEP tubes. In a typical reaction,  $5 \times 10^{-4}$  mole of uranium hexafluoride was condensed onto a known quantity of the silyl which had been dried over molecular sieves and stored under vacuo. Reactions started at the melting point of trimethylsilyl methyl sulphide, when a green colouration developed at the interface between the reactants. The colouration continued to develop as the reaction mixtures warmed to room temperature, whereupon, green solids were deposited with the simultaneous evolution of a white gas. The IR spectra of the volatiles was found to be independent of the reactant stoichiometry; a typical spectrum is shown in Fig. 4.5, which shows the presence of trimethylsilyl fluoride and methyl fluoride. The solid products were isolated by vacuum distillation, and were analysed using X-ray powder photography, vibrational and mass spectroscopy. Mass spectra of the solids showed the fragmentation pattern of elemental sulphur, but no peaks assignable to uranium fluorides were obtained, presumably due to their high molecular weights and melting points. Vibrational data of the solid products are shown in Table 4.9 along with the literature data for uranium tetrafluoride, uranium pentafluoride and sulphur. Comparison of the X-ray powder diffraction



**FIGURE 4.5** [Table 4.7]

The infrared spectrum of the volatile products isolated from interactions between UF<sub>6</sub> and Me<sub>3</sub>SiSMe.

TABLE 4.7

Infrared stretching frequencies ( $\text{cm}^{-1}$ ) of the volatile products formed during the reduction of  $\text{UF}_6$  by  $\text{Me}_3\text{SiSMe}$

<u>Observed</u>	<u>MeF [354]</u>	<u>Me<sub>3</sub>SiF [355]</u>
3000sh	3005 $\nu_4$ ; (C-H) str.	
2970m	2964 $\nu_1$ ; (C-H) str.	2968 $\nu_{\text{asym}}$ (C-H) str.
2910w		2907 $\nu_{\text{sym}}$ (C-H) str.
	1475 $\nu_2$ } (C-H) deform.	
	1471 $\nu_5$ }	
1445mbr		1450
		1425
		1415
1274sh		
1260s		1264 PQR
1200w	1195 $\nu_6$ ( $\text{CH}_3$ ) rock.	
1050m	1048 $\nu_3$ (C-F) str.	
912vs		912 $\nu(\text{Si-F})$ str.
900sh		
860s		858
760s		760

TABLE 4.8

Indexed X-ray powder diffraction pattern for  $\beta\text{-UF}_5$

<u>hkl</u>	<u><math>\sin^2\theta</math></u>	<u>d-values</u>	<u>I/I<sub>0</sub></u>
200	0.01850	5.6682	5
101	0.02706	4.6777	25
220	0.03678	4.0198	10
211	0.04517	3.6272	100
310	0.04567	3.6074	50
321	0.08162	2.6984	25
420	0.09124	2.5522	5
112	0.09770	2.4663	10
411	0.09968	2.4417	35
202	0.10657	2.3615	35
501, 431	0.1358	2.0916	40
440	0.1456	2.0206	5
521, 530	0.1543	1.9628	75
402	0.1609	1.9219	15
600	0.1639	1.9044	10
332	0.17055	1.8667	35
422, 620	0.18179	1.8081	10
611	0.1899	1.7691	15

TABLE 4.9

Raman spectra of the solid products isolated from interactions between UF<sub>6</sub> and Me<sub>3</sub>SiSMe

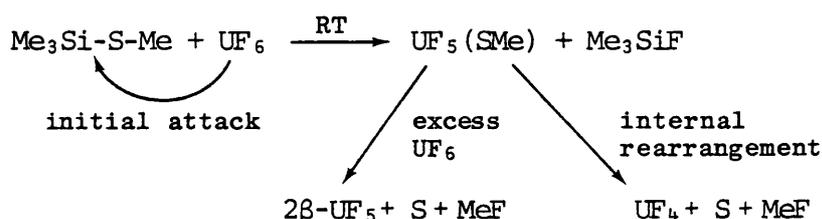
<u>UF<sub>4</sub> [356, 357]</u>	<u>β-UF<sub>5</sub> [20, 358]</u>	<u>S<sub>8</sub> [359, 360]</u>	<u>Me<sub>3</sub>SiSMe:UF<sub>6</sub> ratio</u> (1:1) <u>UF<sub>4</sub>/S</u>	<u>(1:2)</u> <u>β-UF<sub>5</sub>/S</u>
614s	623s		615s	622s
	610s	475 474 471 437	472m, br	612s
430m, br 340m	280m	248 243 218 191	430m, br ~340m, br	476m
180sh		152 86	224w 180m, br 148m	283m- 150m

patterns of the products with those of pure samples of uranium tetra- and pentafluorides (Tables 4.5 and 4.8) confirmed their identifications. The results are summarised below:-

<u>UF<sub>6</sub>:Me<sub>3</sub>SiSMe Ratio</u>	<u>Colour of Solid Product</u>	<u>Products of the Reaction</u>
2:1	pale green	β-UF <sub>5</sub> , Me <sub>3</sub> SiF, S, MeF
	$2\text{UF}_6 + \text{Me}_3\text{SiSMe} \longrightarrow$	$2\beta\text{-UF}_5 + \text{Me}_3\text{SiF} + \text{S} + \text{MeF}$
1:1	green	UF <sub>4</sub> , Me <sub>3</sub> SiF, S, MeF
	$\text{UF}_6 + \text{Me}_3\text{SiSMe} \longrightarrow$	$\text{UF}_4 + \text{Me}_3\text{SiF} + \text{S} + \text{MeF}$

### Discussion

The reactions between the two molar ratios of the reactants proceeded in the same manner, even though the ultimate products were not the same.



Presumably uranium hexafluoride initially attacks the Si-S bond, the weakest link in the trimethylsilyl methyl sulphide molecule, forming trimethylsilyl fluoride and an unstable uranium methyl sulphide fluoride intermediate, UF<sub>5</sub>.SMe. The reactant stoichiometry appears to determine how the intermediate behaves. If an excess of uranium hexafluoride is present, then it will attack UF<sub>5</sub>.SMe forming uranium pentafluoride, methyl fluoride and elemental sulphur. The UF<sub>5</sub>.SMe itself can undergo rearrangement when no excess of uranium hexafluoride is present with the evolution of methyl fluoride, leaving behind uranium tetrafluoride and elemental sulphur.

There are no reports of any uranium-fluorine species which contain a uranium-sulphur bond; which may explain why uranium fluorides and

sulphur are formed from the decomposition of  $UF_5 \cdot 5Me$  instead of uranium thiotetrafluoride. The thermodynamic stabilities of uranium thiofluorides are discussed in the next chapter. The data indicates that they are unstable with respect to decomposition into lower uranium fluorides and elemental sulphur.

#### 4.4.2 Uranium Hexafluoride with Trimethylsilyl Methyl Sulphide in Acetonitrile

##### Summary

Reactions involving both 1:1 and 2:1 molar ratios of uranium hexafluoride to trimethylsilyl methyl sulphide in dry acetonitrile yielded green solids of composition,  $UF_4 \cdot MeCN$ .

The reaction between uranium hexafluoride and trimethylsilyl methyl sulphide was repeated using anhydrous acetonitrile as the solvent. All reactions were carried out in prefluorinated FEP tubes fitted with ChemCon valves. Uranium hexafluoride was condensed onto a solution of trimethylsilyl methyl sulphide in acetonitrile at  $-196^\circ C$  and left to warm to room temperature. A reaction was observed to take place at the melting point of the solvent, with the formation of a green colloidal material.

Trimethylsilyl fluoride was observed in the IR spectra of the volatile products along with bands assignable to the solvent; no vibrational bands were observed associated with methyl fluoride. Green solids were isolated by vacuum distillation. Infrared spectra of the solid products were found to be independent of the reactant stoichiometry; a typical spectrum is shown in Table 4.10 along with the literature data for uranium tetrafluoride and acetonitrile. It can be seen from a comparison of the spectra that the solid product contains co-ordinated acetonitrile (Chapter 3). However, it is interesting to

TABLE 4.10

The infrared spectrum of UF<sub>4</sub>.MeCN compared with those of UF<sub>4</sub> and MeCN

<u>UF<sub>4</sub>.MeCN</u>	<u>MeCN [316,317]</u>	<u>UF<sub>4</sub> [361]</u>	<u>Assignment</u>
2960 w			(C-H) str. $\nu_5$
	2297		comb. ( $\nu_3+\nu_4$ )
2340 m+	2257		(C≡N) str. $\nu_2$
	2208		comb. ( $2\nu_4+\nu_8$ )
1620 vw			
1420 } 1370 } br,m	1376		} CH <sub>3</sub> def. $\nu_3$
1255 vw			
1090 w			
1035 m	1040		CH <sub>3</sub> rock; $\nu_7$
950 s	920		(C-C) str; $\nu_4$
850 w			
754 m-	750		
630 w,br		620 w,br	} (U-F) str.
450 s,sh		400 s,br	
420 vs,br		340 s,br	
	380		(C-CN) def; $\nu_8$

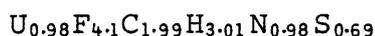
Chemical Analysis

	U	F	C	H	N	S
(%)						
UF <sub>4</sub> .MeCN (found)	62.39	20.84	6.39	0.81	3.67	5.91
(calculated)	67.03	21.40	6.77	0.85	3.94	-

note that the band at  $955\text{ cm}^{-1}$  associated with  $\nu(\text{C-C})$  of co-ordinated acetonitrile is very strong. Initially it was thought that this band was due to some form of hydrolysis, but other workers [319] have noted such intense absorptions in this region for  $\text{UF}_5 \cdot \text{MeCN}$  and  $\text{UF}_5 \cdot n\text{MeCN}$ ; Table 4.11. The strong band centred around  $400\text{ cm}^{-1}$ ,  $\nu(\text{U-F})$ , obscures any bands associated with any elemental sulphur which may be present.

Mass spectra of the solid products showed the presence of acetonitrile and elemental sulphur, but no peaks assignable to uranium tetrafluoride were observed, presumably due to its lack of volatility. The green solids were amorphous to X-rays.

Chemical analysis of the green product is shown in Table 4.9 from which the following empirical formula was obtained:-



which can be rewritten as  $\text{UF}_4 \cdot \text{MeCN} + \text{S}$ .

### Discussion

Presumably a similar mechanism occurs for this reaction as the one described earlier for the direct reaction between uranium hexafluoride and trimethylsilyl methyl sulphide. In this case, the situation is further complicated by the presence of acetonitrile. Again, the uranium hexafluoride presumably initially attacks the Si-S bond in the silyl group, with the evolution of trimethylsilyl fluoride and the formation of an intermediate,  $\text{UF}_5 \cdot \text{SMe}$ . Decomposition of the intermediate occurs rapidly forming  $\text{UF}_4 \cdot \text{MeCN}$ , methyl fluoride and elemental sulphur. Surprisingly, no uranium pentafluoride acetonitrile adducts were formed when an excess of uranium hexafluoride was present, which suggests that the solvent is involved in the mechanism of the decomposition of the intermediate. Assuming that methyl fluoride is formed, even though its presence was not detected, the overall reaction

TABLE 4.11

The infrared spectrum of UF<sub>4</sub>.MeCN compared  
with those of UF<sub>5</sub>.MeCN and UF<sub>5</sub>.nMeCN

<u>UF<sub>4</sub>.MeCN</u>	<u>UF<sub>5</sub>.MeCN [319]</u>	<u>UF<sub>5</sub>.nMeCN [319]</u>
2960 w		
2340 m+	2330 vs	2327 vs
	2320 vs	2321 vs
		2302 vs
		2291 vs
		2265 sh,w
		2245 w
1600 vw		
1420 m,br		
1370 m,br		
1255 vw		
1090 w	1114 w	1110 w
1035 m	1034 s	1030 m
950 s	967 vs	961 vs
		942 sh
850 w		
754 m-	730 m	783 w
		715 m
630 w,br		
	597 s	
	580 s	
		546 s
		525 s
		513 s
		500 s
450 sh,s		
420 vs,br		
	384 m	388 s,br

between uranium hexafluoride and trimethylsilyl methyl sulphide can be represented by the following equation:-



#### 4.4.3 Interactions between Tungsten Hexafluoride with Trimethylsilyl Methyl Sulphide

##### Introduction

To date tungsten thiotetrafluoride has only been synthesised from tungsten hexafluoride at elevated temperatures. It was hoped that interactions between tungsten hexafluoride and trimethylsilyl methyl sulphide would lead to a clean, simple, low temperature method the preparation of tungsten thiotetrafluoride via the thermal decomposition of the presumably formed initial product;  $\text{WF}_5 \cdot \text{SMe}$ , cf.  $\text{MoCl}_5(\text{SR})$ .

##### Interactions between Equimolar Quantities of Tungsten Hexafluoride and Trimethylsilyl Methyl Sulphide

In a typical reaction about  $5 \times 10^{-4}$  mole of tungsten hexafluoride was condensed onto an equimolar quantity of trimethylsilyl methyl sulphide in a prefluorinated FEP tube at  $-196^\circ\text{C}$ . The reactants were allowed to warm to room temperature with constant mixing. Rapid reactions occurred at ambient temperatures, with the deposition of a brown solid. Trimethylsilyl fluoride was identified as the only volatile product by IR spectroscopy. The vibrational data of the brown product from these reactions is given in Table 4.12, along with the published spectra of both tungsten thiotetrafluoride [179] and methyl fluoride [354]. Comparison of the spectra clearly suggests that the brown solid product contains terminal and bridging tungsten-fluorines and a methyl group. Mass spectra of the solid showed the presence of both  $\text{WF}_5^+$  and  $\text{SMe}^+$  ions; however, the assumed parent ion,  $\text{WF}_5\text{SMe}^+$ , was not observed.

TABLE 4.12 [Fig. 4.6]

The infrared spectrum of the brown product isolated from reactions between equimolar quantities of  $WF_6$  and  $Me_3SiSMe$  compared with those of  $WSF_4$  and  $MeF$

<u>Brown Product</u>	<u><math>WSF_4</math></u>	<u>MeF [354]</u>
		3005
2940 w		2964
		1475
		1471
1415 w		
1300 m		
		1195
		1048
1010 m		
948 m		
880 w+		
855 w+		
	720 sh	
	700 s	
690 m	690 sh	
	670 s	
	655 sh	
645 s	645 vs	
620 m+	625 sh	
590 s		
575 sh	575 m	
	560 sh	
515 s		
	535 s	
	515 s	
455 m+		

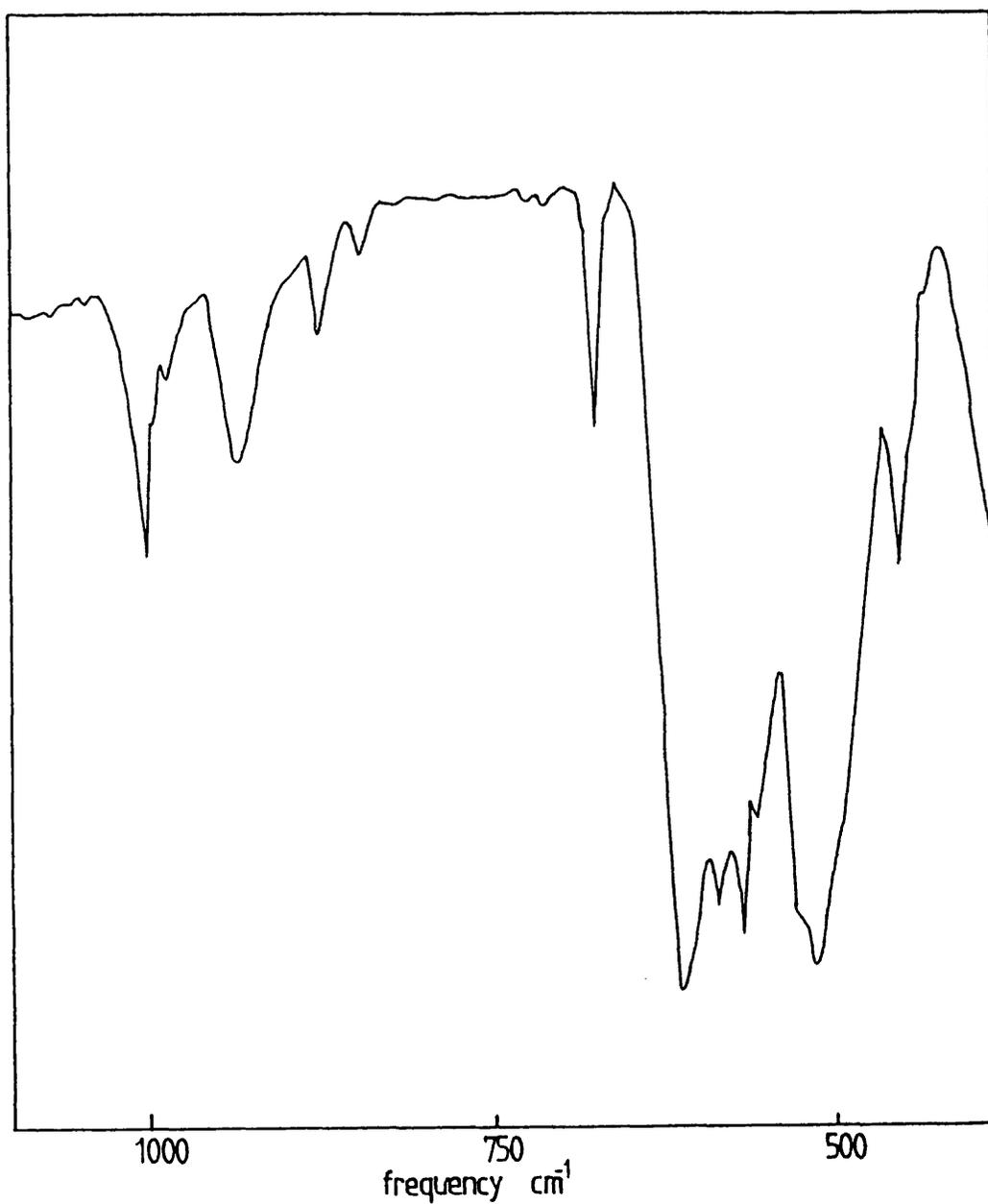


FIGURE 4.6

The infrared spectrum of the solid brown product obtained from reactions between equimolar quantities of  $\text{WF}_6$  and  $\text{Me}_3\text{SiSMe}$ .

Even though the above reaction was not fully characterised, the available data suggests that the products are  $WF_5 \cdot SMe$  and trimethylsilyl fluoride. Since the solid product was insoluble in acetonitrile, Genetron, carbon tetrachloride and tungsten hexafluoride further analysis by  $^{19}F$  nmr and esr spectroscopy was impossible. Attempts to thermally decompose the presumably formed  $WF_5 \cdot SMe$  to tungsten thio-tetrafluoride were unsuccessful.

#### Tungsten Hexafluoride with Trimethylsilyl Methyl Sulphide

In a final attempt to characterise the interaction between tungsten hexafluoride and trimethylsilyl methyl sulphide, the reaction was repeated in anhydrous acetonitrile and was followed by  $^{19}F$  nmr spectroscopy. The spectra obtained were found to be dependent upon the reactant stoichiometry (Figs. 4.7 and 4.8). When an excess of trimethylsilyl methyl sulphide was present, a complex spectrum was obtained, which is similar in many respects to that reported by Kokunov et al. [158] from interactions between tungsten hexafluoride and methyl sulphide in acetonitrile. The three singlets at -83.2, -58.6 and +158.1 ppm (relative to  $CFCl_3$ ) were assigned to  $WSF_4$ ,  $WF_4(SMe)_2$  and  $Me_3SiF$  respectively by comparison with previously reported data [158,179,363], while the intense  $A_4X$  spectrum (a doublet and a *quintet*) suggests that  $WF_5 \cdot SMe$  is the principal product. A much simpler spectrum was obtained when an excess of the hexafluoride was present (Fig. 4.8), with signals assignable to  $WF_6$ ,  $WF_5 \cdot SMe$  and  $Me_3SiF$ ; Table 4.13.

#### Discussion

The principal products from the reaction of tungsten hexafluoride with trimethylsilyl methyl sulphide are the monosubstituted mercapto-fluoride complex,  $WF_5 \cdot SMe$  as a result of the cleavage of the Si-S bond

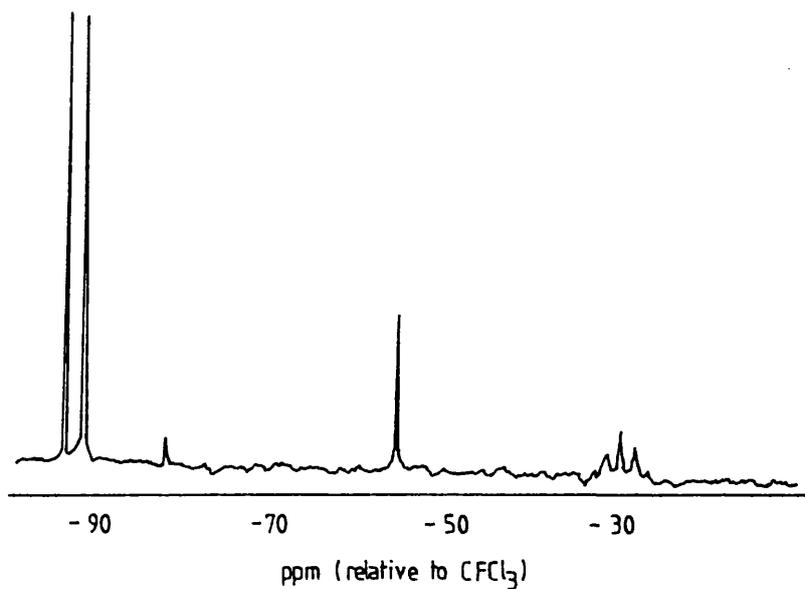


FIGURE 4.7

$^{19}\text{F}$  nmr spectrum obtained from interactions between an excess of  $\text{Me}_3\text{SiSMe}$  and  $\text{WF}_6$  in MeCN recorded at  $0^\circ\text{C}$ .

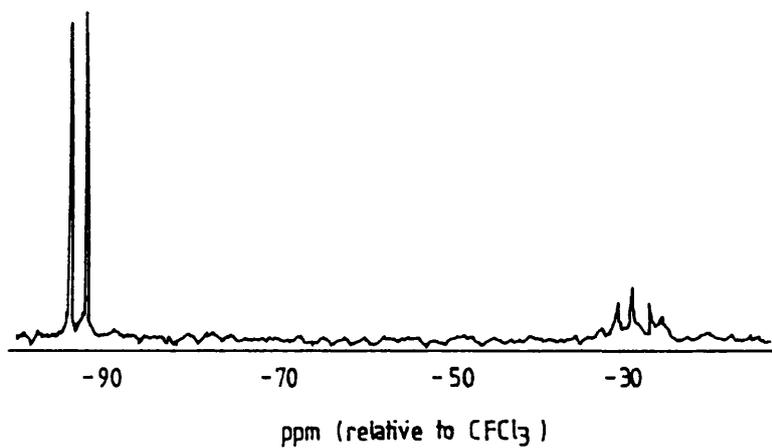


FIGURE 4.8

$^{19}\text{F}$  nmr spectrum obtained from interactions between an excess of  $\text{WF}_6$  and  $\text{Me}_3\text{SiSMe}$  in MeCN recorded at  $0^\circ\text{C}$ .

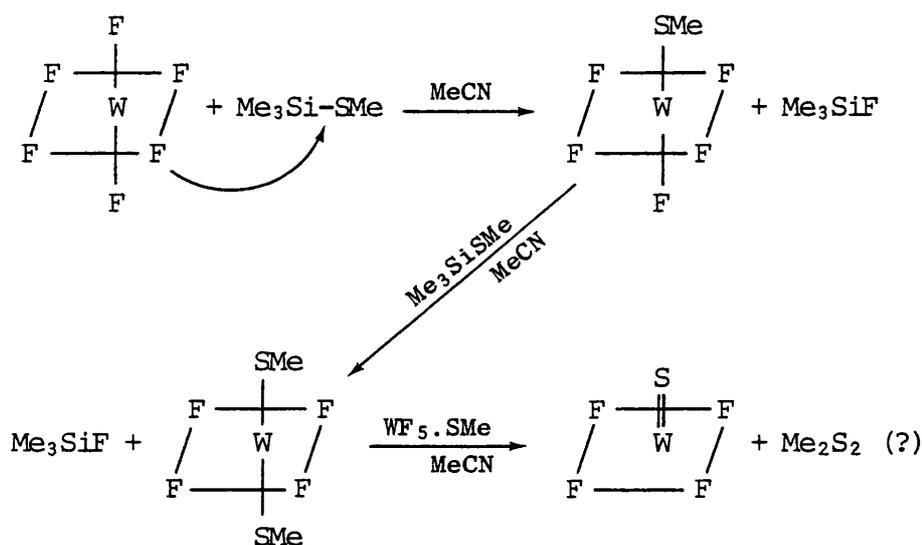
TABLE 4.13

<sup>19</sup>F Nmr parameters for WF<sub>5</sub>(SMe) and WF<sub>4</sub>(SMe)<sub>2</sub>

<u>Sample</u>	<u>Solvent</u>	<u>δ/ppm</u>	<u>Multiplet Structure</u>	<u>Coupling Constant</u>	<u>Assignment</u>	<u>Ref.</u>
WF <sub>6</sub> + Me <sub>3</sub> SiSMe (XS)	MeCN	-98.4	II	} JW-F = 37±4 Hz	WF <sub>5</sub> SMe	
		-38.0	V		WSF <sub>4</sub>	
		-83.2	I	WF <sub>4</sub> (SMe) <sub>2</sub>		
		-58.6	I	Me <sub>3</sub> SiF		
		+158.1	I			
WF <sub>6</sub> + Me <sub>3</sub> SiSMe (XS)	MeCN	-168.7	I	} JW-F = 44±4 Hz	WF <sub>6</sub>	
		-96.8	II		WF <sub>5</sub> (SMe)	
		-37.2	V			
		-156.7	I	Me <sub>3</sub> SiF		
WSF <sub>4</sub>	MeCN	-85.1	I		WSF <sub>4</sub>	179
WF <sub>6</sub> + Me <sub>2</sub> S <sub>2</sub>	MeCN	-96.5	II	} JW-F = 39 Hz	WF <sub>5</sub> (SMe)	158
		-35.4	V		WF <sub>4</sub> (SMe) <sub>2</sub>	
		-57.5	I			
WF <sub>6</sub>	MeCN	-165.2	I	JW-F = 48 Hz	WF <sub>6</sub>	362
Me <sub>3</sub> SiF	MeCN	+155.5	I	JH-F = 7 Hz	Me <sub>3</sub> SiF	363

(XS) = excess

in the silyl molecule and trimethylsilyl fluoride. When there is an excess of the silyl in the system both the mono- and bi-substituted mercaptofluoride complexes are formed. The small quantities of tungsten thiotetrafluoride formed is presumably a result of the interaction between the mono- and bi-substituted complexes (reaction scheme, Fig. 4.9).



**FIGURE 4.9**

The proposed reaction scheme for the interactions between  $\text{WF}_6$  and  $\text{Me}_3\text{SiSMe}$  in MeCN.

#### 4.4.4 Interactions between Uranium Hexafluoride and Bis-Trimethylsilyl Sulphide

##### Summary

Reactions involving 1:2 and 2:1 molar ratios of uranium hexafluoride to bis-trimethylsilyl sulphide both yielded uranium tetrafluoride and elemental sulphur; in the latter case uranium pentafluoride is also formed.

The reactions between uranium hexafluoride and bis-trimethylsilyl sulphide were studied in prefluorinated FEP tubes fitted with ChemCon

valves. Uranium hexafluoride was condensed onto a known quantity of bis-trimethylsilyl sulphide,  $\text{Me}_3\text{SiSSiMe}_3$ , and the systems were allowed to warm to room temperature. Reactions started at the melting point of the silyl when a green colouration began to develop at the interface between the reactants. This colouration continued to develop, until the mixtures reached room temperature when green solids were deposited.

Infrared spectra of the volatile products showed only the presence of trimethylsilyl fluoride and unreacted uranium hexafluoride (when an excess of this reactant was used). Green non-volatile solids were isolated by vacuum distillation and were characterised by X-ray powder photography, vibrational and mass spectroscopy.

Mass spectra of the solid products revealed only the presence of elemental sulphur. The vibrational spectra of the products are shown in Table 4.14 and clearly show that uranium tetrafluoride is formed irrespective of the reactant stoichiometry. Comparison of the X-ray powder diffraction patterns of the solid products isolated from reactions involving a 2:1 excess of bis-trimethylsilyl sulphide with those of pure samples of uranium penta- and tetrafluorides confirmed the presence of uranium tetrafluoride. However, the solid products isolated from reactions using a 2:1 molar excess of uranium hexafluoride were semi-amorphous to X-rays and the powder photographs obtained were of such poor quality that no such comparisons could be made. Anhydrous acetonitrile was condensed onto a known quantity of this product. Approximately 22-24% of the solid mixture was taken into solution. Uranium tetrafluoride and elemental sulphur are both insoluble in acetonitrile while uranium pentafluoride is highly soluble. Thus the observation of some solid going into solution suggests the presence of  $\beta$ -uranium pentafluoride, which was confirmed by the observation of peaks

TABLE 4.14

Raman spectra of the solid products isolated from interactions between UF<sub>6</sub> and (Me<sub>3</sub>Si)<sub>2</sub>S

<u>UF<sub>4</sub> [356,357]</u>	<u>β-UF<sub>5</sub> [20,358]</u>	<u>S<sub>β</sub> [359,360]</u>	<u>UF<sub>6</sub> : (Me<sub>3</sub>Si)<sub>2</sub>S ratio</u>	
			<u>(2:1)</u>	<u>(1:2)</u>
614 s	623 s		625 sh 615 s 608 sh	612 s
430 m,br 340 m		475 474 471 437	470 m,br ~435 m,br ~340 m,br 277 m-	473 m,br 425 m,br 338 m
180 sh	280 m	248 243 218 191	238 w	224 w-
		152 86	154 m,br	148 m

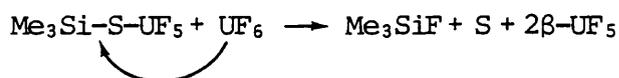
at 625, 610 and 280  $\text{cm}^{-1}$  in the Raman spectrum of the solid material in addition to vibrational bands associated with both uranium tetrafluoride and elemental sulphur.

### Discussion

Uranium hexafluoride presumably attacks one of the Si-S bonds in the bis-trimethylsilyl sulphide molecule releasing trimethylsilyl fluoride, with the formation of an intermediate;  $\text{Me}_3\text{Si-S-UF}_5$ . Since uranium tetrafluoride and elemental sulphur are the predominant products, it suggests that the intermediate has a very short lifetime and rapidly decomposes:-



When an excess of uranium hexafluoride is present, it can attack the intermediate with the formation of  $\beta$ -uranium pentafluoride:-



However, that fact that only 22-24% of the solid product contains  $\beta$ -uranium pentafluoride when a 2:1 molar excess of uranium hexafluoride was used suggests that either the intermediate is very unstable with respect to decomposition or that the reduction of uranium hexafluoride to the tetrafluoride occurs directly without proceeding via an intermediate with the simultaneous release of two molecules of trimethylsilyl fluoride.

❧

CHAPTER  
5

Thermochemistry of  $\text{MF}_6$ ,  $\text{MCl}_n\text{F}_{6-n}$ ,  
 $\text{MO}_n\text{F}_{6-2n}$  and  $\text{MS}_n\text{F}_{6-2n}$  ( $M = \text{U, Mo, W}$ )

## 5.1 INTRODUCTION

The chemistry of the hexafluorides would probably have remained in relative obscurity except for the discovery of uranium fission in 1939, which promoted uranium hexafluoride to a position of high industrial importance. Hexafluorides display a full range of chemical behaviour from complete inertness to extraordinary reactivity. Sulphur, tellurium and selenium hexafluorides are noted for their inertness. In contrast, the metal hexafluorides are among the most reactive of species and include amongst them some of the most powerful known oxidative fluorinating agents.

Striking similarities occur between the second and third row transition metal hexafluorides. The first member of each series is thermodynamically stable with respect to dissociation, but the terminal member is markedly unstable, Fig. 5.1. Weinstock [3] showed that a relationship also exists between chemical reactivity and vapour pressure of the metal hexafluorides, Fig. 5.2. In both series, the first member has the highest vapour pressure and is thermally and chemically the most stable. Vapour pressure, chemical and thermal stabilities of the metal hexafluorides decrease going from left to right along the periodic series. Among the transition series, the 5d group is the most stable and these hexafluorides are much more stable and volatile than their opposite numbers in the 4d and 5f series.

## 5.2 BOND STRENGTHS FROM VIBRATIONAL SPECTROSCOPY

The infrared and Raman spectra of all the metal hexafluorides have been recorded in the vapour phase and have been interpreted on the basis of octahedral symmetry. Bearing in mind that Jahn-Teller distortions are apparent in several of the compounds, the  $A_{1g}(\nu_1)$  mode

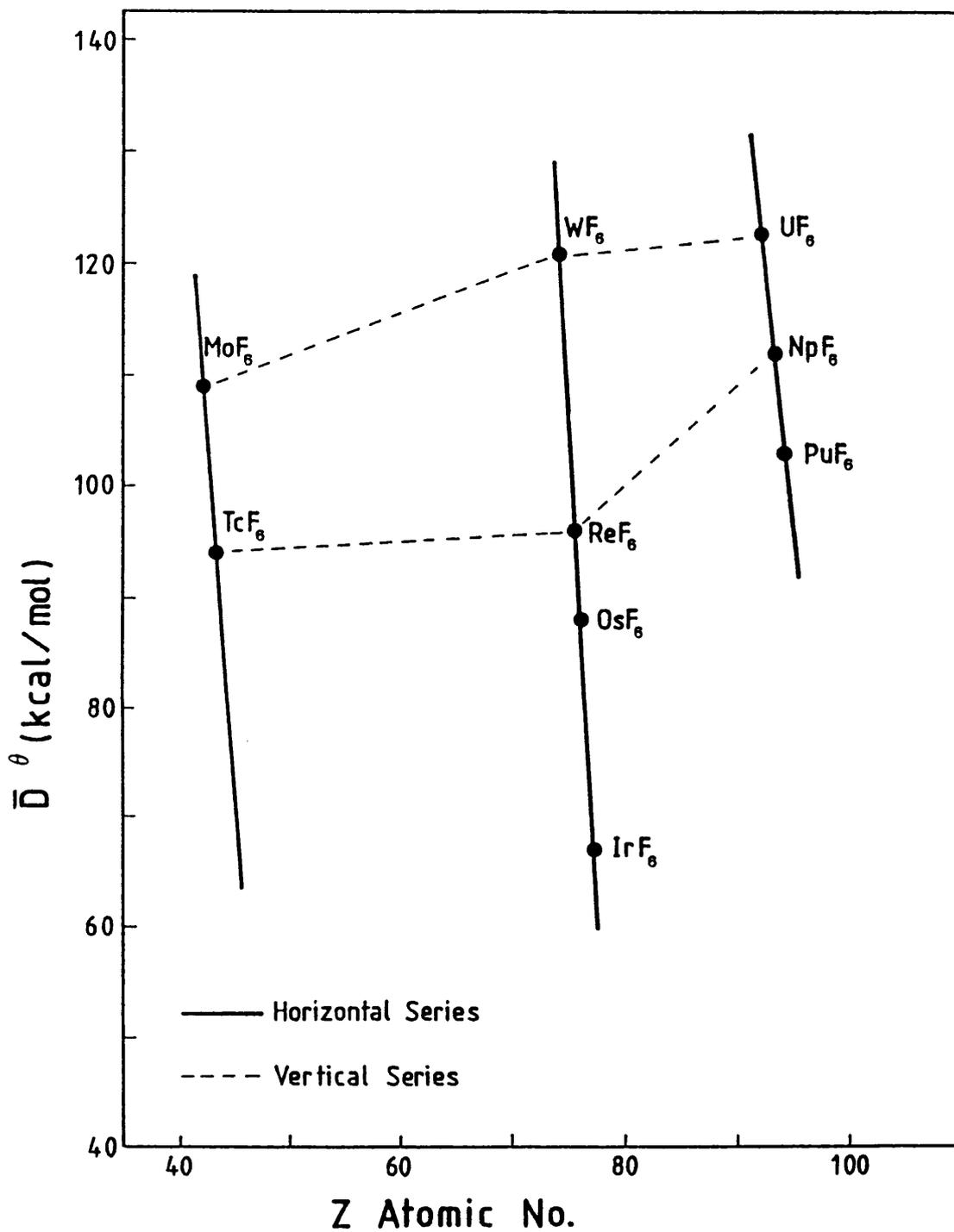


FIGURE 5.1

Variation of the average bond energies ( $\bar{D}^\theta$ , kcal/mol) of  $MF_6$  molecules with the atomic number of the element M in the vertical and horizontal series of the hexafluorides.

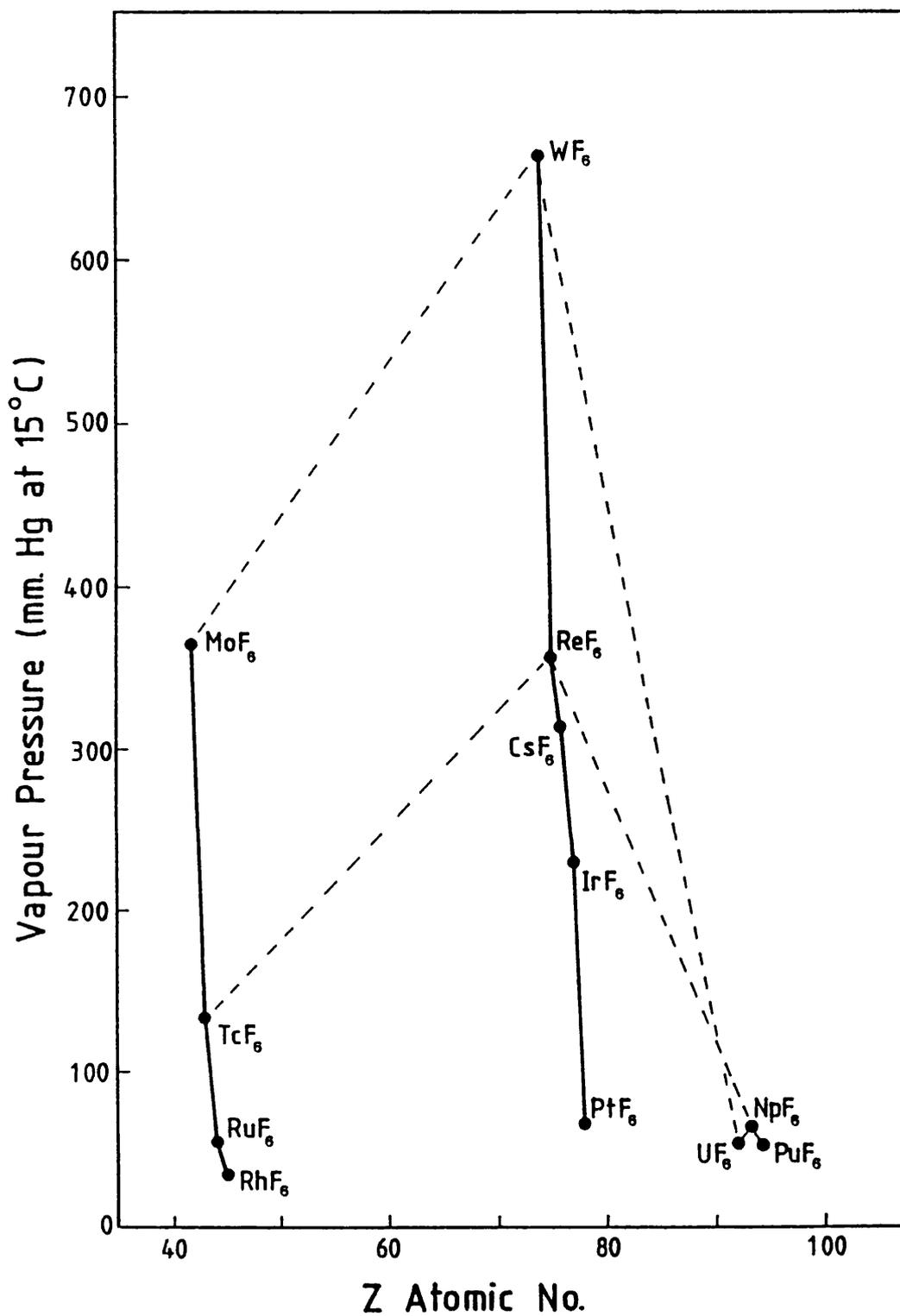


FIGURE 5.2

Variation of the vapour pressure (mmHg; 15°C) of MF<sub>6</sub> molecules with the atomic number of the element M in the vertical and horizontal series of the hexafluorides.

mode is the completely symmetrical vibration and may be taken as the frequency most likely to provide a measure of the bond strength, since the vibration does not change the symmetry of the molecule, nor does it involve movement of the heavy central atom. It is clear that the  $A_{1g}$  frequency and hence the bond strength drops markedly with an increase in  $Z$  (atomic number) in each transition series, Fig. 5.3. This sequence fits exactly with the known chemical reactivity of the hexafluorides.

### 5.3 AVERAGE BOND DISSOCIATION ENERGIES

The average bond energy,  $\bar{D}^\ominus$  of  $MF_n$  molecules can be defined by the formula:-

$$\bar{D}^\ominus = \frac{E^\ominus}{n} \quad \dots [5.1]$$

where  $n$  is the number of bonds, and  $E^\ominus$  is the heat of atomisation of the molecule which can be evaluated from the enthalpy change associated with reaction [5.2] using equation [5.3]



$$\bar{D}^\ominus = \frac{1}{n} \Delta H_f^\ominus [M(g)] + n\Delta H_f^\ominus [F(g)] - \Delta H_f^\ominus [MF_n(g)] \quad \dots [5.3]$$

The values of  $\bar{D}^\ominus$  are not known for all hexafluorides and the accuracy of the calculation or estimation of others is low. For example, one may mention the discrepancy between the data of different workers for the heat of formation of gaseous plutonium hexafluoride: -460 kcal/mol [364], -473 kcal/mol [365], -411.2 kcal/mol [366], and -418±8 kcal/mol [367]. The last value was recommended by Rand [367] as the most accurate.

Analysis of the average bond energies in Table 5.1 shows that the bond energies decrease in the horizontal series from left to right.

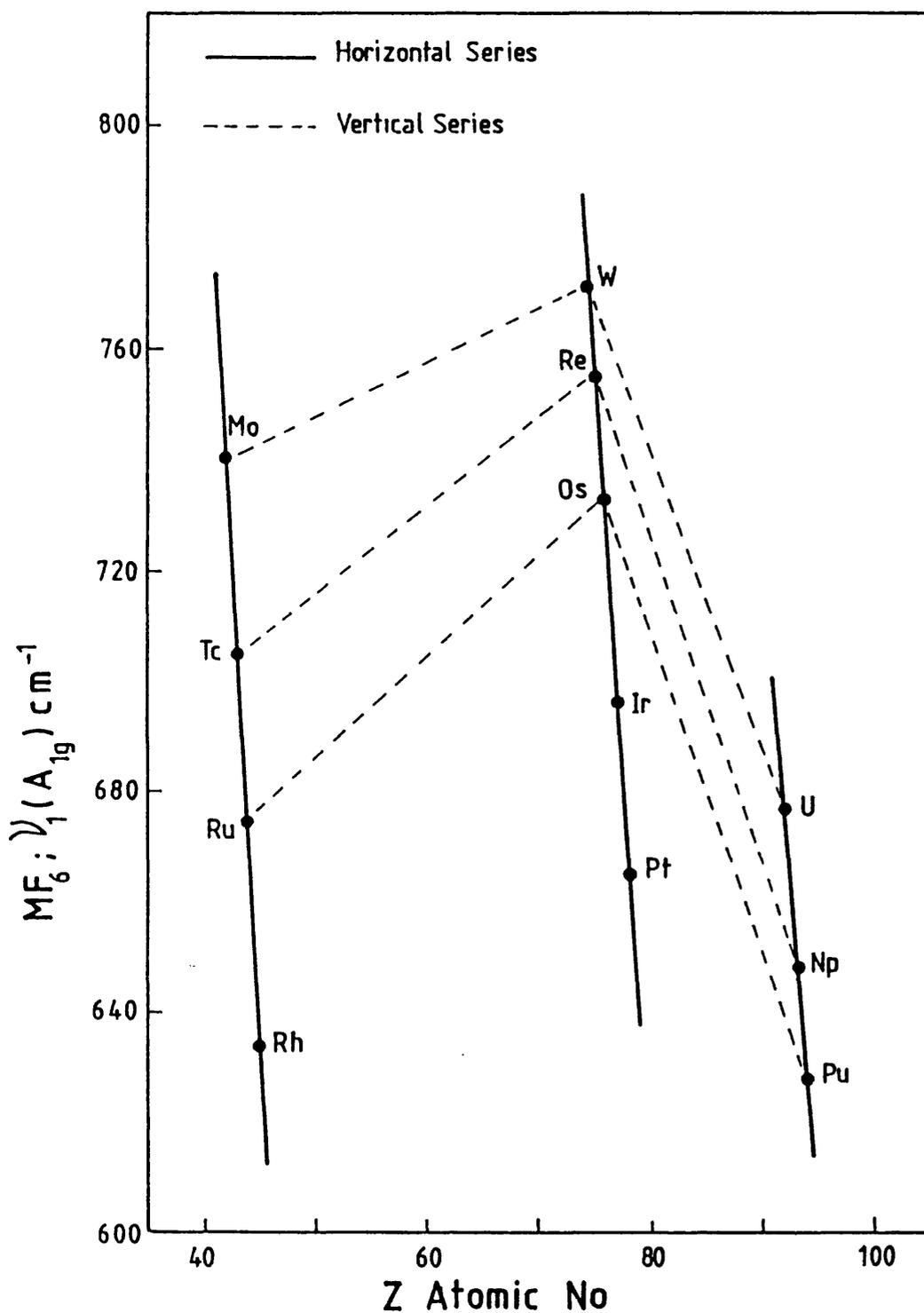


FIGURE 5.3

Variation of  $\nu_1(A_{1g})$  ( $\text{cm}^{-1}$ ) of  $\text{MF}_6$  molecules with the atomic number of the element M in the vertical and horizontal series of the hexafluorides.

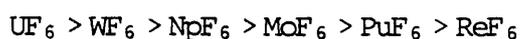
TABLE 5.1

Heats of formation, vapour pressure and average bond energies of metal hexafluorides

Metal Hexafluorides MF <sub>6</sub>	Atomic No. of M	Enthalpy of atomisation of M [368] kcal/mol	Vapour Pressure mmHg (15°C) [3]	$\Delta H_f^\ominus$ [MF <sub>6</sub> (g)] kcal/mol	$\bar{D}^\ominus$ (M <sup>VI</sup> -F) Average Bond Energy kcal/mol
MoF <sub>6</sub>	42	157.3 ± 0.3	361	-372.3 [369]	107.2
TcF <sub>6</sub>	43		135	-300 [364]	94.7 [373]
RuF <sub>6</sub>	44	155.5 ± 1.5	58		
RhF <sub>6</sub>	45	133 ± 1	38		
WF <sub>6</sub>	74	203 ± 1	698	-411.5 [370]	121.4
ReF <sub>6</sub>	75	185 ± 1.5	358	-322.6 [371]	103.6
OsF <sub>6</sub>	76	188 ± 1.5	312	-225 [364]	87.8
IrF <sub>6</sub>	77	160 ± 1	227	-130 [364]	67.3
PtF <sub>6</sub>	78	135.2 ± 0.3	66		
UF <sub>6</sub>	92	126 ± 3	56	-513.49 [372]	125.6
NpF <sub>6</sub>	93		64	-461 [364]	
PuF <sub>6</sub>	94	87.1 ± 4	53	-418 [367]	103.2

In the vertical series the average bond energy increases in the series of hexafluorides of 4d, 5d and 5f elements, Fig. 5.1.

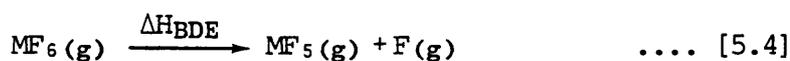
Thus if it is supposed that the average bond energy characterises the thermal stability and reactivity of the hexafluoride molecules, then the hexafluorides can be arranged in the following series in terms of decreasing thermal stability:



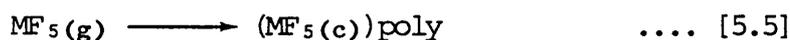
It is worth noting that the enthalpies of formation of the metal hexafluorides also exhibit a similar trend, except that the positions of  $\text{WF}_6$  and  $\text{NpF}_6$  are reversed, Fig. 5.4.

#### 5.4 BOND DISSOCIATION ENERGIES ( $\text{MF}_6$ ; M = U, Mo, W)

The first bond dissociation energy ( $\Delta\text{H}_{\text{BDE}}$ ) of metal hexafluorides is defined by the equation:-



However, since the  $\text{MF}_5$  molecules formed initially polymerise spontaneously:-



the effective first bond dissociation energy is obtained from a combination of equations [5.4] and [5.5].



A value of  $32 \pm 7$  kcal/mol has been calculated [10] for the first effective bond dissociation energy of uranium hexafluoride, this being the same order of magnitude as the bond energy of elemental fluorine (36.6 kcal/mol [374]), from the values  $68.4 \pm 3.5$  kcal/mol and  $-36.6 \pm 3$  kcal/mol [10] evaluated from the measured enthalpy changes associated with equations [5.5] and [5.6] respectively.

The first effective bond dissociation energies; FEBDE for molybdenum

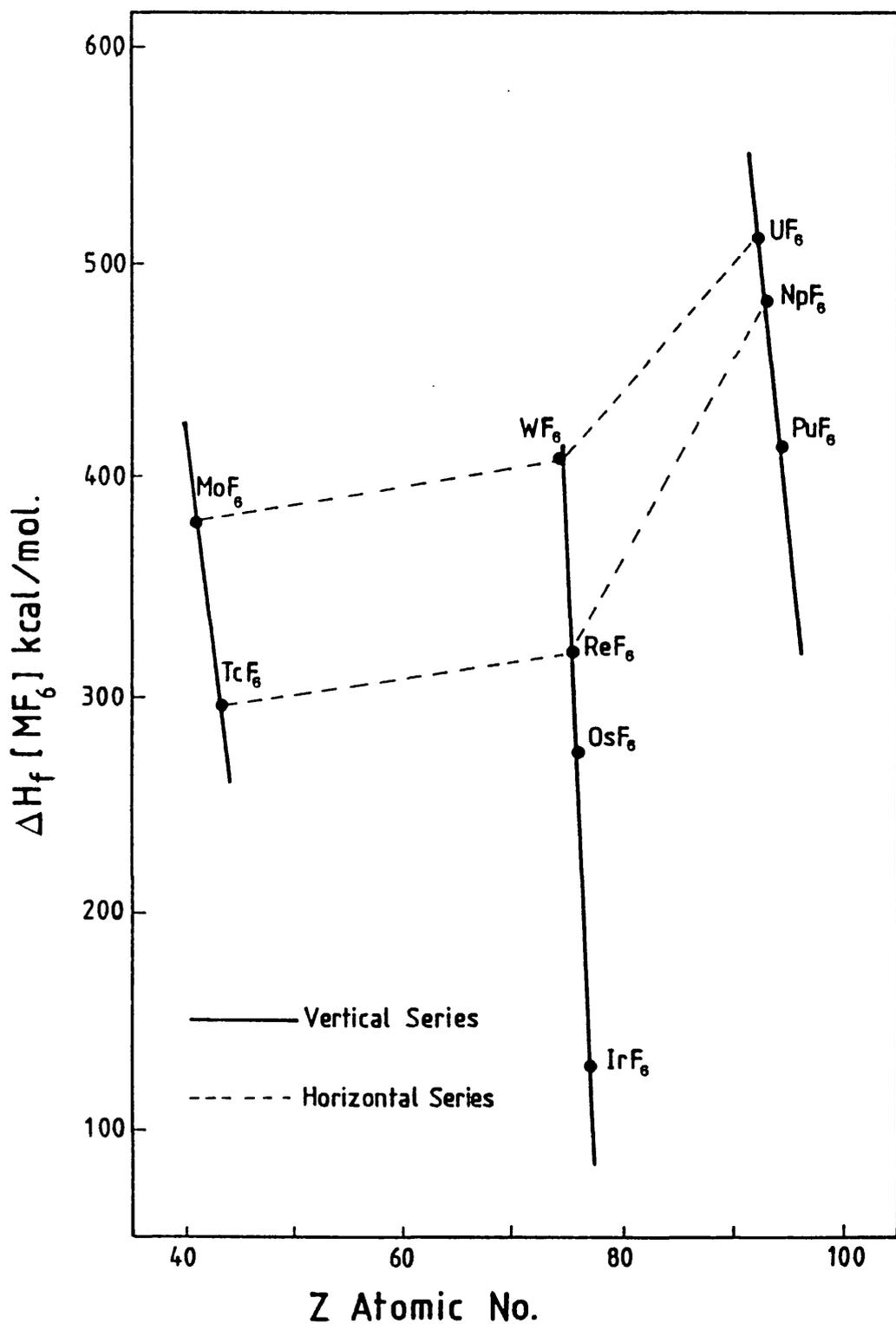


FIGURE 5.4

Variation of the enthalpies of formation ( $\Delta H_f^\ominus$ , kcal/mol) of  $MF_6$  molecules with the atomic number of the element M in the vertical and horizontal series of the hexafluorides.

TABLE 5.2

Standard enthalpies of formation ( $\Delta H_f^\ominus$  kcal/mol), average bond energies and partial dissociation energies of uranium, molybdenum and tungsten fluorides

M	$\Delta H_f^\ominus$ [MF <sub>6</sub> (g)]	$\bar{D}^\ominus$ (M <sup>VI</sup> -F)	$\Delta H_f^\ominus$ [MF <sub>5</sub> (s)]	$\Delta H_f^\ominus$ [MF <sub>5</sub> (g)]	$\bar{D}^\ominus$ (M <sup>V</sup> -F)	$\Delta H_f^\ominus$ [MF <sub>4</sub> (s)]	$\Delta H_f^\ominus$ [MF <sub>4</sub> (g)]	$\bar{D}^\ominus$ (M <sup>IV</sup> -F)	$\Delta H_{BDE}^\ominus$	$\Delta H_{RFBDE}^\ominus$	$\Delta H_{SBDE}^\ominus$	$\Delta H_{SRBDE}^\ominus$
U	-513.49±0.43 [372]	125.6±0.6	α -492.2±1.6 [378] β -497.9±1.5	-460.6±3.4 <sup>B</sup> [5]	136.3±1.4	-459±0.9 [379]	-377.8±0.6 <sup>B</sup> [5]	145±1	71.9±3.9	α 36.3±2.1 β 34.6±1.9	173.7±1.2	92.5±1.5
Mo	-372.3±0.2 [369]	107.2±0.2	-331.6±1.1 [6]	-296.4±0.6 <sup>B</sup> [380]	118.9±0.8	hatched	-228.1±2.0 <sup>B</sup> [380] -228.0±3.9 [381]	126.7±3.3	94.9±0.9	59.7±1.4	182.3±2.3 <sup>d</sup> 182.3±4.2 <sup>E</sup>	hatched
W	-411.5±0.4 [370]	121.4±0.3	-346.1 <sup>+2.6</sup> -1.0 [382]	-309.1±2.0 <sup>B</sup> [8]	121.4±2.8	-292 <sup>b</sup>	-237±5 <sup>C</sup> [383] -222.0±2.5 <sup>B</sup> [18]	129.0±6.3	121.4±2.5	84.4±3.1	212.5±5.5 <sup>f</sup> 227.5±2.9 <sup>g</sup>	~158

<sup>a</sup> estimated from mass spectroscopy; <sup>b</sup> see text; <sup>c</sup> calculated from W-F reactions and systems using published thermodynamic data;  
<sup>d</sup> calculated using  $\Delta H_f^\ominus$  [MoF<sub>4</sub>(g)] = -228.1±2 kcal/mol; <sup>e</sup> calculated using  $\Delta H_f^\ominus$  [MoF<sub>4</sub>(g)] = -228.0±3.9 kcal/mol;  
<sup>f</sup> calculated using  $\Delta H_f^\ominus$  [WF<sub>4</sub>(g)] = -237±5 kcal/mol; <sup>g</sup> calculated using  $\Delta H_f^\ominus$  [WF<sub>4</sub>(g)] = -222±2.5 kcal/mol.

$\Delta H_{BDE}^\ominus$  (bond dissociation energy) is the enthalpy change associated with: MF<sub>6</sub>(g) → MF<sub>5</sub>(g) + F(g)  
 $\Delta H_{RFBDE}^\ominus$  (relative first bond dissociation energy) is the enthalpy change associated with: MF<sub>6</sub>(g) → MF<sub>5</sub>(c) + F(g)  
 $\Delta H_{SBDE}^\ominus$  (second bond dissociation energy) is the enthalpy change associated with: MF<sub>6</sub>(g) → MF<sub>4</sub>(g) + 2F(g)  
 $\Delta H_{SRBDE}^\ominus$  (second relative bond dissociation energy) is the enthalpy change associated with: MF<sub>6</sub>(g) → MF<sub>4</sub>(c) + 2F(g)

and tungsten hexafluorides cannot be evaluated since the enthalpies of polymerisation of the pentafluorides [equation 5.5] are unknown.

However, the enthalpies of polymerisation of gaseous antimony, niobium and tantalum pentafluorides:-



have been estimated by molecular weight measurements to be in the range -4 to -8 kcal/mol [375]. Presumably the values for molybdenum and tungsten pentafluorides will also be relatively small. Thus the relative first bond dissociation energies, RFBDE [Table 5.2] can be used to give a good indication of the FEBDE's for the hexafluorides of molybdenum and tungsten. This seems a fair assumption since there is good agreement between the FEBDE and the RFBDE [Table 5.2] for uranium hexafluoride.

The heats and free energies of formation of  $\text{WF}_2$ ,  $\text{WF}_4$  and  $\text{WF}_5$  have been estimated as an aid to understanding the nature of chemical transport reactions in incandescent filament light sources [376,377]. Thermochemical data for lower fluorides have also been derived from measurements of tungsten transport from heated filaments in fluorine containing atmospheres with the selected heats of formation being those which give the best iterative fit to the transport data at various temperatures [384]. More recently, Hildenbrand [8] derived thermochemical data for gaseous tungsten fluorides from high temperature mass spectroscopic studies. The data derived from transport measurements and mass spectroscopic studies are compared in Table 5.3. From the derived enthalpies of formation one can evaluate the individual bond dissociation energies for tungsten fluorides, Table 5.3. Agreement is reasonably good regarding the heats of formation of  $\text{WF}$ ,  $\text{WF}_2$ ,  $\text{WF}_3$  and

TABLE 5.3

Derived heats of formation and bond dissociation energies of tungsten fluorides [8]

Gaseous Species	Derived heats of formation (kcal/mol)		Bond Dissociation Energies (kcal)		
	$\Delta H_f^\ominus$ <sup>a</sup>	$\Delta H_f^\ominus$ <sup>b</sup>	Bond	$D^\ominus$ <sup>c</sup>	$D^\ominus$ <sup>d</sup>
WF	>92	86	W-F	<130	~136
WF <sub>2</sub>	-20.6±3.2	-25	FW-F	>132	~130
WF <sub>3</sub>	-121.2±2.8	-127	F <sub>2</sub> W-F	119.6±6.5	~119
WF <sub>4</sub>	-220.0±2.5	-246	F <sub>3</sub> W-F	119.8±6.3	~138
WF <sub>5</sub>	-309.1±2.0	-334	F <sub>4</sub> W-F	106.1±6.6	~107
			F <sub>5</sub> W-F	121.4±2.5 <sup>e</sup>	

<sup>a</sup> derived from mass spectroscopic data [8];

<sup>b</sup> derived from transport data [384];

<sup>c</sup> evaluated from the derived heats of formation listed in <sup>a</sup>;

<sup>d</sup> evaluated from the derived heats of formation listed in <sup>b</sup>;

<sup>e</sup> evaluated using  $\Delta H_f^\ominus [WF_6(g)] = -411.5 \pm 0.4$  kcal/mol.

the bond dissociation energies;  $D(W-F)$ ,  $D(FW-F)$ ,  $D(F_2W-F)$ ,  $D(F_4W-F)$ , but large differences appear for the heats of formation of  $WF_4$ ,  $WF_5$ , and the bond dissociation energy,  $D(F_3W-F)$ . Even so, it can be seen that with the exception of  $D(F_4W-F)$ , the bond dissociation energies are remarkably constant. Hildenbrand [8] rationalised the low value for  $D(F_4W-F)$  in terms of the valence excitation energy required at the fifth step in going from the  $5d^46s^2$ ,  $^5D_3$  tetravalent ground state of the tungsten atom to the upper hexavalent state.

Thermochemical data for gaseous fluorides of uranium [5], and molybdenum [381] given in Tables 5.5 and 5.4 respectively have also been derived from high temperature mass spectroscopic studies by Hildenbrand.

The individual bond dissociation energies of molybdenum fluorides evaluated from the derived heats of formation [Table 5.4] show a similar trend to those exhibited by tungsten fluorides. This trend can be interpreted as an indication that the fluorine ligands tend to stabilise the +4 oxidation state somewhat more than the +6 state, the  $F_5Mo-F$  and  $F_4Mo-F$  bonds being significantly weaker than the others. Both molybdenum and tungsten fluoride individual bond dissociation energies show the  $F_4M-F$  bond to be the weakest.

In many of its reactions uranium hexafluoride is reduced to either the penta- or tetrafluoride (which is generally dependent upon the stoichiometric ratio of the reactants) while its reaction partner is usually oxidatively fluorinated. This behaviour is expected since the  $F_5U-F$  and  $F_4U-F$  bonds are relatively weak especially by comparison with the average bond energies of  $125.6 \pm 0.6$  and  $149.7 \pm 1$  kcal/mol in uranium hexafluoride and uranium tetrafluoride respectively. Thus the  $F_3U-F$ ,  $F_2U-F$ ,  $FU-F$  and  $U-F$  bonds are consequently stronger. This goes some

TABLE 5.4

Derived heats of formation and bond dissociation energies of molybdenum fluorides [381]

Gaseous Species	Derived heats of formation (kcal/mol) $\Delta H_f^\ominus$	Bond Dissociation Energies (kcal) Bond $D^\ominus$
MoF	65.0±2.2	Mo-F 111.3±2.8
MoF <sub>2</sub>	-40.2±2.9	FMo-F 124.2±5.2
MoF <sub>3</sub>	-141.5±3.5	F <sub>2</sub> Mo-F 120.3±6.5
MoF <sub>4</sub>	-228.0±3.9	F <sub>3</sub> Mo-F 105.5±7.5
MoF <sub>5</sub>	-296.7±8.6	F <sub>4</sub> Mo-F 87.7±12.6
		F <sub>5</sub> Mo-F 94.6±8.9 <sup>a</sup>

<sup>a</sup> evaluated using  $\Delta H_f^\ominus[\text{MoF}_6(\text{g})] = -372.3 \pm 0.4$  kcal/mol.

TABLE 5.5

Derived heats of formation and bond dissociation energies of uranium fluorides [5]

Gaseous Species	Derived heats of formation (kcal/mol)	Bond Dissociation Energies (kcal) Bond $D^\ominus$
UF <sub>4</sub>	-377.8±0.6	F <sub>5</sub> U-F 71.9±3.9 <sup>a</sup>
UF <sub>5</sub>	-460.6±3.4	F <sub>4</sub> U-F 101.8±5

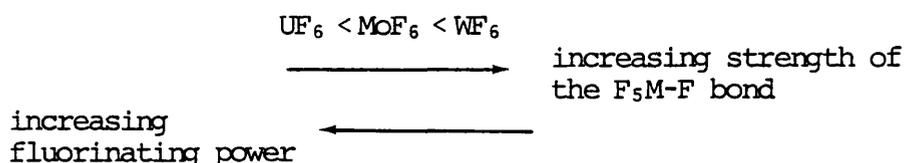
<sup>a</sup> evaluated using  $\Delta H_f^\ominus[\text{UF}_6(\text{g})] = -513.49 \pm 0.43$  kcal/mol.

way to explain the high chemical and thermodynamic stability of uranium tetrafluoride. The chemical stabilities of uranium hexafluorides should increase in the following series:-



which is borne out from their known chemical behaviour.

A comparison of the bond dissociation energies,  $D(F_5M-F)$ ,  $D(F_4M-F)$ , and the RFBDE's of the hexafluorides clearly demonstrate that molybdenum hexafluoride should be a stronger fluorinating agent than tungsten hexafluoride but not as powerful as uranium hexafluoride, i.e. the partial dissociation of the hexafluorides is most favourable for uranium and that the first bond dissociation energies can be arranged in the following series:-



Even though the individual bond dissociation energies constitute a more objective criterion to explain the known chemical behaviour of the hexafluorides, average bond energies will be used to estimate the enthalpies of formation of substances formed in exchange reactions. In the next section, the enthalpies of formation of compounds both known and unknown, formed from exchange reactions are estimated and compared wherever possible with literature values. The thermodynamic stabilities of these compounds with respect to decomposition and disproportionation are also discussed.

#### 5.5 METAL CHLORIDE FLUORIDES; $MCl_nF_{6-n}$ (M = U, Mo, W; n = 1 or 2)

Previous work on the synthesis and chemical stabilities of uranium-(VI) and tungsten(VI) chloride fluorides are discussed in Chapter 1.

No chloride fluorides of molybdenum(VI) have been isolated.

The enthalpies of formation of the chloride fluorides of uranium(VI) and tungsten(VI) can be estimated from the average bond energies derived from the respective hexachlorides and hexafluorides using the thermochemical cycle shown in Fig. 5.5 [Tables 5.6 and 5.7].

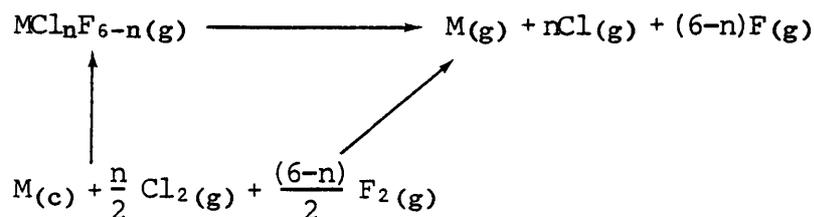


FIGURE 5.5

$$\begin{aligned}
 \text{i.e. } \Delta H_f^\ominus [\text{MCl}_n\text{F}_{6-n}(\text{g})] &= \Delta H_f^\ominus [\text{M}(\text{c})] + n\Delta H_f^\ominus [\text{Cl}(\text{g})] + (6-n)\Delta H_f^\ominus [\text{F}(\text{g})] \\
 &\quad - n\bar{D}^\ominus (\text{M}^{\text{VI}}-\text{Cl}) - (6-n)\bar{D}^\ominus (\text{M}^{\text{VI}}-\text{F}) \quad \dots [5.7]
 \end{aligned}$$

An alternative method for estimating enthalpies of formation is by linear interpolation:-

$$\begin{aligned}
 \Delta H_f^\ominus [\text{MCl}_n\text{F}_{6-n}(\text{i})] &= \frac{n\Delta H_f^\ominus [\text{MCl}_6(\text{i})]}{6} + \frac{(6-n)\Delta H_f^\ominus [\text{MF}_6(\text{i})]}{6} \quad \dots [5.8] \\
 &\quad (\text{i} = \text{gas or crystalline})
 \end{aligned}$$

The estimated and measured enthalpies of formation of uranium(VI) and tungsten(VI) chloride fluorides are listed in Tables 5.6 and 5.7 respectively. Agreement between the measured and estimated values for tungsten(VI) chloride fluorides is reasonably good especially when the uncertainties in the literature concerning the enthalpy of formation of tungsten hexachloride is taken into account.

Combining these results with the data for  $\beta$ -UF<sub>5</sub> and UF<sub>4</sub> [Table 5.2], the thermodynamic stabilities of uranium(VI) chloride fluorides with respect to decomposition can be predicted from the standard enthalpy changes associated with the following reactions:-

TABLE 5.6

Estimated standard enthalpies of formation (kcal/mol) of uranium(VI) chloride fluorides

Compound	$\Delta H_f^\ominus$	$\bar{D}^\ominus(\text{U}^{\text{VI}}-\text{F})$	$\bar{D}^\ominus(\text{U}^{\text{VI}}-\text{Cl})$	$\Delta H_f^\ominus \text{ }^a$	$\Delta H_f^\ominus \text{ }^b$
UF <sub>6</sub>	g	-513.49±0.43 [372]	125.6±0.6		
	s	-525.49±0.43 [372]			
UClF <sub>5</sub>	g			-467.5	-467.3
	s				-480.5
UCl <sub>2</sub> F <sub>4</sub>	g			-421.3	-421.2
	s				-435.5
UCl <sub>6</sub>	g	-236.6±0.5 [385]	89.4±0.6		
	s	-255.4±0.5 [385]			

<sup>a</sup> enthalpies of formation estimated using  $\bar{D}^\ominus(\text{U}^{\text{VI}}-\text{F})$ ,  $\bar{D}^\ominus(\text{U}^{\text{VI}}-\text{Cl})$  derived from UF<sub>6</sub> and UCl<sub>6</sub>;

<sup>b</sup> enthalpies of formation estimated by linear interpolation using the enthalpies of formation of UF<sub>6</sub> and UCl<sub>6</sub>.

TABLE 5.7

Estimated enthalpies of formation (kcal/mol) of tungsten(VI) chloride fluorides

Compound	$\Delta H_f^\ominus$	$\bar{D}^\ominus(W^{VI}-F)$	$\bar{D}^\ominus(W^{VI}-Cl)$	estimated enthalpies of formation	
				$\Delta H_f^\ominus^a$	$\Delta H_f^\ominus^b$
WF <sub>6</sub>	g	-411.5±0.4 [370]	121.4±0.3		
	s	-418.2±0.2 [370]			
WClF <sub>5</sub>	g			-362.6	-366.8
	s	-391±3 <sup>d</sup> [ 6 ]			-372.2
WCl <sub>2</sub> F <sub>4</sub>	g			-314.0	-313.7
	s	-353±3 <sup>d</sup> [ 6 ]			-322.1
WCl <sub>6</sub>	g	-118.0 [386]	82.5		
	s	-141.9 [386]			-326.1

<sup>a</sup> enthalpies of formation estimated using  $\bar{D}^\ominus(W^{VI}-F)$ ,  $\bar{D}^\ominus(W^{VI}-Cl)$  derived from WF<sub>6</sub> and WCl<sub>6</sub>;<sup>b</sup> enthalpies of formation estimated by linear interpolation using the enthalpies of formation of WF<sub>6</sub> and WCl<sub>6</sub>;<sup>c</sup> enthalpies of formation estimated using  $\bar{D}^\ominus(W^{VI}-F)$ ,  $\bar{D}^\ominus(W^{VI}-Cl)$  derived from WF<sub>6</sub> and WCl<sub>6</sub>, where  $\Delta H_f^\ominus[WCl_6(s)] = -163$  kcal/mol;  $\Delta H_f^\ominus[WCl_6(g)] = -143$  kcal/mol [364];<sup>d</sup> literature values for these compounds in their liquid state.

	$\Delta H^\ominus$ (kcal/mol)	
$\text{UF}_5\text{Cl}(\text{s}) \rightarrow \beta\text{-UF}_5(\text{s}) + \frac{1}{2}\text{Cl}_2(\text{g})$	-17.4	.... [ 5.9]
$\text{UF}_5\text{Cl}(\text{g}) \rightarrow \beta\text{-UF}_5(\text{s}) + \frac{1}{2}\text{Cl}_2(\text{g})$	-30.6	.... [5.10]
$\text{UF}_4\text{Cl}_2(\text{s}) \rightarrow \text{UF}_4(\text{s}) + \text{Cl}_2(\text{g})$	-23.5	.... [5.11]
$\text{UF}_4\text{Cl}_2(\text{g}) \rightarrow \text{UF}_4(\text{s}) + \text{Cl}_2(\text{g})$	-37.8	.... [5.12]

Thus in both the crystalline and gaseous state  $\text{UF}_5\text{Cl}$  and  $\text{UF}_4\text{Cl}_2$  are predicted to be thermodynamically unstable with respect to the formation of  $\beta\text{-UF}_5$  and  $\text{UF}_4$ , respectively and to the evolution of gaseous chlorine. These conclusions are in agreement with the reported chemical stabilities of uranium(VI) chloride fluorides.

Similarly, the measured and estimated enthalpies of formation [Table 5.7] can be used to predict the thermodynamic stabilities of tungsten(VI) chloride fluorides with respect to decomposition from the standard enthalpy changes associated with reactions [5.13] to [5.16] using the thermochemical data for  $\text{WF}_4$  and  $\text{WF}_5$  listed in Table 5.2.

	$\Delta H^\ominus$ (kcal/mol) **	
$\text{WF}_5\text{Cl}(\text{s}) \rightarrow \text{WF}_5(\text{s}) + \frac{1}{2}\text{Cl}_2(\text{g})$	+28.9	.... [5.13]
$\text{WF}_5\text{Cl}(\text{g}) \rightarrow \text{WF}_5(\text{s}) + \frac{1}{2}\text{Cl}_2(\text{g})$	+14.3	.... [5.14]
$\text{WF}_4\text{Cl}_2(\text{s}) \rightarrow \text{WF}_4(\text{s}) + \text{Cl}_2(\text{g})$	+34.1	.... [5.15]
$\text{WF}_4\text{Cl}_2(\text{g}) \rightarrow \text{WF}_4(\text{s}) + \text{Cl}_2(\text{g})$	+21.7	.... [5.16]

The decomposition reactions have large positive enthalpy changes and are thus thermodynamically unfavourable.

The enthalpy of formation of  $\text{WF}_4$  has not been measured experimentally but has been estimated by Burgess et al. [6]. Since the disproportionation of  $\text{WF}_5$  into  $\text{WF}_4$  and  $\text{WF}_6$  goes to a position of equilibrium rather than to completion [6], one can assume that the free energy for the

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\*\* Calculated using the enthalpies of formation of tungsten(VI) chloride fluorides estimated by linear interpolation.

reaction:-



is zero to within 2-3 kcal/mol. From this assumption, estimated entropies\* of  $35 \text{ cal deg}^{-1} \text{ mole}^{-1}$  for  $\text{WF}_4(\text{s})$ , 40 for  $\text{WF}_5(\text{s})$  and 84 for  $\text{WF}_6(\text{g})$  [6], known enthalpies of formation of -346 kcal/mol for  $\text{WF}_5(\text{c})$  [382] and -412 kcal/mol for  $\text{WF}_6(\text{g})$  [370], an enthalpy of formation of -292 kcal/mol can be estimated for  $\text{WF}_4$ .

Since molybdenum hexachloride is unknown, estimations of the enthalpies of formation of molybdenum(VI) chloride fluorides cannot be made. However, from the known chemical behaviour of the hexafluorides, it can be assumed that molybdenum(VI) chloride fluorides will be more stable with respect to decomposition than the analogous uranium compounds, but less stable than the analogous tungsten compounds. Thus the thermodynamic and chemical stabilities of the metal chloride fluorides;  $\text{MCl}_n\text{F}_{6-n}$  ( $\text{M} = \text{U}, \text{Mo}, \text{W}; n = 1 \text{ or } 2$ ) increase in the series:-



#### 5.6 METAL OXIDE FLUORIDES; $\text{MO}_n\text{F}_{6-2n}$ ( $\text{M} = \text{U}, \text{Mo}, \text{W}; n = 1 \text{ or } 2$ )

Literature values for the standard enthalpies of formation of oxide fluoride compounds of uranium, molybdenum, and tungsten are listed in Table 5.8. As enthalpies of sublimation of several of these compounds are not known, it is impossible to give data relating solely to the gaseous or to the solid state. The values in this Table give some idea of the uncertainties and doubts in these enthalpies.

Combining these values with the auxiliary data listed in Table 5.13,

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\* Entropies of tungsten tetrafluoride and tungsten pentafluoride were estimated by Latimer's method; "The oxidation states of the Elements and their Potentials in Aqueous Solution", 2nd. edn., Prentice-Hall, New Jersey, 1952.

TABLE 5.8

Standard enthalpies of formation ( $\Delta H_f^\ominus$  kcal/mol) of oxide fluoride compounds of uranium(VI), molybdenum(VI) and tungsten(VI)

	URANIUM		MOLYBDENUM		TUNGSTEN	
	SOLID	GAS	SOLID	GAS	SOLID	GAS
MF <sub>6</sub>	-525.49±0.43 [372]	-513.49±0.43 [372]	-388.6 [389] <sup>f</sup>	-372.3±0.2 [369]	-418.2±0.6 [370]	-411.5±0.4 [370]
MOF <sub>4</sub>	-460.1±0.1 [390]		-329.9±0.3 [7]		-358.6±4 [7]	-312.5±11.1 <sup>a, c, e</sup> [391] -342.1 <sup>e</sup> [7]
MO <sub>2</sub> F <sub>2</sub>	-395.6±0.6 [390]		-260.3±1.5 [392]	-267.6±15.6 <sup>a, c, e</sup> [391]		-211.9±11.1 <sup>a, c, e</sup> [391] (ca. -222 <sup>b</sup> ) [393]
MO <sub>3</sub>	-292.6±0.6 [394]		-178.08 [395]	(ca. -85 <sup>d</sup> ) [396]	-201.46±0.2 [397]	(ca. -70 <sup>d</sup> ) [396]

<sup>a</sup> indirect estimates from mass spectroscopy;

<sup>b</sup> indirect estimates from gas transport measurements;

<sup>c</sup> calculated using the enthalpies of atomisation derived by Zmbov *et al.* [391] and the auxiliary data listed in Table 5.13;

<sup>d</sup> calculated by Dellien *et al.* [396] from the work of G. De Maria, R. P. Burns, J. Drowart, M. G. Inghram; J. Chem. Phys. 32 [1960] 1373;

<sup>e</sup>  $\Delta H_f^\ominus$  [WOF<sub>4</sub>(g)] calculated from the reported  $\Delta H_f^\ominus$  [WOF<sub>4</sub>(s)] value using a value of 16.5 kcal/mol for the enthalpy of sublimation of WOF<sub>4</sub>;

<sup>f</sup> refers to the hexafluoride in the liquid state.

the standard enthalpies of formation of the oxide fluorides can be estimated using the average bond energies,  $\bar{D}^{\ominus}(\text{M}^{\text{VI}}=\text{O})$ ,  $\bar{D}^{\ominus}(\text{M}^{\text{VI}}-\text{F})$  derived from the respective metal trioxides and hexafluorides, and by linear interpolation. The estimated and literature values are compared in Table 5.9. Agreement is poor especially between the values for the enthalpies of formation of gaseous oxide fluorides. This is presumably a consequence of the large uncertainties in the literature concerning the enthalpies of formation of the gaseous trioxides of molybdenum and tungsten. However, from the measured heats of formation of  $\text{MoOF}_4(\text{g})$  and  $\text{WOF}_4(\text{g})$  the respective metal-oxygen bond energies can be evaluated since it is known that these compounds vapourise directly to a monomeric gas [7]. If the average metal-fluorine bond energy is assumed to be the same as in the hexafluorides, metal-oxygen bond energies of 177 kcal/mol in  $\text{MoOF}_4(\text{g})$  and 165, 195 kcal/mol in  $\text{WOF}_4(\text{g})$  [Table 5.10] can be evaluated. The latter compares with a value of 186 kcal/mol in  $\text{WOCl}_4(\text{g})$  [388]. These values are considerably higher than those derived from the respective metal trioxides. The estimated enthalpies of formation of gaseous  $\text{MoO}_2\text{F}_2$  and  $\text{WO}_2\text{F}_2$  using these average values for the bond strengths are in good agreement with those which have been derived experimentally; Table 5.9.

The thermodynamic stabilities of the dioxide difluorides with respect to disproportionation can be predicted from the standard enthalpy changes associated with reactions [5.18] to [5.25] using the thermochemical data in Table 5.9. Due to the large variations in the estimated enthalpies of formation of these compounds, only thermochemical data derived experimentally are used in these calculations.

TABLE 5.9

Estimated standard enthalpies of formation of metal oxide fluorides;  $MO_nF_{6-2n}$   
(M = U, Mo, W; n = 1 or 2)

		$\Delta H_f^\ominus$ (kcal/mol)	$\bar{D}^\ominus(M^{VI}-F)$	$\bar{D}^\ominus(M^{VI}=O)$	Estimated enthalpies of formation		
					$\Delta^\ominus H_f^a$	$\Delta^\ominus H_f^b$	$\Delta^\ominus H_f^c$
UF <sub>6</sub>	g	-513.49±0.43 [372]	125.6±0.6				
	s	-525.49±0.43 [372]					
UOF <sub>6</sub>	g						
	s	-460.1±0.1 [390]					
UO <sub>2</sub> F <sub>2</sub>	g						
	s	-395.6±0.5 [390]					
UO <sub>3</sub>	g						
	s	-292.6±0.6 [394]					
MoF <sub>6</sub>	g	-372.3±0.2 [369]	107.2±0.2				
		-388.6 [389]					
MoOF <sub>4</sub>	g						
	s	-329.9±3 [ 7 ]					
MoO <sub>2</sub> F <sub>2</sub>	g	-267.6±15.6 [391]					
	s	-260.3±1.5 [392]					
MoO <sub>3</sub>	g	(ca. -85) [396]		140.2			
	s	-178.08 [395]					
WF <sub>6</sub>	g	-411.5±0.4 [370]	121.4±0.3				
	s	-418.2±0.6 [370]					
WOF <sub>4</sub>	g	-312.5±11.1 [391]					
	s	-358.6±4 [ 7 ]					
WO <sub>2</sub> F <sub>2</sub>	g	-211.9±11.1 [391] (ca. -222) [393]					
	s						
WO <sub>3</sub>	g	(ca. -70) [396]		150.6			
	s	-201.46±0.2 [397]					

<sup>a</sup> enthalpies of formation estimated using  $\bar{D}^\ominus(M^{VI}-F)$ ,  $\bar{D}^\ominus(M^{VI}=O)$  derived from MF<sub>6</sub> and MO<sub>3</sub>;

<sup>b</sup> enthalpies of formation estimated by linear interpolation using the enthalpies of formation of MF<sub>6</sub> and MO<sub>3</sub>;

<sup>c</sup> enthalpies of formation estimated using  $\bar{D}^\ominus(M^{VI}-F)$ ,  $\bar{D}^\ominus(M^{VI}=O)$  derived from MF<sub>6</sub> and MOF<sub>4</sub> [Table 5.8];

<sup>d</sup> enthalpies of formation estimated by linear interpolation using  $\Delta H_f^\ominus[MoF_6(l)] = -388.6$  kcal/mol.

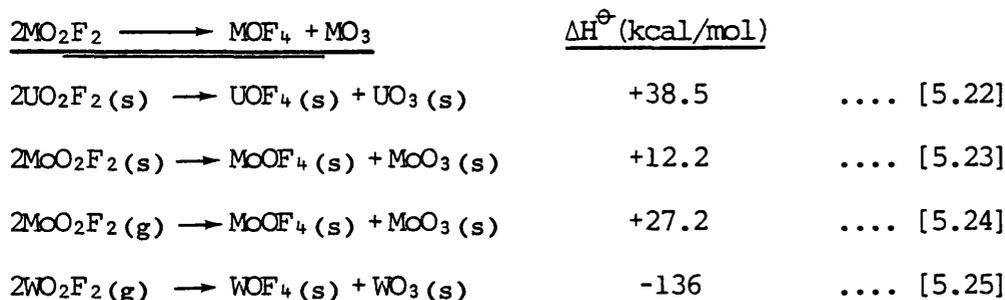
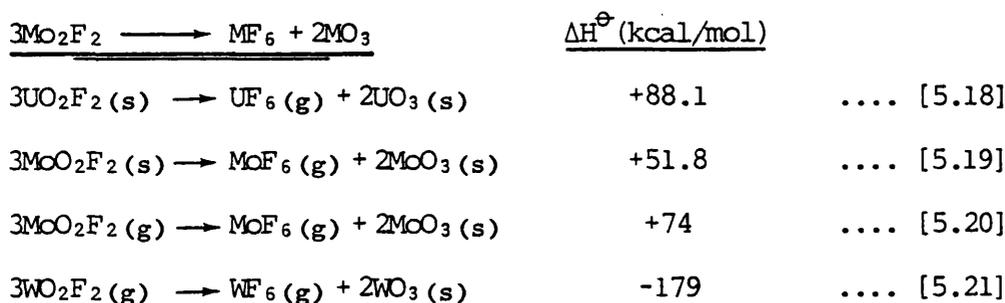
TABLE 5.10

Average bond dissociation energies (kcal/mol) calculated from the measured enthalpies of formation of molybdenum(VI) and tungsten(VI) fluorides and oxide fluorides

Compound	$\Delta H_f^\ominus$	$\bar{D}^\ominus(M^{VI}-F)$	$\bar{D}^\ominus(M^{VI}=O)$
WF <sub>6</sub> (g)	-411.5±0.4 [370]	121.4	
MoF <sub>6</sub> (g)	-372.3±0.2 [369]	107.2	
WOF <sub>4</sub> (g)	-312.5 [391]	121.4	165.4
	-342.1 <sup>a</sup> [ 7 ]	121.4	195.0
MoOF <sub>4</sub> (g)	-313.4 <sup>b</sup> [ 7 ]	107.2	177.4

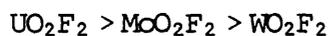
<sup>a</sup>  $\Delta H_f^\ominus$  [WOF<sub>4</sub>(g)] calculated from the reported  $\Delta H_f^\ominus$  [WOF<sub>4</sub>(s)] using a value of 16.5 kcal/mol for the enthalpy of sublimation of WOF<sub>4</sub> [398];

<sup>b</sup>  $\Delta H_f^\ominus$  [MoOF<sub>4</sub>(g)] calculated from the reported  $\Delta H_f^\ominus$  [MoOF<sub>4</sub>(s)] assuming a value of 16.5 kcal/mol for the enthalpy of sublimation of MoOF<sub>4</sub>.



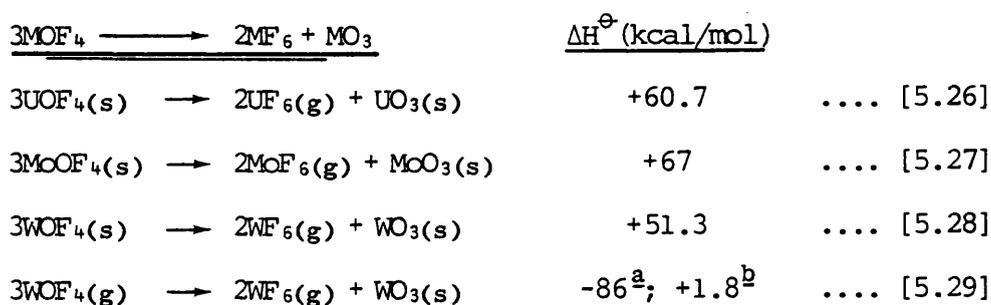
Thus assuming small entropy changes the disproportionation of uranium and molybdenum dioxide difluorides set out in the above equations are thermodynamically unfavourable. However, the enthalpy changes for gaseous tungsten dioxide difluoride suggest that it is thermodynamically unstable with respect to disproportionation into  $\text{WF}_6$  and  $\text{WO}_3$  [equation 5.21] or into  $\text{WOF}_4$  and  $\text{WO}_3$  [equation 5.25]. It is thus possible that the Gibbs free energy changes for the disproportionation of tungsten dioxide difluoride may be negative, which may explain the inability of workers [392] to prepare pure samples of this compound easily.

The thermodynamic stabilities of the metal dioxide difluorides with respect to disproportionation decrease in the following series:-



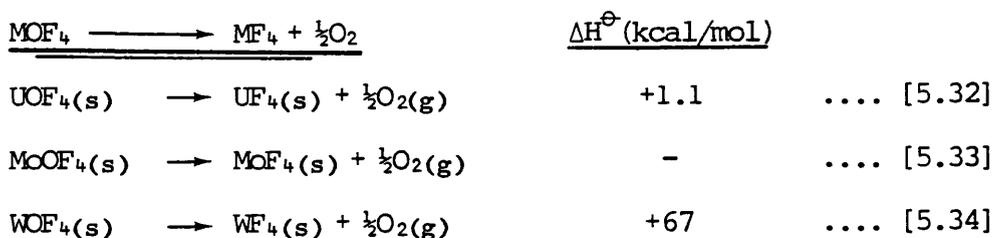
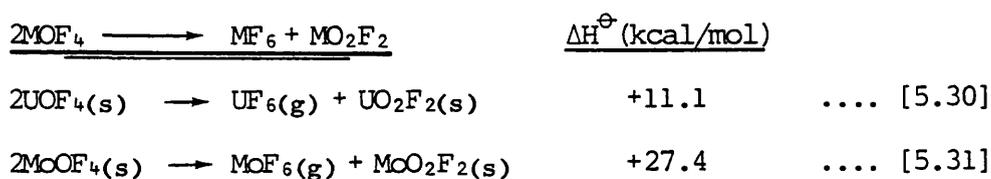
which is in agreement with their known chemical behaviour.

Similarly, the thermodynamic stabilities of the metal oxide tetrafluorides with respect to decomposition and disproportionation can be predicted from the standard enthalpy changes associated with equations [5.26] to [5.34] using the data listed in Tables 5.2 and 5.9.



<sup>a</sup> calculated using ΔH<sub>f</sub><sup>⊖</sup> [WOF<sub>4</sub>(g)] = -312.5 kcal/mol;

<sup>b</sup> calculated using ΔH<sub>f</sub><sup>⊖</sup> [WOF<sub>4</sub>(g)] = -342.1 kcal/mol.



The thermodynamic stabilities of the oxide tetrafluorides of uranium, molybdenum and tungsten predicted from the disproportionation and decomposition reactions [5.26 to 5.34] decrease in the series:-

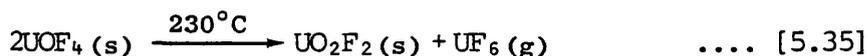


which is in accord with their known chemical behaviour.

Positive enthalpy changes are obtained for the decomposition of the oxide tetrafluorides of uranium and tungsten into the corresponding tetrafluoride and to the evolution of gaseous oxygen. Again, assuming small entropy changes, the Gibbs free energy changes for these reactions will be markedly positive with the reactions being thermodynamically unfavourable. The analogous enthalpy change for molybdenum oxide tetrafluoride could not be calculated since there is no available value for the enthalpy of formation of solid molybdenum tetrafluoride.

The enthalpy change associated with reaction [5.29] is either negative or close to zero depending upon the value employed for the enthalpy of formation of gaseous tungsten oxide tetrafluoride. This implies that gaseous tungsten oxide tetrafluoride is unstable with respect to disproportionation into  $WF_6$  and  $WO_3$ . Both molybdenum and tungsten oxide tetrafluorides have been well characterised [398,399]; they are thermally stable, white crystalline solids and are sufficiently volatile to permit easy sublimation in vacuo. The discrepancy between the known and predicted stability of gaseous tungsten oxide tetrafluoride must be accounted for by structural and bonding considerations.

Uranium oxide tetrafluoride is involatile and thermally unstable [82]:-



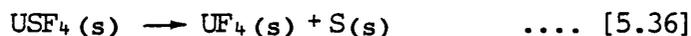
It is worth noting that the standard enthalpy change for equation [5.30] is very close to the enthalpy of sublimation, 11.9 kcal/mol of uranium hexafluoride [4]. Thus from a 'thermochemical' view, uranium oxide tetrafluoride behaves as a very loosely bound 1-1 complex of  $UO_2F_2$  and  $UF_6$ . This is in agreement with Malm et al. [400] who observed the disproportionation of uranium oxide tetrafluoride and its complexes at room temperature and suggested that chemically it behaves like a mixture of  $UF_6$  and  $UO_2F_2$ . This is also borne out by the work of Laycock and Holloway [401].

#### 5.7 METAL THIOFLUORIDES; $MS_nF_{6-2n}$ (M=U, W; n=1 or 2)

The enthalpies of formation of uranium hexafluoride and uranium(VI) sulphide were used to estimate the corresponding values for crystalline  $USF_4$  and  $US_2F_2$  by linear interpolation. Since there is no readily

available data for the enthalpy of vapourisation of uranium(VI) sulphide, the average bond energies,  $\bar{D}^\ominus(U^{VI}=S)$ ,  $\bar{D}^\ominus(U^{VI}-F)$  could not be used to estimate the enthalpies of formation of uranium thiofluorides.

The decomposition of uranium thiotetrafluoride:-



from the thermodynamic data in Tables 5.2 and 5.11 has a standard enthalpy change of -68 kcal/mol. Hence the Gibbs free energy for this reaction assuming a small entropy change is markedly negative, the reaction being thermodynamically favourable. The enthalpy changes associated with the disproportionation reactions of uranium(VI) thiofluorides would be meaningless since  $UF_6$  and  $US_3$  (the products of disproportionation) were used to determine the enthalpies of formation of the thiofluorides via linear interpolation. Thus at room temperature, uranium thiotetrafluoride is thermodynamically unstable with respect to decomposition into uranium tetrafluoride and elemental sulphur.

A summary of the attempted methods for the synthesis of uranium thiotetrafluoride from uranium hexafluoride are shown in Fig. 5.5. It is interesting to note that uranium hexafluoride is always reduced to  $\beta$ - $UF_5$  or  $UF_4$  or their adducts (depending upon the reactant stoichiometry) with the sulphur-containing reaction partner remaining as elemental sulphur or sulphur fluorides if elevated temperatures were used. This is in agreement with the thermodynamic data presented in this study.

No values could be estimated for molybdenum thiofluorides since there is no readily available data for the enthalpy of formation of molybdenum(VI) sulphide.

The thermodynamic data for tungsten thiofluorides listed in Table 5.12 have been derived from high temperature mass spectroscopic studies

TABLE 5.11

Estimated standard enthalpies of formation (kcal/mol)  
of uranium(VI) thiofluorides

Compound	$\Delta H_f^\ominus$	$\Delta H_f^{\ominus a}$
UF <sub>6</sub> (s)	-525.49±0.43 [372]	
USF <sub>4</sub> (s)		-392
US <sub>2</sub> F <sub>2</sub> (s)		-258.5
US <sub>3</sub> (s)	-125 [402]	

<sup>a</sup> enthalpies of formation estimated by linear interpolation using the enthalpies of formation of UF<sub>6</sub> and US<sub>3</sub>.

TABLE 5.12

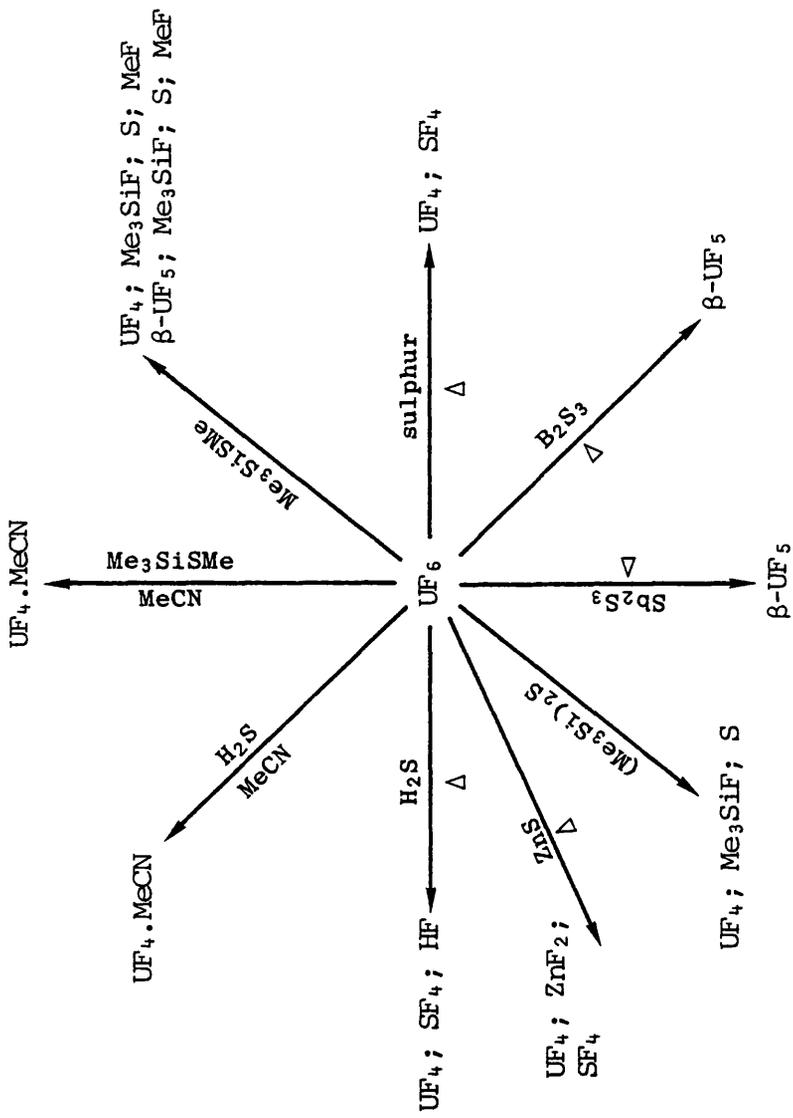
Derived enthalpies of formation (kcal/mol) and bond  
dissociation energies of tungsten thiofluorides

Compound	$\Delta H_f^\ominus a$	Bond	$\bar{D}^\ominus$
WSF <sub>2</sub> (g)	-80.1±3.9 [ 8 ]	F <sub>3</sub> W=S	115.2±6.1
WSF <sub>3</sub> (g)	-170.2±3.2 [ 8 ]	F <sub>2</sub> W=S	125.7±7.1
WSF <sub>4</sub> (g)	-271.8±9 [403]	F <sub>2</sub> SW=S	104.8±8.1
WSF <sub>4</sub> (s)	-290.9±9.1 [403]	F <sub>2</sub> SW-F	109.1±7.1
WS <sub>2</sub> F <sub>2</sub> (g)	-118.7±4.2 [ 8 ]	F <sub>4</sub> W=S	131.3±11.2 <sup>b</sup>
		(W <sup>VI</sup> =S)	124.64±5.5 <sup>c</sup>

<sup>a</sup> estimated from mass spectroscopy;

<sup>b</sup> calculated assuming that the average W-F bond energy in WSF<sub>4</sub> is the same as in WF<sub>6</sub>;

<sup>c</sup> average bond energy calculated assuming that the average W-F bond energy in WS<sub>2</sub>F<sub>2</sub> is the same as in WF<sub>6</sub>.

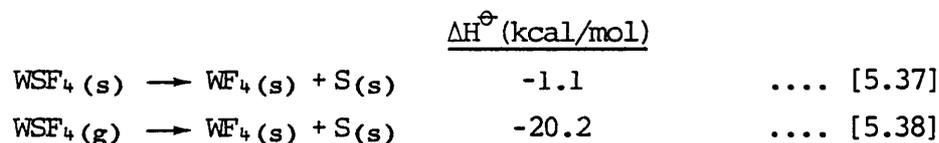


**FIGURE 5.5**

A systematic representation of the methods used for the attempted synthesis of uranium(VI) sulphur fluorides.

[8]. From the derived heats of formation, average bond energies and various individual bond dissociation energies can be evaluated. It is interesting to note that  $D(F_2SW=S)$  in  $WS_2F_2$  derived from mass spectroscopic studies is significantly smaller than the  $(W^{VI}=S)$  bond energies evaluated from the enthalpies of formation of gaseous  $WSF_4$  and  $WS_2F_2$ ; Table 5.12.

The thermodynamic stability of tungsten thiotetrafluoride with respect to decomposition can be predicted from the standard enthalpy changes associated with reactions [5.37] and [5.38].



The negative enthalpy changes suggest that tungsten thiotetrafluoride is thermodynamically unstable with respect to decomposition into tungsten tetrafluoride and elemental sulphur. However, since solid tungsten thiotetrafluoride is chemically stable at room temperature [179], the Gibbs free energy for reaction [5.37] must be positive.

Since there is no accurate value for the enthalpy of formation of tungsten(VI) sulphide, the thermodynamic stabilities of tungsten(VI) thiofluorides with respect to disproportionation could not be estimated. However, since both molybdenum and tungsten thiotetrafluorides have been characterised [179,180], the thermodynamic stability of the thiotetrafluorides must decrease in the series:-



TABLE 5.13

Auxiliary Thermodynamic Data<sup>a</sup>

Species	$\Delta H_f^\ominus$ (kcal/mol)
F(g)	18.978±0.07
O(g)	59.563±0.024
Cl(g)	28.997±0.002
S(g)	66.211±0.06

<sup>a</sup> CODATA recommended key values for thermodynamics, 1977; J. Chem. Thermodyn. 10 [1978] 903.



# CHAPTER 6

The  $\text{MF}_6$  (M = U, Mo, W) reactions  
with Urea and Thiourea

## 6.1 FLUORINATION OF UREA BY METAL HEXAFLUORIDES

### 6.1.1 Introduction

Fluoro-nitrogen compounds such as  $\text{NF}_3$ ,  $\text{N}_2\text{F}_2$ , and  $\text{N}_2\text{F}_4$  have been prepared by the direct fluorination of certain compounds containing N-H bonds, including urea, alkali metal amides, hydrazine, and diamine, in the presence of a metal catalyst [404]. At  $0^\circ\text{C}$ , the direct fluorination of urea yields a yellow corrosive liquid containing 16% of fluorine active to hydrogen iodide and about 45-55% of total fluorine. Distillation of this mixture gives difluoroamine,  $\text{F}_2\text{NH}$ , but no organic compounds containing a N-F bond [405]. N N'-difluorourea has been obtained from both the direct fluorination of urea at  $0^\circ\text{C}$  in the presence of  $\text{MgF}_2$  [406] and from the fluorination of aqueous solutions of urea [407]. The fluorination of urea by  $\text{AgF}_2$  under an atmosphere of nitrogen at room temperature yields a colourless gas which was shown by infrared spectroscopy to contain both carbonyl and N-F groups [408], while the electrochemical fluorination of urea by anhydrous hydrogen fluoride gives  $\text{NF}_3$ ,  $\text{COF}_2$ ,  $\text{CO}$ , and  $\text{N}_2$  as the principle products [409].

To date there have been no published studies on the fluorination of urea by metal hexafluorides. It was hoped that the differences in the fluorinating ability of the hexafluorides of uranium, molybdenum, and tungsten, discussed in Chapter 5, would be evidenced experimentally by their behaviour towards urea.

### 6.1.2 Present Study

A large excess (approximately 12-fold) of the desired hexafluoride was condensed onto a known quantity of 'oven dried' urea in pre-fluorinated FEP tubes at  $-196^\circ\text{C}$  and allowed to warm to room temperature

with constant mixing.

Uranium and molybdenum hexafluorides reacted vigorously with urea at ambient temperatures with the evolution of a large quantity of heat to yield a green solid and a yellow viscous liquid respectively. No reaction was observed for tungsten hexafluoride. When the reactions had terminated, the volatiles were transferred into a separate seasoned FEP tube.

#### UF<sub>6</sub> with H<sub>2</sub>NCONH<sub>2</sub>

Vibrational spectroscopy and X-ray powder diffraction studies identified the green non-volatile solid isolated from the reaction between uranium hexafluoride and urea as uranium tetrafluoride.

#### MoF<sub>6</sub> with H<sub>2</sub>NCONH<sub>2</sub>

Over a period of several days under dynamic vacuum, the yellow viscous liquid slowly solidified. While recording its Raman spectrum, it was observed that the 'heating effect' of the laser caused sublimation, with bright yellow crystalline material being deposited at the top of the FEP tube. The Raman and IR data of both the initial and sublimed material along with the published spectra of molybdenum tetrafluoride and pentafluoride are given in Table 6.1. Comparison of the spectra suggests that the initial product is molybdenum pentafluoride contaminated with molybdenum tetrafluoride and possibly other fluorides, while the sublimed material is pure molybdenum pentafluoride. This was confirmed by X-ray powder photography. Mass spectra of the sublimed material showed the expected splitting pattern up to and including MoF<sub>5</sub><sup>+</sup> along with peaks associated with molybdenum oxyfluoride species. This may be explained in terms of the method employed in introducing the sample into the spectrometer, since the capillary

TABLE 6.1

Vibrational spectra of the solid products isolated from reactions between molybdenum hexafluoride and urea

MoF <sub>6</sub> [410]		MoF <sub>6</sub> [411]	Initial Product		Sublimed Product	
Raman	IR	IR	Raman	IR	Raman	IR
759 vs	970 w 890 w 845 w		763 vs 757 sh		762 vs	
746 sh 737 vs	745 vs	738 m,sh 731 s,sh 723 s	739 s	750 vs 740 sh	735 vs	750 vs
704 s 696 vs	698 vs			720 sh 710 vs	701 s	700 vs
563 w	647 vs	554 m,br	525 m,br	545 m,br		655 sh 510 m,br
406 w	520 w 480 vw		453 w,br 421 w,br		410 w,br	
294 w 250 sh 241 s			364 w			
	200 m 160 m		264 sh 239 m 227 w		254 sh 235 s	
			165 w		182 m	

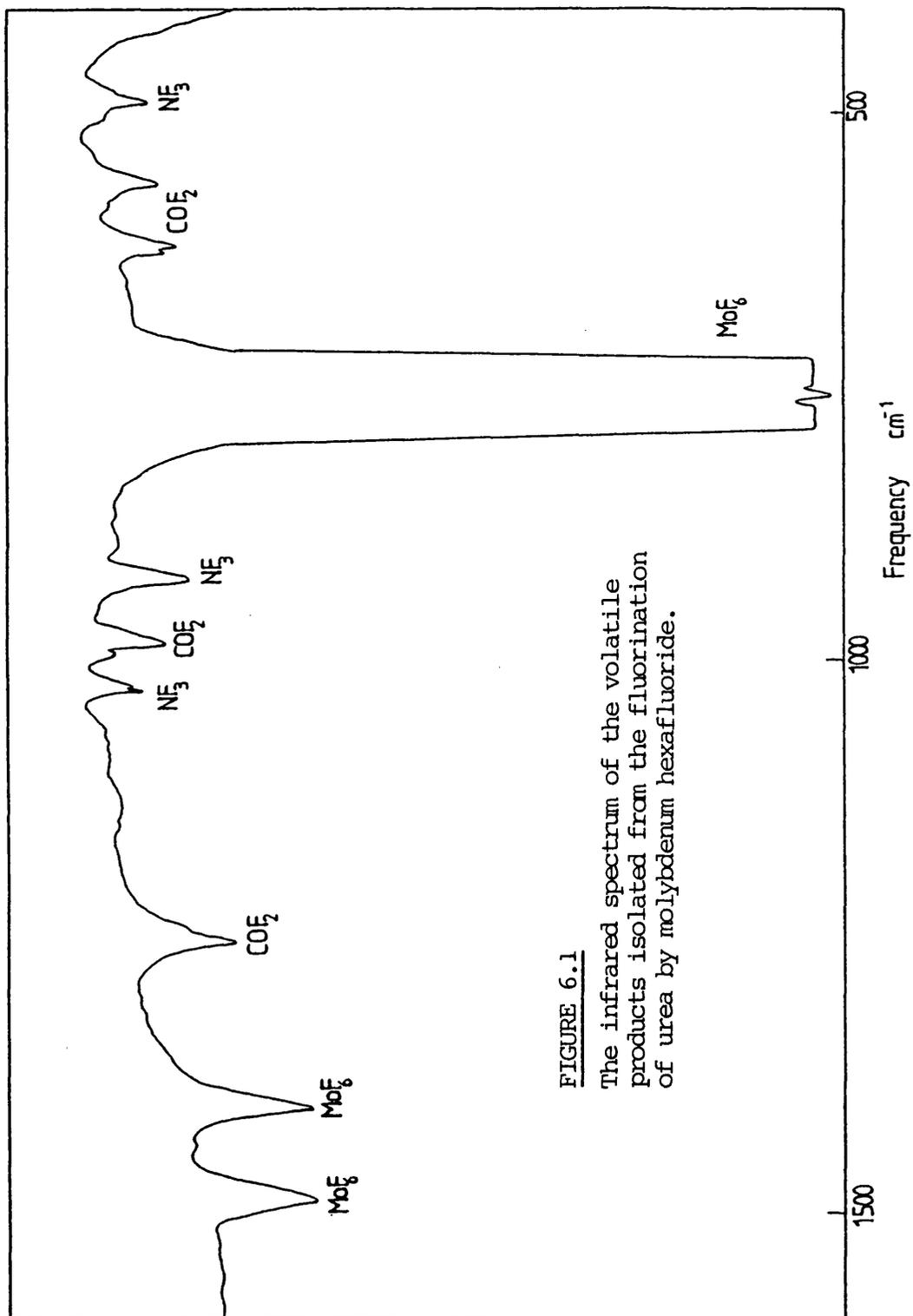
containing the sample must be broken in the atmosphere before insertion into the mass spectrometer ionisation chamber.

### 6.1.3 Volatile Products

The infrared spectra of the volatile products obtained from the fluorination of urea by both uranium and molybdenum hexafluorides were identical. The position of the absorptions in a typical spectrum [Fig. 6.1] are shown in Table 6.2 and clearly indicate the presence of hydrogen fluoride, nitrogen trifluoride and carbonyl fluoride, as well as unreacted molybdenum hexafluoride. The vibrational-rotational band of monomeric hydrogen fluoride consisted of a series of lines separated by approximately  $40\text{ cm}^{-1}$  centred around  $3960\text{ cm}^{-1}$ . During earlier experiments when only a 2-4 fold excess of the hexafluoride was present, the volatile products occasionally detonated when being condensed into a separate FEP tube. This suggests the presence of  $\text{HNF}_2$  and/or  $\text{H}_2\text{NF}$  which are thermally unstable and are known to explode when rapidly cooled [405]. No attempt was made to confirm the presence of these volatiles.

### 6.1.4 Discussion

The differences in the fluorinating ability of the hexafluorides of uranium and molybdenum hexafluorides compared with tungsten hexafluoride is clearly demonstrated by their chemical behaviour towards urea. Presumably, the hexafluorides initially attack the weakest link in the urea molecule, the C-N bonds, to form carbon monoxide, hydrogen fluoride and fluoro-substituted derivatives of urea,  $\text{HNF}_2$  and  $\text{H}_2\text{NF}$ . When a large excess of the hexafluoride is present, nitrogen trifluoride, carbonyl fluoride and hydrogen fluoride are the observed volatile products. Thus the reactions of the hexafluorides of uranium and



**FIGURE 6.1**

The infrared spectrum of the volatile products isolated from the fluorination of urea by molybdenum hexafluoride.

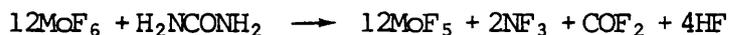
TABLE 6.2

Infrared stretching frequencies ( $\text{cm}^{-1}$ ) of the volatile products formed during the fluorination of urea by molybdenum hexafluoride at room temperature

Observed	MoF <sub>6</sub> [280]	COF <sub>2</sub> [412]	NF <sub>3</sub> [413]
3960 <sup>a</sup>			
1930		1928 $\nu_2$	
1480	1479 $\nu_1 + \nu_3$		
1390	1390 $\nu_2 + \nu_3$		
1250		1249 $\nu_4$	
1035			} 1031 $\nu_1$
1030			
970		965 $\nu_1$	
910			907 $\nu_3$
		774	
740	741 $\nu_3$		
640			642 $\nu_2$
635		} 626 $\nu_3$	
620			
580		584 $\nu_5$	
505			} 497 $\nu_4$
495			
490			

<sup>a</sup> see text

molybdenum with urea can be represented by the equations:-



The failure of tungsten hexafluoride to react with urea was surprising since it has been used for the selective fluorination of many organic compounds [414-417].

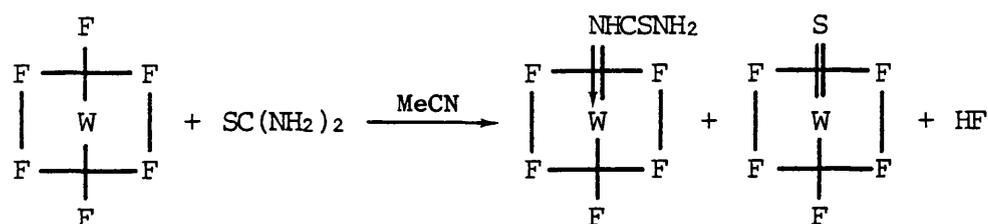
## 6.2 PREPARATION OF MF<sub>5</sub>.2L (M=U, Mo, W; L=thiourea) COMPLEXES

### 6.2.1 Introduction

Uranium hexafluoride is reported to be reduced by thiourea in acetonitrile at ambient temperatures to yield a pale green complex; UF<sub>5</sub>.2SC(NH<sub>2</sub>)<sub>2</sub>. Vibrational data of the adduct suggested that thiourea

is coordinated to the uranium through the sulphur atom [62]. This adduct is the only reported uranium fluorine species containing a uranium-sulphur bond and clearly, in light of the work discussed in Chapter 4, warranted reinvestigation.

The interaction between tungsten hexafluoride and thiourea has been characterised on the basis of  $^{19}\text{F}$  nmr spectroscopy alone from which the following reaction scheme was proposed [71]:-



In this case, coordination through the nitrogen is inferred.

### Present Study

#### 6.2.2 MF<sub>6</sub> (M=U, Mo, W) with thiourea in acetonitrile

##### Summary

Vibrational, esr and  $^1\text{H}$  nmr spectroscopy, mass balance and chemical analysis has established that the hexafluorides of uranium, molybdenum, and tungsten are all reduced by thiourea in acetonitrile, yielding complexes which can be represented by the general formula;  $\text{MF}_5 \cdot 2\text{L}$  (M=U, Mo, W; L=thiourea). The available data has also established that thiourea acts as a unidentate ligand and that coordination to the metal occurs via one of the nitrogen atoms.

An excess of the desired hexafluoride was condensed onto a mixture of vacuum dried thiourea in acetonitrile in prefluorinated FEP tubes at  $-196^\circ\text{C}$ . The systems were allowed to warm to room temperature with constant mixing. Rapid reactions occurred at ambient temperatures with the formation of dark viscous liquids from which non-volatile solids

were isolated upon removal of the solvent and the excess of hexafluoride by vacuum distillation.

### 6.2.3 IR Spectroscopy

The IR data for the three adducts are given in Table 6.3 along with the assigned spectrum of pure thiourea. The spectra are all similar but, due to their complexity, they cannot be confidently assigned, except for the  $\nu(\text{N-H})$  str. modes centred around  $3330\text{ cm}^{-1}$ .

No hydrogen fluoride was observed in the IR of the volatile products which, along with the spectra of the adducts, indicate that the  $-\text{NH}_2$  groups in the coordinated thiourea remain intact.

One of the most striking features of the spectra of the adducts are the group of peaks in the  $1000\text{-}1700\text{ cm}^{-1}$  region. These bands cannot be definitively assigned but it is worth noting that pure thiourea possesses four strong vibrational bands at  $1086$ ,  $1413$ ,  $1473$  and  $1673\text{ cm}^{-1}$  assigned to  $\delta(\text{N-H})$ ,  $\nu(\text{C-S})$  str.,  $\nu(\text{C-N})$  str. and  $(\text{N-H})$  bending modes respectively [418,419]. In the adducts, the two nitrogen atoms in the coordinated thiourea have differing chemical environments which will cause the above stretching and bending modes to be both split and shifted. These bands will be shifted to both higher and lower frequencies compared with the neutral molecule depending upon whether the  $-\text{NH}_2$  in coordinated thiourea is free or coordinated to the metal.

Broad absorptions were observed in the  $500\text{-}600\text{ cm}^{-1}$  region for all the adducts, which is the region where both metal-fluorine stretches; in-plane skeletal deformations and out-of-plane vibrations of thiourea occur. Exposure of the solids to the atmosphere simplified the spectra in this region with the disappearance of the  $\nu(\text{M-F})$  str. and the appearance of  $\nu(\text{M=O})$  str. at approximately  $1000\text{ cm}^{-1}$ , plus the distinctive spectrum of thiourea.

TABLE 6.3

Infrared data for MF<sub>5</sub>.2L complexes

Thiourea [418, 419]	UF <sub>5</sub> .2L	MoF <sub>5</sub> .2L	WF <sub>5</sub> .2L	Assignment
3365 s	3400	3400	3390 sh	$\nu_{13}$ ; $\nu(\text{NH})b_2$
3258 s			3330 m-	$\nu_1$ ; $\nu(\text{NH})a_1$
3157 s	m-,br	m-,br	3240 w+	$\nu_{14}$ ; $\nu(\text{NH})b_2$
3097 sh	3100	3100	2975 w	$\nu_2$ ; $\nu(\text{NH})a_1$
2670 w				comb. ( $\nu_4 + 2\nu_{11}$ )
2119 w				comb. ( $\nu_9 + \nu_{15}$ )
2045 w				comb. ( $\nu_4 + \nu_{11}$ )
1826 w				comb. ( $\nu_5 + \nu_6$ )
	1675 m-	1710 w-	1670 m,br	
	1664 m-	1670 m-		
	1625 m-	1650 m-	1620 sh	
1617 s		1620 m-		$\nu_3$ ; $\delta(\text{N-H})a_1$ ; $\nu_{15}$ ; $\delta(\text{N-H})b_2$
1473 s				$\nu_{16}$ ; $\nu(\text{C-N})b_2$
1413 s				$\nu_4$ ; $\nu(\text{C-S})a_1$
	1405 m	1410 m	1414 m	
	1390 m		1380 m	
1205 w				comb. ( $\nu_8 + \nu_{11}$ )
	1170 w	1170 w	1165 w-	
	1100 m	1095 m	1095 m-	
1086 s				$\nu_5$ ; $\rho(\text{NH})a_1$ ; $\nu_{17}$ ; $\rho(\text{NH})b_2$
	1020 m-	1015 m-	1020 m-	
		1005 sh		
	960 m-	950 m-	994 m-	
		790 w-	795 w-	
730 s				$\nu_6$ ; $\nu(\text{C-N})a_1$
	745 m-	745 m-	745 w+,br	
	695 w			
	675 m			
			655 sh,s	$\nu(\text{M-F})$
629 s				$\nu_{11}$ ; $\beta(\text{SCNN})b_1$
			625 s,br	$\nu(\text{M-F})$
	525 s,br	515 s,br		$\nu(\text{M-F})$
		580 s,br		$\nu_{18}$ ; $\delta(\text{CN})b_2$
486 s,br			480 w-	
	458 w			$\nu_7$ ; $\delta(\text{CN})a_1$
463 sh,br		418 w		
411 m		395 w		$\nu_{12}$ ; $\tau(\text{NH})b$

#### 6.2.4 ESR/NMR Spectroscopy

Esr and nmr spectra were recorded on solutions of the adducts in dry acetonitrile in sealed FEP tubes. The esr spectra of the solutions showed the typical response for uranium(V), molybdenum(V), and tungsten(V) species. No hyperfine coupling was observed for any of the species.

Proton nmr spectra of the complexes showed that there are two types of protons present [Fig. 6.2], equal in number, which gives further evidence for the coordination of one of the  $-NH_2$  groups in thiourea to the metal atom. Since the metal atom (oxidation state V) in the

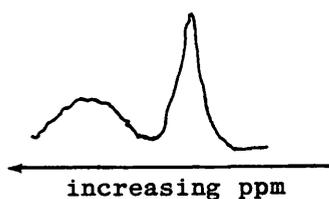


Figure 6.2

complexes is paramagnetic, the protons furthest away give a much sharper response than those bound to the nitrogen atom involved in the coordination to the metal.

The  $^{19}F$  nmr spectra of the complexes were recorded at low temperatures ( $\sim 15^\circ C$ ), but showed only broad intense signals which could not be resolved. Attempts to follow the reactions by  $^{19}F$  nmr spectroscopy were also unsuccessful even at low temperatures.

#### 6.2.5 Discussion

The hexafluorides of uranium, molybdenum, and tungsten are reduced to oxidation state V by thiourea in acetonitrile at room temperature. A mass balance on the systems showed that two molecules of thiourea react with one molecule of the hexafluoride in each case. Infrared and  $^1H$  nmr spectra of the complexes established that the  $-NH_2$  groups of co-

ordinated thiourea remain intact. Only one of the  $\text{-NH}_2$  groups of thiourea is involved in coordination to the metal via the lone pair of electrons on the nitrogen atom. Chemical analysis confirmed that the complexes can be represented by the general formula;  $\text{MF}_5 \cdot 2\text{L}$  [Table 6.4]. A balanced equation for the reactions cannot be written since a fluorine atom cannot be accounted for. However, this phenomenon has been previously observed during studies of the reactions of metal hexafluorides in solution [99].

Since the results of this study differ in some aspects with those previously reported [6.2.1], some explanation is clearly required. The only difference in the results of this investigation of the  $\text{UF}_6\text{-H}_2\text{NCSNH}_2\text{-MeCN}$  system compared with those of a previous study [62] is the type of coordination present in the  $\text{UF}_5 \cdot 2\text{L}$  complex. On the basis of far infrared data ( $150\text{-}400\text{ cm}^{-1}$ ), the Russians concluded that thiourea is coordinated to the uranium through the sulphur atom. Since they characterised this system only by far infrared spectroscopy and chemical analysis, little evidence seems to be given to support this conclusion.

There are, however, major disagreements in the results of this study of the  $\text{WF}_6\text{-H}_2\text{NCSNH}_2\text{-MeCN}$  system compared with those of a previous investigation [71]. Comparison of experimental data is impossible since no solid products were isolated; the reaction system being characterised on the basis of  $^{19}\text{F}$  nmr spectroscopy alone. Little evidence is given to support their interpretation of the spectra. The reasoning behind the assignment of the group of signals ( $\text{A}_4\text{X}$ -type) to  $\text{WF}_5(\text{HNCSNH}_2)$  is especially puzzling. Also, it is difficult to envisage a mechanism by which both  $\text{WF}_5(\text{HNCSNH}_2)$  and  $\text{WSF}_5^-$  can be formed from interactions between tungsten hexafluoride and thiourea in acetonitrile.

TABLE 6.4

Chemical analysis of the ternary adducts  
 Found (calculated)

Compound	Carbon	Hydrogen	Nitrogen	Fluorine	Colour
Cu[UF <sub>6</sub> ] <sub>2</sub> .5MeCN	12.35 (12.35)	1.64 (1.55)	6.98 (7.20)	22.08 (23.43)	Pale blue
Cu[UF <sub>6</sub> ] <sub>2</sub> .6MeCN	13.06 (14.22)	1.69 (1.79)	7.69 (8.29)	22.72 (22.49)	Green
Zn[UF <sub>6</sub> ] <sub>2</sub> .4MeCN	10.22 (10.29)	1.43 (1.3)	5.85 (6.00)	23.74 (24.42)	Pale green
Zn[UF <sub>6</sub> ] <sub>2</sub> .5MeCN	11.63 (12.32)	1.56 (1.55)	6.97 (7.19)	23.62 (23.4)	Green

Clearly, insufficient data and evidence is given by previous workers to support the majority of their conclusions.

In this study, a wide range of techniques ( $^1\text{H}$  nmr, esr, mass balance, IR, and chemical analysis) were used to characterise the  $\text{MF}_6\text{-H}_2\text{NCSNH}_2\text{-MeCN}$  systems with all the available data suggesting that the solid products isolated from these reactions can be represented by the general formula,  $\text{MF}_5\cdot 2\text{L}$ .<sup>†</sup> Thus the claim that a uranium fluorine species containing a uranium-sulphur bond is formed from the reaction between uranium hexafluoride and thiourea appears to be incorrect.

---

N.B.

<sup>†</sup> Nevertheless, this is somewhat surprising since the proposed general formula of the complexes suggests 7-coordinate uranium, molybdenum and tungsten.



CHAPTER  
7

Sorption

## 7.1 INTRODUCTION

Sorption is the most researched non-distillative method for the purification of uranium hexafluoride [225-228,231,232,263,264,420-431]. Most of the studies on the sorptive purification of uranium hexafluoride have been carried out almost exclusively in fixed-bed systems where pellets of the sorbent are held in towers or trays under static or dynamic flow conditions.

Most investigations of sorbent systems start with 'scoping tests', which are, in effect, screening trials, used to determine the suitability of a particular material as a sorbent. These tests are usually carried out in static conditions with only one contaminant present. The relative capability of the sample material to selectively sorb significant quantities of an impurity during the preliminary exposure determines whether the proposed sorbent undergoes further testing. The purpose of this present study was to investigate the sorption of liquid hexafluorides on various materials, since work on liquid phase sorption has either not been carried out or has not been reported.

## 7.2 ABSORPTION, ADSORPTION AND SORPTION

The uptake of gases by solids may be divided into two types: that of adsorption, where the gas is retained on the surface of the solid, and that of absorption where the interior of a non-porous solid is penetrated. Study of adsorption, both theoretically and experimentally, has been widespread while only rudimentary data is available on the somewhat more complicated process of absorption.

Adsorption itself can be further divided into physical adsorption and chemisorption. In physical adsorption the adsorbed gas is held to

the solid surface by relatively weak Van der Waal-type forces. This type of adsorption is similar to the condensation of a pure vapour in that in both processes the rate is almost instantaneous. A second similarity is that the quantity of heat released on adsorption is approximately the latent heat of vapourisation (5-10 kcal/mol) of the adsorbing material.

Chemisorption more closely resembles a chemical reaction than condensation. The binding forces between the gas and the solid are normally stronger than those in physical adsorption; this is reflected in the heat of adsorption, which is usually greater than 10 kcal/mol but less than the heat of reaction for typical chemical reactions, which is about 100 kcal/mol. Chemisorption normally proceeds at a rate which is lower than that of physical adsorption and, in most cases, an activation energy is observed as in most chemical reactions.

Adsorption normally results in the deposition of a monolayer or, at most, a few monolayers of the adsorbing gas whereas absorption often results in complete reaction of the original solid.

Experimentally it is often difficult to differentiate between absorption and adsorption processes, especially when only a small quantity of gas is retained on the solid. In order to alleviate this problem the term 'sorption' which is an abbreviation of both absorption and adsorption has become widely used to describe such systems and will be used throughout this Chapter. Sorption is also used in a general sense in many of the reports referred to in this Chapter and can be understood to mean absorption, adsorption, chemisorption or any combination of all three as appropriate.

The principles underlying physical adsorption, chemisorption and absorption are still to this day not completely understood which appears

to be borne out by the dearth of theoretical papers.

### 7.3 GAS-SOLID REACTIONS (e.g. absorption of a gas by a sorbent)

In any gas-solid reaction, the following general steps must be taken into consideration:-

- ( i ) initial reaction on the surface of the solid,
- ( ii ) adsorption of the gas onto the product,
- (iii) transport of unreacted material to the reaction interface,
- ( iv ) reaction at the interface.

The gaseous molecules strike the surface with rapid complex formation. This process probably occurs on active surface sites, i.e. small areas of high potential energy. From these nuclei, further reaction occurs by surface diffusion until the entire surface is covered by a layer of the complex. At the same time, there may be some penetration of the solid, but the rate is much slower than the lateral growth because of the retarding effect of the complex formed. After the surface reaction is complete the gas must be adsorbed onto the complex in order for further reaction to take place. There must also be a diffusion of material through the complex so that further growth can occur at either the complex/gas or complex/solid interface. Thus different rates of sorption, reaction mechanisms, rate determining steps occur depending upon the gas, the sorbent and its physical state.

Nearly all of the available data on the rates of sorption can be represented by one of three relationships:-

- ( i ) Linear law:- where the rate of sorption is controlled by the rate of reaction between the gas and the sorbent.
- ( ii ) Parabolic law:- where the rate of sorption is inversely proportional to the thickness of the reaction product.
- (iii) Logarithmic law:- where the rate of sorption decreases exponentially with the quantity of the gas sorbed.

Presumably the sorption of liquids by solids are governed by similar mechanisms and relationships.

#### 7.4 SORBENT PREPARATION

Sorbent temperature, depth of pellet bed, flow velocity, sorbent surface area and residence time can all influence the sorption of a particular material. The physical structure of the sorbent pellet plays an important rôle in determining the sorption characteristics of a material. Too much attention is often focussed on the material from which the pellets are fabricated, whilst the forming and heat treating processes which the pellets undergo are generally ignored. Sorbent preparation, however, has often been quoted as being the single most important factor that influences sorption efficiency. A summary of reported sorbent pre-treatments is given in Table 7.1. The importance of the physical structure of sodium fluoride in the sorption of uranium hexafluoride has been well defined [427] and, presumably, the underlying theory developed in this study can be generalised to include other sorption systems.

#### 7.5 SORBENT SELECTION

It is desirable that the sorbent pellets formed are not only suitably reactive and porous, but that they be mechanically strong enough to withstand repeated use without deterioration. An efficient sorbent pellet must also have a high surface to volume ratio, high void fraction and be sufficiently active to be able to withstand variations of feed gas impurity content.

The material from which potential pellets are fabricated must ideally be inexpensive and available in bulk. Uranium retention and

TABLE 7.1

## Sorbent Pretreatments

PELLET TYPE	STARTING MATERIAL	FORMING	PREPARATIVE METHOD		DRYING	SURFACE AREA (m <sup>2</sup> /g)	REFERENCE
			SINTERING	FLUORINATING			
Na <sub>3</sub> AlF <sub>6</sub>	cryolite	tumble 1% stearic acid 10% water		N <sub>2</sub> , F <sub>2</sub> , 350°C 3 hours		0.54	[420]
Na <sub>3</sub> AlF <sub>6</sub>	cryolite	extruded 1% stearic acid 10% water	air	dry ambient Ar, F <sub>2</sub> , 200°C 2-4 hours		1.68	[421]
MgF <sub>2</sub>	MgF <sub>2</sub>	tumble 1-2% stearic acid 10-12% water	N <sub>2</sub> , 400-600°C 3-5 hours	F <sub>2</sub> , 250°C several hours	N <sub>2</sub> , 400-500°C		[422]
MgF <sub>2</sub>	MgF <sub>2</sub>	tumble			N <sub>2</sub> , > 350°C	44	[423]
MgF <sub>2</sub>	MgF <sub>2</sub>	tumble	N <sub>2</sub> , 400°C 2 hours	F <sub>2</sub> , 120°C 2 hours		44	[424]
MgF <sub>2</sub>	MgF <sub>2</sub>	granulate (5-10% water)	N <sub>2</sub> , 100-300°C	ClF <sub>3</sub> ; < 300°C	vacuo 350°C 2-3 hours		[425]
MgF <sub>2</sub>	MgF <sub>2</sub>	tumble (5% water)	in air	with F <sub>2</sub>	in N <sub>2</sub>	111	[426]
CaF <sub>2</sub>	drierite	compaction		F <sub>2</sub> , several hours		200	[423]
CaF <sub>2</sub>	CaSO <sub>4</sub>			with F <sub>2</sub>			[424]

the optimum operating temperature must also be taken into consideration from an economic standpoint. In essence, an efficient sorbent for impurities in uranium hexafluoride must also be an inefficient sorbent for uranium hexafluoride itself.

7.6 SORPTION OF  $UF_6$ ,  $MoF_6$ ,  $WF_6$  FROM THE MELT BY SODIUM FLUORIDE;  
Table 7.2

Sodium fluoride has received more attention than any other sorbent for the sorption of the hexafluorides of uranium, molybdenum and tungsten from the gas phase. The previous work on these systems is discussed in some detail in Chapter 1.

PRESENT STUDY

A known quantity of vacuum-dried sodium fluoride powder was introduced into a prefluorinated sealed nickel or stainless steel reactor and pre-treated by heating in an atmosphere of fluorine to 300°C for several hours. Upon cooling, and evacuation to high vacuum, a sufficient excess of the desired hexafluoride to ensure the presence of liquid at 100°C was condensed onto the pre-treated sodium fluoride at -196°C. The systems were allowed to warm slowly to room temperature prior to being heated to 100°C by means of a thermostatically controlled furnace. Since it is reported that the maximum sorption of both uranium and molybdenum hexafluorides by sodium fluoride occurs at 100°C, all reactions discussed here were carried out at this temperature. Contact times varied between 2-4 hours. The reactors were evacuated upon cooling until a constant vapour pressure was attained. The weight changes associated with the sorption processes indicated that the sodium fluoride retained only approximately 1% by weight of the metal hexafluorides.

TABLE 7.2

Sorption of uranium and molybdenum hexafluorides by sodium fluoride

Impurity	Carrier Gas	Sorption Temp. °C	Desorption Temp. °C	Remarks	Reference
UF <sub>6</sub>	N <sub>2</sub>	100	400	~100 wt. % recovery in 10 mins. at 400°C	[232]
UF <sub>6</sub>	BrF <sub>3</sub> /BrF <sub>5</sub>	150		complete sorption, severe caking	[429]
UF <sub>6</sub>	N <sub>2</sub>	150	300-400	good sorbent, good recovery	[430]
UF <sub>6</sub>	none	<180		very efficient	[228]
UF <sub>6</sub>	none	200	350-500	good sorption and recovery	[231]
UF <sub>6</sub>	N <sub>2</sub>	100-150		efficiency decreases with no. of cycles	[235]
UF <sub>6</sub>	N <sub>2</sub>	30-100		good performance	[427]
UF <sub>6</sub>	N <sub>2</sub>	100		at low U concentrations, sorption is determined by flow rate	[431]
MoF <sub>6</sub>	none	100	300-400	maximum sorption rate at 100°C	[232]
MoF <sub>6</sub>	N <sub>2</sub> /UF <sub>6</sub>	100	150	desorbs whilst UF <sub>6</sub> is retained on pellets	[420]
MoF <sub>6</sub>	N <sub>2</sub> /UF <sub>6</sub>	100	150-400	similar sorption properties to UF <sub>6</sub>	[244]
MoF <sub>6</sub>	UF <sub>6</sub>	100		high U loadings on pellets	[255]

Sorption of uranium hexafluoride by sodium fluoride resulted in a pale yellow product whereas both molybdenum and tungsten hexafluorides yielded white products. The IR spectra of the non-volatile, highly air sensitive solids are shown in Table 7.3. Since the complexes were only obtained in low yields, structural analysis by X-ray powder diffraction was impossible. Attempts to obtain pure samples of the complexes by increasing the stoichiometric excess of the hexafluoride were unsuccessful.

It has been reported that molybdenum hexafluoride can be separated from uranium hexafluoride by joint sorption at 100°C followed by selective desorption at 150°C [244,245]. This procedure was repeated in a static system using equimolar quantities of the hexafluorides. Sodium fluoride powder was used rather than pellets due to its higher surface area. It was pre-treated by the same method as described above.

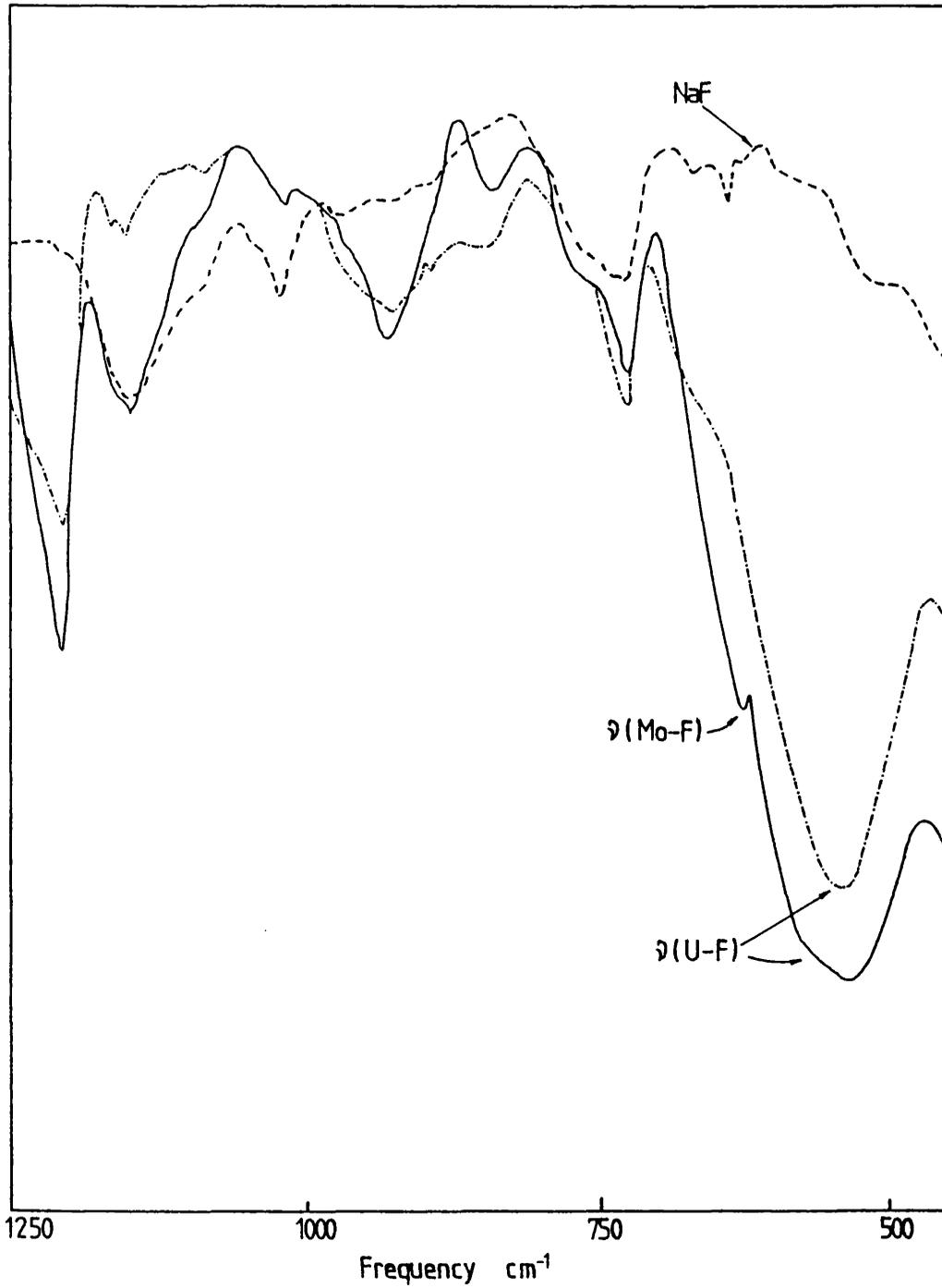
Sorption and desorption of the hexafluorides on sodium fluoride was followed by IR spectroscopy, since the weight changes associated with the processes were too small to be meaningful. When the  $UF_6$ -NaF- $MoF_6$  complex was heated to 150°C, a small quantity of a gas was evolved which was identified by IR spectroscopy as molybdenum hexafluoride. The amount of gas evolved was insufficient to be accurately measured.

Comparison of the IR spectra of the complexes [Table 7.3; Fig. 7.1] clearly show that both molybdenum and uranium hexafluorides are sorbed on sodium fluoride at 100°C since the  $\nu_3$  vibrations associated with the metal hexafluoroanions at 620 and 515  $cm^{-1}$  respectively are present. The disappearance of the band at 620  $cm^{-1}$  suggests that little molybdenum hexafluoride remains after the complex had been heated to 150°C. This is in agreement with the claims made by other workers [244,245].

TABLE 7.3

Infrared spectra (1350-450  $\text{cm}^{-1}$ ) of the complexes formed from the sorption of liquid uranium, molybdenum and tungsten hexafluorides by sodium fluoride powder at 100°C

UF <sub>6</sub> /NaF complex	MoF <sub>6</sub> /NaF complex	WF <sub>6</sub> /NaF complex	Assignment
1310 w 1210 m 1170 vw 1165 vw 1025 w 925 w,br 725 m-	1305 w 1210 m  1020 w 920 w 720 w 670 m- 620 vs,br	1300 vw 1200 m  1015 w 915 w 720 w  595 s,br	$\nu_3$ [MoF <sub>6</sub> ] <sup>-</sup> $\nu_3$ [WF <sub>6</sub> ] <sup>-</sup> $\nu_3$ [UF <sub>6</sub> ] <sup>-</sup>
515 vs,br			



**FIGURE 7.1**

Infrared spectra (1250-450 cm<sup>-1</sup>) showing the effect of heating the complex formed from the joint sorption of liquid uranium and molybdenum hexafluorides by sodium fluoride powder at 100°C.

## 7.7 SCOPING TESTS

Scoping tests were carried out on various materials;  $MgF_2$ ,  $CaF_2$ ,  $Na_3AlF_6$ ,  $MgF_2 + 5\% NiF_2$ ,  $BaF_2$ , supplied by British Nuclear Fuels plc. These tests were carried out in static systems, with the metal hexafluorides ( $UF_6$ ,  $MoF_6$ ,  $WF_6$ ) in the liquid phase. Table 7.4 summarises the previous work on the sorptive capabilities of the above potential sorbents. The following procedure was used for all the present tests:-

*— The sorbent pellets were dried at elevated temperatures under dynamic vacuum and heated to 300°C in an atmosphere of fluorine prior to being introduced into a nickel bucket contained in a prefluorinated nickel or stainless steel reactor. An excess of the appropriate hexafluoride was condensed onto approximately 0.2g of the sorbent. The sorbent-sorbate systems were heated by means of a thermodynamically controlled water bath to 80±2°C for one hour. After cooling, the reactors were evacuated to high vacuum and the exposed pellets were sealed in seasoned FEP tubes and sent to British Nuclear Fuels plc for chemical analysis.*

The results of the scoping tests indicated preferential retention of molybdenum and tungsten on cryolite [Table 7.5].

TABLE 7.4

Sorption of uranium and molybdenum hexafluorides by various sorbents

Sorbent	Impurity	Carrier Gas	Sorption Temp. °C	Desorption Temp. °C	Remarks	Reference
MgF <sub>2</sub>	MoF <sub>6</sub>	UF <sub>6</sub> + other volatile fluorides	65-100		sorbent can be regenerated by water wash	[246]
MgF <sub>2</sub>	UF <sub>6</sub>	N <sub>2</sub>	20		physical sorption - monolayer	[261]
BaF <sub>2</sub>	MoF <sub>6</sub>	N <sub>2</sub> + mixed volatile fluorides	100-300		only partial sorption	[428]
BaF <sub>2</sub>	UF <sub>6</sub>	N <sub>2</sub>	>157	>220 (decomp.)	poor sorbent	[247]
NiF <sub>2</sub>	NbF <sub>5</sub>	N <sub>2</sub> /UF <sub>6</sub>	120		down to 1 ppm in outlet, no U retention	[422]
NiF <sub>2</sub>	TiF <sub>4</sub>	N <sub>2</sub> /UF <sub>6</sub>	120		down to 1 ppm in outlet gas stream	[422]

TABLE 7.5

The results of the scooping tests

Test Material	B/M Time	Granulating Additive	Sintering Temp. °C	Sintering Time	Resulting Granules	% Uranium Retention	% Molybdenum Retention	% Tungsten Retention
MgF <sub>2</sub>	Nil	Water	800	5 mins.	strong, porous	0.9	0.42	0.33
CaF	Nil	Dilute Celacol	1000	5 mins.	strong	0.1	0.35	0.084
BaF <sub>2</sub>	2 hrs.	Saturated Starch solution	1000	2 mins.	small, strong	0.1	0.101	0.065
MgF <sub>2</sub> + 5% NIF <sub>2</sub>	½ hr.	1% Stearic Acid [solid]	1150-1200	5 mins.	strong	0.2	0.096	0.198
Na <sub>3</sub> AlF <sub>6</sub>	2 hrs.	2% Celacol Powder	700	5 mins.	small, strong	0.3	8.97	8.69



# CHAPTER 8

The Chemistry of Ruthenium Fluorides:  
Investigation of Methods of Removal of  
traces of  $\text{RuF}_5$  from mixtures of  
Volatile Fluorides

## 8.1 RUTHENIUM FLUORIDES: A REVIEW

The known fluorine derivatives of ruthenium include five binary fluorides;  $\text{RuF}_3$ ,  $\text{RuF}_4$ ,  $\text{RuF}_5$ ,  $\text{RuF}_6$ ,  $\text{RuF}_8$ ; an oxide fluoride,  $\text{RuOF}_4$  and complex salts of three anions;  $[\text{RuF}_6]^{3-}$  (K);  $[\text{RuF}_6]^{2-}$  (Na, K, Rb, Cs, Ba);  $[\text{RuF}_6]^-$  (NO, Li, Na, K, Rb, Cs, Ca, Ba, Sr, Ag, Tl). There are no reports of any complex oxide fluorides.

### 8.1.1 Ruthenium Trifluoride

Ruthenium trifluoride is the non-volatile product from the reduction of ruthenium pentafluoride in an alumina tube by iodine at  $150^\circ\text{C}$  or by elemental sulphur at  $200^\circ\text{C}$  [432]. The volatiles are removed over a period of up to 12 hours by pumping which not only removes impurities, but also promotes crystal growth. X-ray powder diffraction studies have shown that ruthenium trifluoride adopts a rhombohedral lattice, but the unit cell parameters vary according to the experimental conditions of preparation; Table 8.1.

TABLE 8.1

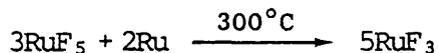
Lattice parameters of ruthenium trifluoride [433]

<u>Method of preparation</u>	<u>a(Å)</u>	<u><math>\alpha</math></u>
excess $\text{RuF}_5$	5.386	54.79
excess $\text{RuF}_5$	5.392	54.78
small excess $\text{I}_2$	5.403	54.67
large excess $\text{I}_2$	5.408	54.67
large excess S	5.407	54.66

Even though the differences between individual values are small, they are significant overall and it is considered [433] that the variation is caused by the presence in the lattice of cations with oxidation states other than III. On the basis of X-ray diffraction studies it has been suggested that ruthenium trifluoride consists of almost regular octahedra of F atoms about each Ru atom; the octahedra being

joined by the sharing of all corners [433].

The reduction of ruthenium pentafluoride by ruthenium metal at elevated temperatures also yields the trifluoride according to the equation [434]:-



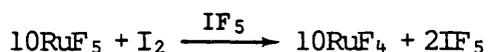
Since the heterogenous reduction with ruthenium metal is incomplete, twice the theoretical quantity of ruthenium pentafluoride is required [434].

Ruthenium trifluoride may also be prepared by the homogeneous reduction of the pentafluoride by perfluorocyclobutene in perfluoro-1,2-dimethyl cyclohexane at 70°C [434].

At 650°C, ruthenium trifluoride begins to disproportionate with the formation of a greenish-yellow sublimate, and is reported to melt at approximately 1000°C [434].

### 8.1.2 Ruthenium Tetrafluoride

When an excess of ruthenium pentafluoride dissolved in pure iodine pentafluoride is allowed to react with an approximately stoichiometric amount of iodine, reduction takes place with the formation of the tetrafluoride according to the equation:-



Little heat is evolved. It is essential that an excess of ruthenium pentafluoride is used, otherwise further reduction to the trifluoride occurs. Removal of the excess of ruthenium pentafluoride and iodine pentafluoride leaves a pale yellow residue of the relatively non-volatile ruthenium tetrafluoride. Imperfect crystals were obtained, probably due to the presence of iodine, and as a consequence, there is no available data on the crystal structure of the compound. It is

blackened immediately by moist air and is more reactive than ruthenium trifluoride, but can be conveniently handled in dry Pyrex [435].

Ruthenium tetrafluoride reacts violently with water depositing ruthenium dioxide, but no tetraoxide is formed. It attacks glass at temperatures greater than 280°C without melting, forming an unidentified volatile compound and a black residue. The observed magnetic moment of the tetrafluoride at ordinary temperatures is higher than the spin only value for two unpaired electrons [435].

### 8.1.3 Ruthenium Pentafluoride

Ruthenium pentafluoride was first prepared in 1925 by Ruff and Vidic [436] by the action of elemental fluorine on ruthenium sponge in a nickel or alumina reactor at an elevated temperature. This remains the most convenient synthetic method [432,434-436]. The analogous fluorination of ruthenium dioxide also yields the pentafluoride [437]. An alternative less satisfactory preparative technique is to treat ruthenium sponge with bromine trifluoride at room temperature. The reaction, which is vigorous, is moderated by the addition of bromine [438]. The product, besides the complex,  $\text{RuF}_5 \cdot \text{BrF}_3$  which decomposes to ruthenium pentafluoride at 120°C, also contains ruthenium oxide tetrafluoride which is difficult to completely separate from the pentafluoride.

The original melting and boiling points of ruthenium pentafluoride estimated by Ruff and Vidic [436] were too high; the revised values are given in Table 8.2.

Single crystal studies on ruthenium pentafluoride have shown that it adopts a tetrameric configuration with a distorted version of the molybdenum pentafluoride structure [Fig. 8.1]. It is monoclinic of

TABLE 8.2

Physical properties of ruthenium pentafluoride

Property	RuF <sub>5</sub>	Reference
M.pt.	86.5°C	[435]
B.pt.	227°C	[435]
Vapour pressure equation	$\log p = 9.54 - 3329/T$ (90-160°C)	[435]
Enthalpy of vapourisation $\Delta H_{\text{vap}}$ (kcal/mol)	15.23	[435]
Entropy of vapourisation $\Delta S_{\text{vap}}$ (cal/mol <sup>-1</sup> K <sup>-1</sup> )	30.5	[435]
Enthalpy of formation $\Delta H_f$ (kcal/mol)	-213.4±0.35	[439]

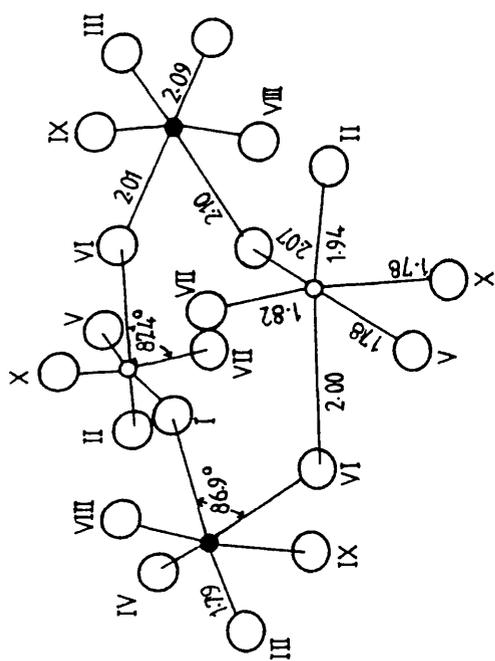


FIGURE 8.1

Crystal structure of  $\text{RuF}_5$  [436]

$\text{Ru}_I - \text{Ru}_I = 5.11 \pm 0.002 \text{ \AA}$

$\text{Ru}_{II} - \text{Ru}_{II} = 5.45 \pm 0.002 \text{ \AA}$

$\text{F}_I - \text{Ru}_I - \text{F}_{VI} = 87^\circ 22' \pm 2.5^\circ$

$\text{F}_I - \text{Ru}_{II} - \text{F}_{VI} = 86^\circ 52' \pm 2.5^\circ$

Average bridging bond length  $2.05 \text{ \AA}$

Average terminal bond length  $1.90 \text{ \AA}$

Average bond angle at bridging fluorine  
 $132^\circ$

dimensions,  $a = 12.47 \pm 0.01$ ,  $b = 10.01 \pm 0.1$ ,  $c = 5.42 \pm 0.01 \text{ \AA}$ ,  $\alpha = 99^\circ 50' \pm 30'$ , belong to the space group  $P2_1/a = C_{2h}^5$ ;  $z = 8$  [436] and has been shown by X-ray powder photography to be isostructural with  $\text{OsF}_5$ ,  $\text{RhF}_5$ ,  $\text{IrF}_5$ ,  $\text{PtF}_5$  and  $\text{AuF}_5$  [440].

The heat of formation of ruthenium pentafluoride has been determined by Hubbard et al. [439] to be  $-213.4 \text{ kcal/mol}$  from fluorine bomb calorimetry. Ruthenium pentafluoride forms a green solid and liquid and, apparently, a colourless vapour [435]. The liquid, especially if traces of impurities are present, readily supercools. Visible and UV absorption spectra suggests a near octahedral environment for the Ru atom in liquid ruthenium pentafluoride [441]. The magnetic moment of the pentafluoride is  $3.04 \text{ BM}$  at room temperature, which is very close to the spin only value expected for a  $d^3$  octahedral configuration [435].

The vapour pressure of liquid ruthenium pentafluoride has been determined [435] over the temperature range,  $90\text{-}160^\circ\text{C}$ , and the variation with temperature is given by:-

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

Ruthenium pentafluoride is sensitive to the smallest traces of atmospheric moisture, and rapidly blackens if any is present. It attacks glass above its melting point to form a black solid, and an unidentified red liquid, but is somewhat more stable in quartz [435]. With water, complete hydrolysis occurs with the formation of  $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ ,  $\text{RuO}_4$  and  $\text{HF}$  [438]. Presumably complex fluoroanions are initially formed (cf.  $\text{ReF}_5$ ,  $\text{OsF}_5$ ), but since  $(\text{RuF}_6)^-$  and  $(\text{RuF}_6)^{2-}$  are both decomposed by water, the hydrolysis can go to completion [438].

Ruthenium pentafluoride is reduced by iodine at  $150^\circ\text{C}$  or by elemental sulphur at  $200^\circ\text{C}$  to the trifluoride [432]. Under milder conditions, the pentafluoride is reduced by iodine in iodine pentafluoride to the tetra-

fluoride [435]. Ruthenium pentafluoride reacts with sulphur tetrafluoride to give the pink solid,  $\text{RuF}_5 \cdot \text{SF}_4$ , which melts at  $150^\circ\text{C}$  to give a red liquid [442]. In view of the low melting point of this adduct, it is possible that it is a covalent compound with fluorine bridges rather than a compound containing discrete ions. The known adducts of ruthenium pentafluoride are given in Table 8.3.

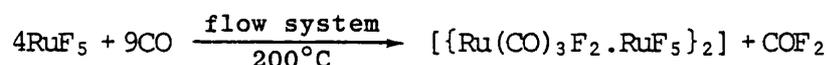
TABLE 8.3  
Adducts of ruthenium pentafluoride

<u>Adduct</u>	<u>M.pt °C</u>	<u>Colour</u>	<u>Reference</u>
$\text{RuF}_5 \cdot \text{BrF}_3$	120 dec.		[443]
$\text{RuF}_5 \cdot \text{SF}_4$	150	pale pink	[442]
$\text{RuF}_5 \cdot \text{XeF}_2$	115-125	pale yellow green	[444,445]
$(\text{RuF}_5)_2 \cdot \text{XeF}_2$	52-56	bright green	[444,445]
$\text{RuF}_5 \cdot (\text{XeF}_2)_2$	98-99	pale yellow green	[444]

The physical properties and Raman spectra of the  $\text{XeF}_2$  adducts of ruthenium pentafluoride can be interpreted in terms of the ionic structures,  $(\text{XeF})^+(\text{RuF}_6)^-$ ,  $(\text{XeF})^+(\text{Ru}_2\text{F}_{11})^-$  and  $(\text{Xe}_2\text{F}_3)^+(\text{RuF}_6)^-$  [444,446]. These  $\text{XeF}_2$  adducts were prepared in bromine pentafluoride solution [444]; the compounds  $\text{XeF}_2 \cdot \text{RuF}_5$  and  $(\text{RuF}_5)_2 \cdot \text{XeF}_2$  have also been prepared directly from the parent fluorides [445]. Attempts to synthesise and isolate  $\text{XeF}_4$  adducts of ruthenium pentafluoride have proved unsuccessful [445]. Also, it is reported that ruthenium pentafluoride reacts with  $\text{KrF}_2$  to form the adducts;  $\text{KrF}_2 \cdot \text{RuF}_5$  and  $\text{KrF}_2 \cdot (\text{RuF}_5)_2$  which, according to Raman spectroscopy, can be formulated as  $(\text{KrF})^+(\text{RuF}_6)^-$  and  $(\text{KrF})^+(\text{Ru}_2\text{F}_{11})^-$  respectively. The adducts are unstable in hydrogen fluoride forming  $\text{Kr}$ ,  $\text{F}_2$ ,  $\text{RuF}_5$  and they decompose rapidly in bromine pentafluoride [447].

In selenium tetrafluoride solution, ruthenium pentafluoride reacts with the 'base'  $\text{TlBrF}_4$  to give the salt  $\text{TlRuF}_6$  [438]. The reaction of

ruthenium pentafluoride with carbon monoxide in a flow system has been reported to yield a yellow-brown moisture-sensitive non-volatile solid of composition;  $[\text{Ru}(\text{CO})\text{F}_{3.5}]$  [448]:-



A further reaction occurs with carbon monoxide at high pressure (100 atm.) and temperature (200°C) to yield a pale involatile crystalline solid;  $[\text{Ru}(\text{CO})_3\text{F}_2]_4$  which has a tetragonal unit cell of dimensions,  $a = 11.055$ ,  $c = 9.376 \text{ \AA}$  [449].

#### 8.1.4 Ruthenium Hexafluoride

Ruthenium hexafluoride was first prepared in 1961 by the induction heating of ruthenium metal in fluorine at 300 mmHg pressure in a quartz reactor fitted with an internal cold finger to rapidly cool the product as it is thermally unstable [450]. The principle product, a dark red-brown solid obtained in 49% yield, was ruthenium hexafluoride. Small amounts of the pentafluoride also formed were removed by vacuum distillation [450].

Solid ruthenium hexafluoride undergoes a solid-state transition at 2.5°C [450]. The high temperature modification is cubic;  $a = 6.11 \pm 0.01 \text{ \AA}$  at 25°C,  $z = 2$  with a calculated density;  $D^{25} = 3.13 \text{ g/cm}^3$ . The low temperature modification is orthorhombic;  $a = 9.44 \pm 0.022$ ,  $b = 8.59 \pm 0.02$ ,  $c = 4.98 \pm 0.02 \text{ \AA}$  at -30°C, with a calculated density;  $D^{-30} = 3.50 \pm 0.03 \text{ g/cm}^3$  [451]. The hexafluoride melts at 54°C, but its boiling point cannot be accurately determined because of dissociation to the pentafluoride and fluorine, but it is known to form a red-brown vapour [450].

The vapour pressure of the solid hexafluoride over a selected temperature range [450] is given below:-

<u>Temp. °C</u>	0.0	4.6	8.6	11.1	14.4	17.6
<u>Pressure (mmHg)</u>	23	32	40	46	56	67

Although ruthenium hexafluoride is thermally unstable and is totally decomposed to the pentafluoride at 200°C, it can be stored for weeks at room temperature in nickel cans with only slight decomposition [450]. The hexafluoride rapidly attacks Pyrex at room temperature, but is less reactive in quartz [450].

In the gaseous state, ruthenium hexafluoride is monomeric from vapour density measurements and like the other transition metal hexafluorides it is octahedral, with  $O_h$  symmetry [452].

The IR spectrum between 230 and 4000  $\text{cm}^{-1}$  of the gaseous hexafluoride in equilibrium with the solid shows bands at 275 ( $\nu_4$ ), 735  $\text{cm}^{-1}$  ( $\nu_3$ ), with combination bands at 997 ( $\nu_3 + \nu_5$ ), and at 1410  $\text{cm}^{-1}$  ( $\nu_1 + \nu_3$ ), from which  $\nu_1$  and  $\nu_5$  were estimated as 675 and 262  $\text{cm}^{-1}$  respectively. Other bands were observed and are thought to be due to impurities [452].

Due to the difficulties in the preparation and long term storage of ruthenium hexafluoride, relatively few studies have been made on its chemical behaviour.

Antimony, arsenic and bismuth trifluorides reduce the hexafluoride to the pentafluoride [453]. A similar reduction occurs with hydrogen in anhydrous hydrogen fluoride [453]. Ruthenium hexafluoride has been shown to react with xenon [456] and oxidises water in hydrogen fluoride to give the oxonium salt;  $(\text{H}_3\text{O})^+(\text{RuF}_6)^-$  and oxygen [454], while the reaction with boric oxide (a popular reagent for the preparation of transition metal oxide fluorides from transition metal fluorides) in an inert solvent gave  $\text{RuF}_5$ ,  $\text{BF}_3$  and  $\text{O}_2$  as identifiable products [96].

Non-stoichiometric ruthenium mixed halides were obtained from reactions of the hexafluoride with boron trihalides [457]. Table 8.4

TABLE 8.4

## Reactions of Ruthenium Hexafluoride

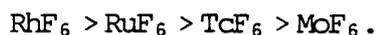
Reagent	Products	Reference
PF <sub>3</sub> /AHF	[Ru(PF <sub>3</sub> )F <sub>4</sub> ] <sub>n</sub> PF <sub>3</sub>	[453]
AsF <sub>3</sub>	RuF <sub>4</sub> ; AsF <sub>5</sub>	[453]
SbF <sub>3</sub>	RuF <sub>5</sub> ; SbF <sub>5</sub> <sup>b</sup>	[453]
BiF <sub>3</sub>	RuF <sub>5</sub> ; BiF <sub>5</sub> <sup>b</sup>	[453]
ClF <sub>3</sub>	ClF <sub>3</sub> .RuF <sub>5</sub> ; ClF <sub>3</sub> .2RuF <sub>5</sub>	[453]
CS <sub>2</sub> <sup>a</sup>	CF <sub>4</sub> ; SF <sub>4</sub>	[453]
H <sub>2</sub> /AHF	RuF <sub>5</sub> → RuF <sub>4</sub> <sup>c</sup>	[453]
Ru/AHF	RuF <sub>5</sub>	[453]
Ru/KF/AHF	KRuF <sub>6</sub>	[453]
H <sub>2</sub> O/AHF	H <sub>3</sub> O <sup>+</sup> .RuF <sub>6</sub> <sup>-</sup>	[454]
B <sub>2</sub> O <sub>3</sub>	RuF <sub>5</sub> ; BF <sub>3</sub> ; O <sub>2</sub>	[96]
NO	NO <sup>+</sup> .RuF <sub>6</sub> <sup>-</sup>	[455]

<sup>a</sup> only volatile products are listed;

<sup>b</sup> only the pentafluorides are reported here, as no attempt was made to determine if adducts had formed between the products themselves;

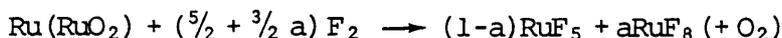
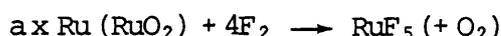
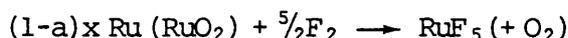
<sup>c</sup> on standing RuF<sub>5</sub> is slowly reduced to RuF<sub>4</sub> by hydrogen in AHF.

gives a comprehensive list of all the published reactions of ruthenium hexafluoride. It is evident from this Table that ruthenium hexafluoride is an extremely powerful oxidant. Taking into account the differences in the chemical reactivities of the hexafluorides of the second row transition metals, the order of oxidant strength is:-



### 8.1.5 Ruthenium Octafluoride

Separation of the products from the fluorination of both ruthenium metal and ruthenium dioxide by microsublimation at low temperature yielded a bright yellow solid, which from chemical analysis was shown to be ruthenium octafluoride [458,459]. The principle product, however, is the pentafluoride:-



The vapour pressure of solid ruthenium octafluoride has been determined over a limited temperature range [458,459] and the variation with temperature is given by:-

$$\log p = 7.67 - 1636/T$$

An IR spectrum of the octafluoride showed bands at 1030 and 385  $\text{cm}^{-1}$  with a combination band at 1285  $\text{cm}^{-1}$ . Force constant calculations have shown that ruthenium octafluoride is cubic [458,459]. It is thermally unstable and rapidly decomposes to lower fluorides at temperatures above approximately  $-50^\circ\text{C}$  [458,459].

### 8.1.6 Ruthenium Fluoride Complexes

#### 8.1.6.1 Oxidation State V [Hexafluororuthenates (V)]

The only definitively characterised complexes of quinquevalent

ruthenium are the nitrosyl, alkali and alkaline earth metal salts of  $[\text{RuF}_6]^-$ . Table 8.5 gives the methods of preparation, lattice parameters and magnetic moments of the known hexafluororuthenate(V) salts. The fluorination of a 1:1 mixture of the appropriate alkali metal chloride, bromide or alkaline earth metal bromate and ruthenium powder by bromine trifluoride at room temperature is the major method of preparation of the salts [438]. The thallium salt has been prepared from a direct combination of thallium fluoride and ruthenium pentafluoride in anhydrous hydrogen fluoride or selenium tetrafluoride [438], whilst nitrosyl hexafluororuthenate(V) is formed from the oxidation of nitric oxide by ruthenium hexafluoride [455].

Except for the silver and thallium salts which are orange in colour, all the other known hexafluororuthenate(V) salts are pale cream.

The magnetic character of the K, Rb, Cs and Ag salts are based on the assumption of  $4d^24sp^3$  hybridisation in  $[\text{RuF}_6]^-$  and have a  $t_{2g}^3$  [460-462] configuration with three unpaired electrons. The spin only value for the magnetic moment should therefore be 3.86 BM, but experimental studies on hexafluororuthenate salts yielded values of approximately 3.7 BM. The lower experimental values are largely attributed to spin orbital coupling effects, but there may also be some antiferromagnetic interactions between the octahedral anions [462].

#### 8.1.6.2 Oxidation State IV [Hexafluororuthenates(IV)]

These salts are generally prepared from the corresponding hexafluororuthenates(V) by reduction with water. After evolution of oxygen and ruthenium tetraoxide has ceased, the solution is cooled and the yellow salts crystallise [438]. Other methods include fusion of a ruthenium nitrosyl nitrate with potassium hydrogen fluoride at 250°C

TABLE 8.5

Lattice parameters and methods of preparation of hexafluororuthenates (V)

SALT	METHOD OF PREPARATION	LATTICE PARAMETERS	MAGNETIC MOMENT BM
LiRuF <sub>6</sub>	LiCl, RuCl <sub>3</sub> and BrF <sub>3</sub> [463]	Rhombohedral: a = 5.39 Å α = 56.0° [463] [LiSbF <sub>6</sub> structure]	
NaRuF <sub>6</sub>	NaCl, RuCl <sub>3</sub> and BrF <sub>3</sub> [463]	Rhombohedral: a = 5.80 Å α = 55.2° [194] a = 5.80 Å α = 54.32° [463] [LiSbF <sub>6</sub> structure]	
KRuF <sub>6</sub>	KBr, Ru metal and BrF <sub>3</sub> [438]	Rhombohedral: a = 4.97 Å α = 97.4° [464] a = 4.95 Å α = 97.4° [194, 461, 463] [KOsF <sub>6</sub> structure]	3.6 [462]
RbRuF <sub>6</sub>	KCl, RuCl <sub>3</sub> and F <sub>2</sub> (flow system), 350°C [461] RbCl, RuCl <sub>3</sub> and F <sub>2</sub> (flow system), 350°C [461]	Rhombohedral: a = 5.07 Å α = 96.9° [194, 461, 463] [KOsF <sub>6</sub> structure]	
CsRuF <sub>6</sub>	CsCl, Ru metal and BrF <sub>3</sub> [438]	Rhombohedral: a = 5.25 Å α = 96.3° [194, 461, 463] [KOsF <sub>6</sub> structure]	3.83 [462]
M(RuF <sub>6</sub> ) <sub>2</sub> (M = Ca, Sr, Ba)	CsCl, RuCl <sub>3</sub> and F <sub>2</sub> (flow system), 350°C [461] M(BrO <sub>3</sub> ) <sub>2</sub> , Ru metal and BrF <sub>3</sub> [438]		
TlRuF <sub>6</sub>	TlF, RuF <sub>5</sub> (solvent = HF or SeF <sub>4</sub> ) [438]	Rhombohedral: a = 5.09 Å α = 96.6° [194] [KOsF <sub>6</sub> structure]	
AgRuF <sub>6</sub>	AgBr, Ru metal and BrF <sub>3</sub> [438]	Tetragonal: a = 4.85 Å c = 9.54 Å [194] [KNbF <sub>6</sub> structure]	3.70 [462]

[465] and fluorination of an equimolar mixture of ruthenium trichloride and barium chloride at 350°C [461].

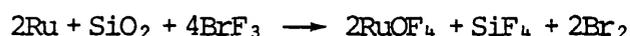
A large number of hexafluororuthenates(IV) have been examined by X-ray powder diffraction techniques; the results are summarised in Table 8.6. The room temperature magnetic moments of the hexafluororuthenates(IV) are about 2.90 BM [466].

#### 8.1.6.3 Oxidation State III [Hexafluororuthenate(III)]

Potassium hexafluororuthenate(III) has been prepared by the fusion of ruthenium trichloride or triiodide with potassium hydrogen fluoride in the absence of oxygen [465,467]. It is a brown solid, having a tetragonal unit cell, a magnetic moment of 1.25 BM [467] and is unstable in water.

#### 8.1.7 Ruthenium Oxide Tetrafluoride

Ruthenium oxide tetrafluoride was reported to be prepared from the action of bromine trifluoride on ruthenium metal in a Pyrex apparatus [435]. This is a violent reaction, the metal burns and is moderated by cooling the reaction bulb with liquid air. It is thought that the oxide tetrafluoride is formed from an oxide film on the metal, and this appears to be confirmed since the principle product is ruthenium pentafluoride [435]. However, it seems more likely due to the high temperature attained during its preparation that ruthenium oxide tetrafluoride is formed from a reaction between Ru metal, BrF<sub>3</sub> and SiO<sub>2</sub> in the Pyrex apparatus, according to the equation:-



Ruthenium oxide tetrafluoride is colourless when completely purified by vacuum sublimation; it is extremely susceptible to hydrolysis, but with small amounts of water it forms a red liquid of unknown composition [435].

TABLE 8.6

Lattice parameters of Hexafluororuthenates (IV)

Compound	Symmetry	Unit-cell parameters	Reference
Na <sub>2</sub> RuF <sub>6</sub>	Hexagonal	a = 9.32 Å, c = 5.15 Å	[468]
K <sub>2</sub> RuF <sub>6</sub> (α) (β)	Cubic	a = 8.37 Å	[469]
	Hexagonal	a = 5.76 Å, c = 4.64 Å	
Rb <sub>2</sub> RuF <sub>6</sub>	Cubic	a = 8.51 Å	[469]
Cs <sub>2</sub> RuF <sub>6</sub>	Hexagonal	a = 6.23 Å, c = 5.00 Å	[469]
BaRuF <sub>6</sub>	Rhombohedral	a = 4.88 Å, α = 98.0°	[461, 464]

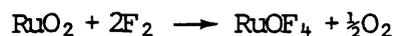
The vapour pressure of ruthenium oxide tetrafluoride as a function of temperature is given by the equations:-

$$\text{Solid RuOF}_4 \quad \log P_{\text{mm}} = 9.82 - 2857/T \quad (20-110^\circ\text{C})$$

$$\text{Liquid RuOF}_4 \quad \log P_{\text{mm}} = 8.60 - 2616/T \quad (120-160^\circ\text{C})$$

The heat and entropy of vapourisation are 11.97 kcal/mol and 26.1 kcal/mol respectively. Ruthenium oxide tetrafluoride melts at 115°C with an estimated boiling point of 184°C from extrapolation of vapour pressure data. It has a magnetic moment of about 2.8 BM at room temperature [435].

More recent studies by a Japanese group [470-473] have suggested that the initial reports are inaccurate and state that ruthenium oxide tetrafluoride is the sole product from the fluorination of ruthenium dioxide.



This is somewhat surprising considering that many other workers [432, 434-436] obtained only the pentafluoride from the fluorination of both ruthenium metal and ruthenium dioxide. Ruthenium oxide tetrafluoride reported to be formed in this way is thermally unstable; it



is reported to lose oxygen at room temperature and decomposes totally at 400°C to the tetrafluoride [471,472].



The Japanese group also quote a different vapour pressure equation

[472] :-

$$\log P_{\text{mm}} = 8.48 - 2.74 \times 10^3/T \quad (0-70^\circ\text{C})$$

The confusion in the literature on the preparation, physical and chemical properties of ruthenium oxide tetrafluoride obviously requires clarification.

## 8.2 PRESENT STUDY

### 8.2.1 Aim

The reason for interest in ruthenium is that possessing volatile fluorides it would be present in any  $\text{UF}_6$  produced from a reprocessed feedstock. Hence, any potential process involving reprocessed feeds would need to consider a means of removing it in order that the  $\text{UF}_6$  meets international specifications.

A survey of the literature seems to suggest that this can be achieved via the formation of alkali, alkaline earth metal ruthenium fluoride complexes. Another possible method is the partial hydrolysis of ruthenium fluoride-uranium hexafluoride mixtures. Both these methods as well as the sorption of ruthenium pentafluoride by cryolite have been studied, and the results are discussed in this Chapter.

### 8.2.2 Preparation of Ruthenium Pentafluoride

The diagram in Fig. 8.2 is the apparatus used for the preparation of ruthenium pentafluoride in quantities suitable for experimental work.

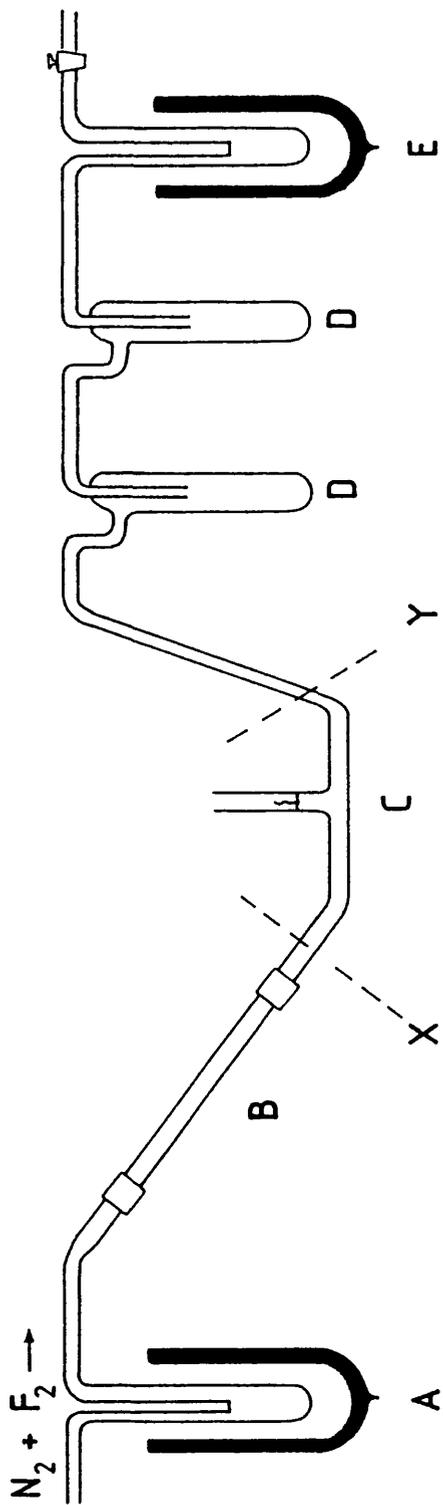


FIGURE 8.2  
Apparatus used for the fluorination of ruthenium powder.

The construction was of Pyrex throughout, with the copper reactor, B, being joined to the glass via compression unions and Neoprene rings.

Approximately 2g of ruthenium metal powder was heated by a hydrogen flame in a porcelain crucible to activate the metal. The ruthenium was allowed to cool under a stream of hydrogen prior to being transferred in a nickel boat to reactor B, and the apparatus was assembled as shown. The system was purged with nitrogen overnight and all traces of moisture were removed by regular flaming with a blow torch.

Trap A was cooled to dry ice temperature, to condense out any fluorocarbons and hydrogen fluoride from the fluorine generating cell. Liquid oxygen or dry ice traps were placed around the traps, D. Fluorine generated from a 60 amp ICI cell, diluted with nitrogen, was passed through the apparatus and the nickel reactor was heated by means of a Bunsen burner. The Neoprene rings were protected by cooling the nickel/glass joints with cotton wool soaked with water.

The temperature of the reactor was maintained at approximately 300°C during the whole reaction. The first indication that a reaction had begun was the appearance of a heavy yellow vapour which condensed into traps, D. After the reaction had finished, these traps were sealed off and attached to a metal vacuum line. Mass and IR spectroscopy identified this yellow vapour as ruthenium tetraoxide.

After about 30 minutes, a black-green viscous liquid began to run into C. The reaction was complete within 3 hours. When the ruthenium metal was exhausted, the fluorine supply was cut off and the apparatus was purged overnight with nitrogen to remove fluorine from the system. Ruthenium pentafluoride was removed from the sloping part of the collection tube, C, by gentle heating with a Bunsen burner. The collector was sealed off at X and Y.

### 8.2.3 Purification of Ruthenium Pentafluoride

Sample tube, C, containing the products of the fluorination was attached to the apparatus shown in Fig. 8.3. The apparatus was evacuated and seasoned with fluorine. Break seal, C, was broken with nickel balls and the system was again evacuated. The nickel balls were returned to the sidearm, S, and S was removed. Heating tapes were carefully wrapped around C and J up to the U-bend. The tapes were maintained at approximately 65°C and the ruthenium pentafluoride distilled as a viscous green liquid into vessel B. The glass about the constriction, Q, was completely cleared of the pentafluoride with a Bunsen burner and the container, B, was sealed off under high vacuum.

The ruthenium pentafluoride was further purified by means of a second low temperature (~40°C) distillation. Sample tube B was attached to the apparatus shown in Fig. 8.4 and a similar procedure was used to that described above. Highly pure crystalline ruthenium pentafluoride was obtained in V and was sealed off under high vacuum.

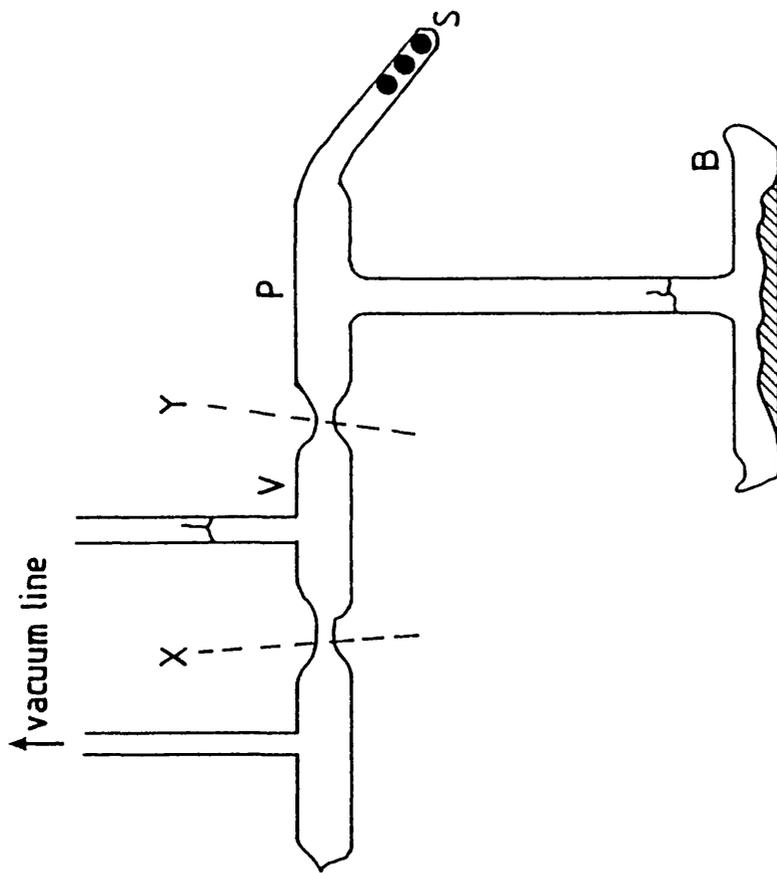
The pentafluoride can be stored for an unlimited period without decomposition in a dry box in sealed prefluorinated FEP or glass tubes.

## 8.3 VIBRATIONAL SPECTRA OF RUTHENIUM PENTAFLUORIDE

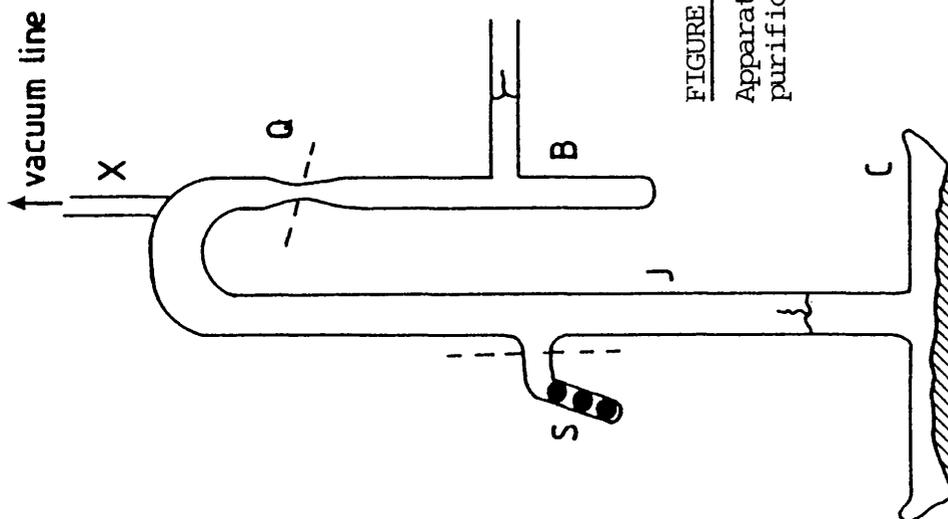
### 8.3.1 Introduction

The transition metals which form pentafluorides include vanadium, niobium, tantalum, chromium, molybdenum, ruthenium, tungsten, technetium, rhodium, rhenium, iridium and platinum. As a class, these pentafluorides have high volatility with melting points below 100°C and boiling points of 200-300°C [474]. The latent heats of vapourisation and entropies of vapourisation are high (Trouton constants),

**FIGURE 8.4**  
 Apparatus used for the final purification  
 of  $\text{RuF}_5$ .



**FIGURE 8.3**  
 Apparatus used for the initial  
 purification of  $\text{RuF}_5$ .



which indicate that association occurs in the liquid state. However, there is little evidence to confirm this or to provide information on the degree or mode of association. Single crystal studies [142,436,475,476,477] have shown that there are three main types of polymerisation in transition metal pentafluorides:-

( i ) Cis-fluorine bridged tetramers with a linear bridge:

MoF<sub>5</sub>, NbF<sub>5</sub>, TaF<sub>5</sub>, and WF<sub>5</sub>.

( ii ) Cis-fluorine bridged tetramers with a bent bridge:

RhF<sub>5</sub>, IrF<sub>5</sub>, PtF<sub>5</sub>, AuF<sub>5</sub>, OsF<sub>5</sub>, and RuF<sub>5</sub>.

(iii) Cis-fluorine bridged endless chains: VF<sub>5</sub>, CrF<sub>5</sub>,

TcF<sub>5</sub>, and ReF<sub>5</sub>.

Of these only the pentafluorides of vanadium, niobium, tantalum and molybdenum have been examined in detail by vibrational spectroscopy [410,478-481]. Tungsten, osmium, iridium, and rhenium pentafluorides have been studied superficially [410,482]. To date there appears to have been no published work on the vibrational spectra of ruthenium pentafluoride.

### 8.3.2 Present Study

Samples for IR spectroscopy were prepared by placing a finely powdered sample between oven dried KBr plates in a dry box. The plates were compressed in a cell holder and the only hydrolysis (hydrolysis gives dark products which are immediately detected) occurred at the edge of the plates well away from the beam of the spectrometer. Attempts to record the IR spectrum of liquid ruthenium pentafluoride by warming the solid when compressed between the plates were unsuccessful, resulting in the complete hydrolysis of the sample.

Solid samples for Raman spectroscopy were contained in seasoned Pyrex capillaries. Since liquid ruthenium pentafluoride does not

solidify in less than a day, samples for Raman studies of the melt were prepared by subliming a small quantity of the pentafluoride into a seasoned Pyrex capillary.

Raman spectra obtained on the solid and liquid are shown in Figs. 8.5 and 8.6 respectively. The spectra of solid ruthenium pentafluoride are completely different from the spectra of the liquid implying that there is a major change in structure between the solid and the liquid. An unpublished low temperature Raman spectrum of gaseous ruthenium pentafluoride [Fig. 8.7] obtained by Holloway and Claassen at the Argonne National Laboratory is virtually the same as that of the liquid, so it is very probable that they have similar structures.

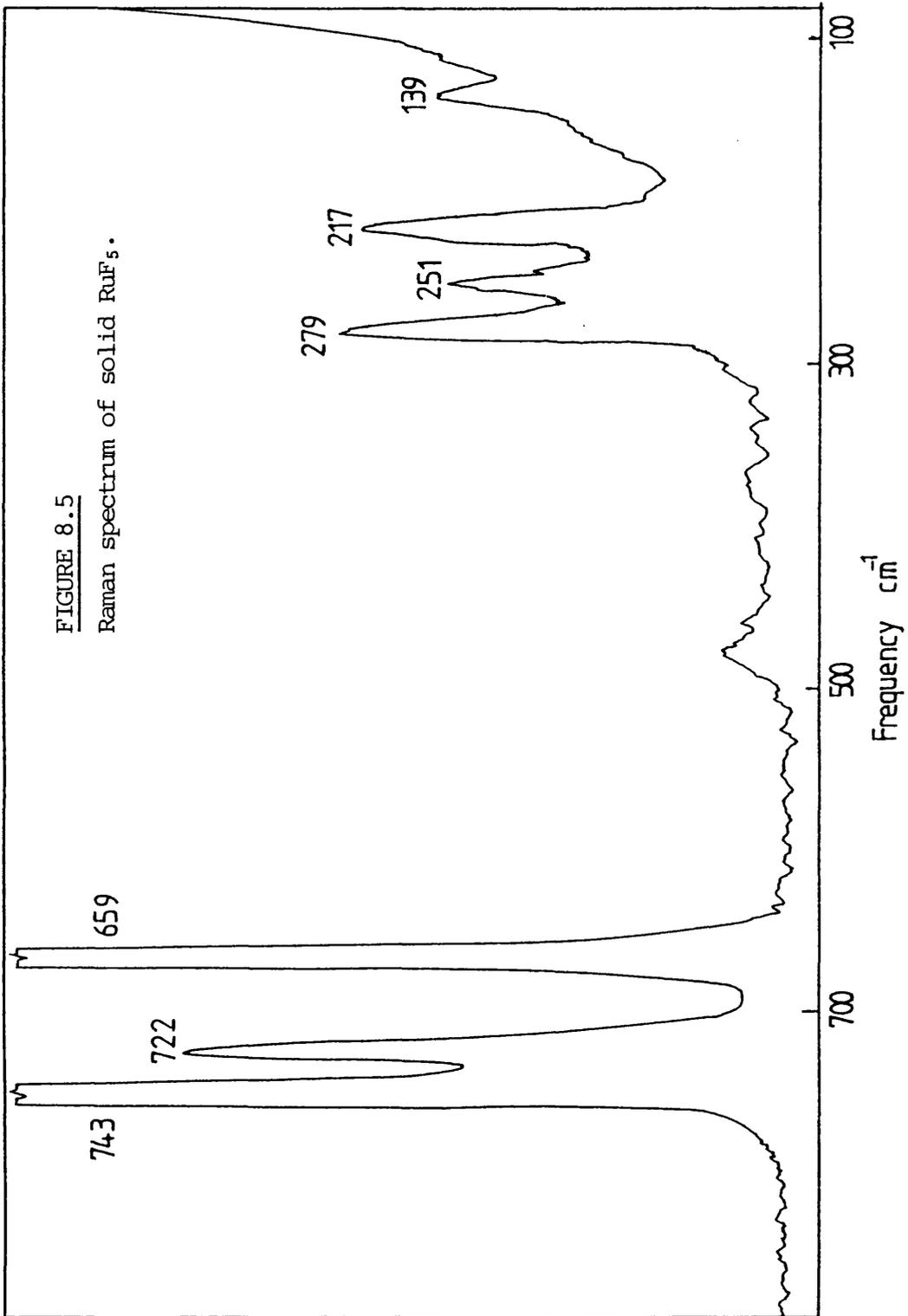
The Raman spectra of solid ruthenium [Table 8.9], molybdenum [410], niobium [479], and tantalum [479] pentafluorides are all very similar but there are major differences in the relative intensities and pattern of the bands. Infra-red spectra of solid rhenium, osmium, iridium [482] and ruthenium pentafluorides [Fig. 8.8] show one common band in each compound, a broad adsorption at approximately  $530\text{ cm}^{-1}$ ; Table 8.8. From this work and previous vibrational spectroscopic studies on tetrameric transition metal pentafluorides [482,483], the assignment of the band as the F-M-F stretching mode appears to be certain. In view of the complexity of the structure, no attempt has been made to assign the Raman and IR spectra of solid ruthenium pentafluoride.

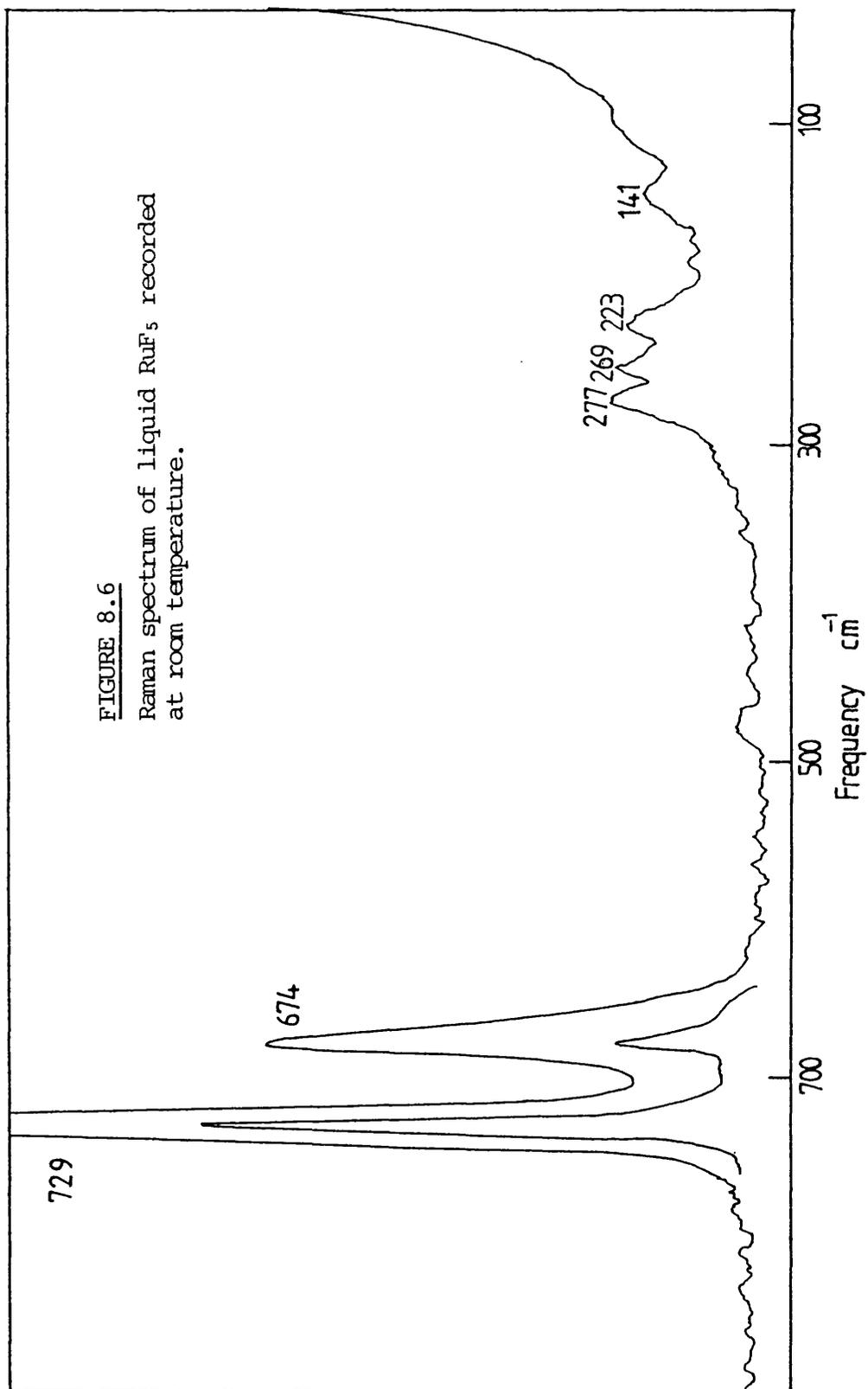
There are major disagreements in the interpretation of the observed spectra of liquid niobium and tantalum pentafluorides; the species present being postulated as either monomeric with  $D_{3h}$  symmetry [478] or cis-fluorine bridged polymers [479].

Visible spectra of liquid ruthenium pentafluoride show peaks

FIGURE 8.5

Raman spectrum of solid  $\text{RuF}_5$ .





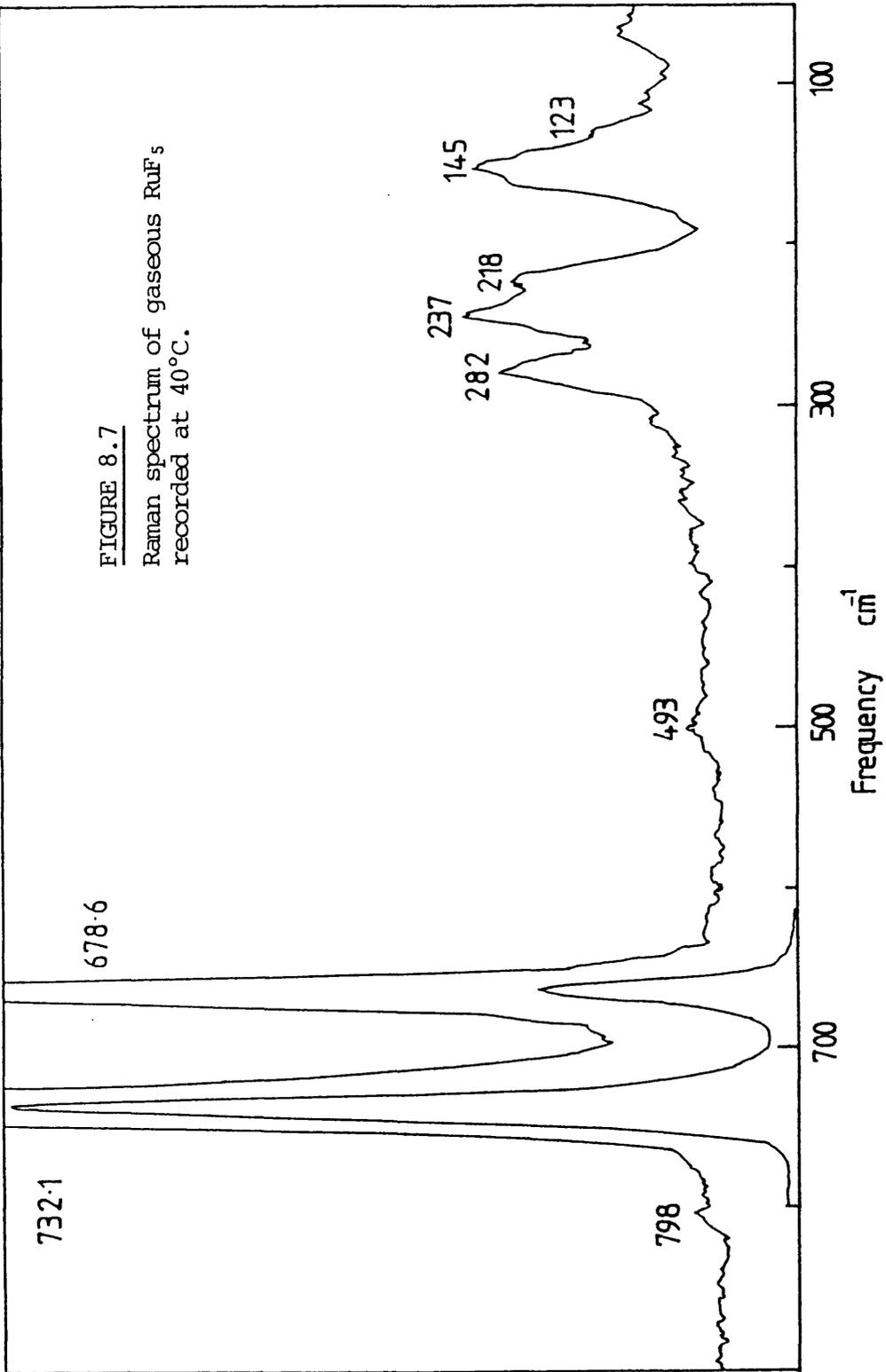


TABLE 8.8

Infra-red spectra of rhenium, osmium, iridium [482] and ruthenium pentafluorides

ReF <sub>5</sub> thin film -196°C	OsF <sub>5</sub> thin film -196°C	IrF <sub>5</sub> thin film -196°C	RuF <sub>5</sub> room temp.
743 m,sh 721 s,sh 693 s	712 m,sh 691 s	715 s,sh 699 s,sh 678 vs 642 vs 533 m,br	750 s,sh 715 vs
660 s 535 m,br	657 s 530 s,br		657 vs 525 s,br

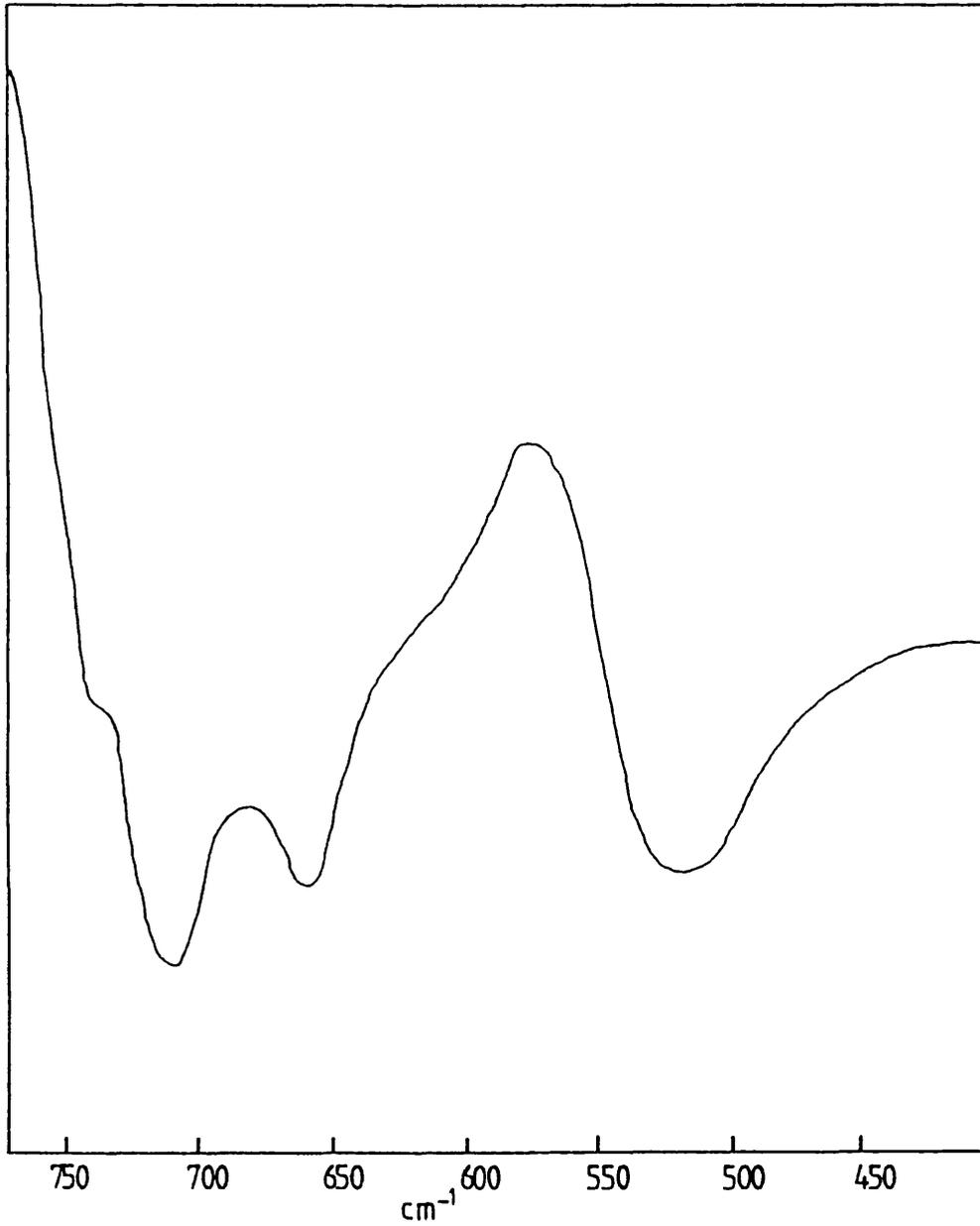


FIGURE 8.8  
Infrared spectrum of solid RuF<sub>5</sub>.

TABLE 8.9

Raman spectra of solid, liquid and gaseous ruthenium pentafluoride

Solid RuF <sub>5</sub> room temp.	Liquid RuF <sub>5</sub> room temp.	Gaseous RuF <sub>5</sub> <sup>a</sup> ~80°C
		798 w
743 vs		
722 m	729 vs	732 vs
659 s	674 s	679 vs
~490 w,br	~490 w,br	493 vw,br
279 m	277 w	282 w
251 m-	269 w	237 w
217 m	223 w	218 w,sh
139 w+	141 w	143 w
		123 sh

<sup>a</sup> see text

characteristic of  $d^3$  octahedral transition metal compounds [441] which, along with its visibly high viscosity, clearly suggests a high degree of association. Polymeric species have been observed in gaseous ruthenium pentafluoride [484].

If we assume that in liquid and gaseous ruthenium pentafluoride polymerisation occurs via cis-fluorine bridges of an 'octahedral' RuF<sub>6</sub> unit, the important features spectroscopically are likely to be vibrations of the C<sub>2v</sub> MF<sub>4</sub> residue together with the fluorine bridging modes which are only likely to be intense in the IR. By analogy with gaseous TeCl<sub>4</sub> [486], we expect two strongly polarised bands in the Raman spectrum, effectively the axial RuF<sub>2</sub> symmetric stretching mode and the equatorial RuF<sub>2</sub> symmetrical stretching mode. In the IR we expect three stretching modes to be intense, the axial RuF<sub>2</sub> anti-symmetrical stretch and the equatorial RuF<sub>2</sub> symmetrical and anti-symmetrical stretches. In addition to this at lower frequencies we expect broad bridging modes. An important feature is that for the stretching region the Raman spectrum of the polymer is likely to be

independent of ring size.

The Raman spectra of both liquid and gaseous ruthenium pentafluoride show two strongly polarised bands in the ruthenium-fluorine stretching region which is in agreement with the presence of a  $C_{2v}$   $RuF_4$  residue, which contrasts sharply with the observation of only one intense band in the stretching region for liquid (monomeric)  $AsF_5$  [485] and for gaseous (monomeric)  $VF_5$  [487]. The observed spectra clearly augurs in favour of cis-fluorine bridged polymeric species in both liquid and gaseous ruthenium pentafluoride.

Even though the spectra of liquid and gaseous cannot be fully assigned, the following deductions can be made from this study:-

- (a) the spectra do not disagree with those expected for a cis-fluorine bridged polymer;
- (b) the presence of monomeric species were not detected in either the liquid or gas at low temperatures.

Clearly a Raman spectroscopic study of gaseous ruthenium pentafluoride as a function of temperature and high temperature (melt) IR spectra would be valuable.

#### 8.4 HYDROLYSIS OF RUTHENIUM PENTAFLUORIDE

The data so far published on the hydrolysis of ruthenium pentafluoride are very few [435,438,488]. In the majority of studies it is assumed that hydrated ruthenium dioxide is the major product, but little or no experimental evidence is given.

Distilled water (1 ml) was added to a small quantity of ruthenium pentafluoride (0.2g) in a seasoned glass reactor fitted with a 'sub-a-seal' by means of a hyperfine syringe. Immediately, a dark brown precipitate was formed, with the evolution of a gas, which was

condensed into a separate prefluorinated glass reactor and was shown by IR and mass spectroscopy to be  $\text{RuO}_4$ . The precipitate was filtered and IR spectra were recorded as it was heated in air to dryness.

The IR of the hydrolysis products exhibited a very broad band ranging from 750 to 400  $\text{cm}^{-1}$  which is the region characteristic of metal-oxygen single bonds [489], along with two other bands at 3350

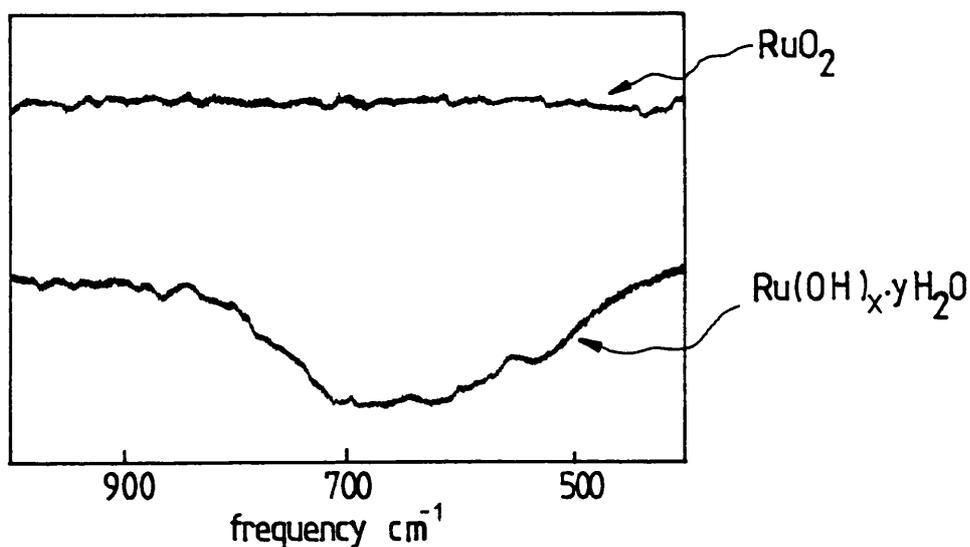


FIGURE 8.9

Infrared spectra of  $\text{RuO}_2$  and  $\text{Ru(OH)}_x \cdot y\text{H}_2\text{O}$ , the initial hydrolysis product.

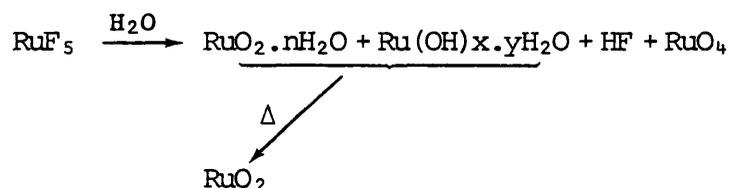
$\text{cm}^{-1}$  and  $1640 \text{ cm}^{-1}$  corresponding to the stretching and bending vibrations of bonded water [490]. Thus it can be concluded that the hydrolysis products possess both hydroxyl groups and bonded water, i.e.  $\text{Ru(OH)}_x \cdot y\text{H}_2\text{O}$ .

The vibrational bands associated with bonded water are initially extremely broad due to hydrogen-bonding. As the precipitate is heated, the broad band at  $3750\text{--}2200 \text{ cm}^{-1}$  changes in length and intensity; shortening occurring in the  $3700\text{--}3200 \text{ cm}^{-1}$  range. Finally, the band disappears on complete dehydration together with those due to the stretching and bending vibrations. The broad band ranging from 700 to

400  $\text{cm}^{-1}$  also becomes less intense as the product is heated and eventually disappears. The IR spectrum of the completely dried hydrolysis product was featureless, and the dehydrated black solid was shown by X-ray powder photography to be ruthenium dioxide. Other workers [491] observed no bands in the IR of anhydrous  $\text{RuO}_2$  which is somewhat surprising considering that  $\nu(\text{Ru}=\text{O})$  is known to occur in the range 950 to 1050  $\text{cm}^{-1}$  [492].

So it seems likely that the initial hydrolysis product contains both hydrated ruthenium dioxide and hydroxide. Ruthenium dioxide was not detected by IR spectroscopy, but there is no reason to suggest it is not formed along with the hydrated hydroxides, since  $\text{RuO}_2$  has been identified as the dried final product of the hydrolysis.

Thus the hydrolysis of ruthenium pentafluoride can be represented by:-



which agrees in principle with some work by the Japanese [473] who suggested from a comparison of spectra that the initial hydrolysis product is  $\text{Ru}(\text{OH})_3 \cdot y\text{H}_2\text{O}$ .

## 8.5 RUTHENIUM FLUORIDE COMPLEXES

### 8.5.1 Reactions between $\text{RuF}_5$ and alkali, alkaline earth metal fluorides in anhydrous hydrogen fluoride

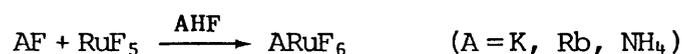
The aim of the present work is to determine if the salts,  $\text{ARuF}_6$ ,  $\text{B}(\text{RuF}_6)_2$  can be prepared from direct interactions between ruthenium pentafluoride and the appropriate main group metal fluoride.

### 8.5.2 RuF<sub>5</sub> with AF (A = K, Rb, NH<sub>4</sub>) in Anhydrous Hydrogen Fluoride

The reactions between ruthenium pentafluoride and AF (A = K, Rb, NH<sub>4</sub>) were studied in prefluorinated FEP tubes fitted with ChemCon valves. Since ruthenium pentafluoride is extremely sensitive to even the smallest traces of moisture, the alkali metal fluorides had to be dried carefully using the following procedure. Typically, 0.3g of the appropriate main group metal fluoride was dried for several days at 250°C under high vacuum and then fluorinated several times at elevated temperatures prior to use.

Anhydrous hydrogen fluoride was condensed onto a 1:1 molar ratio of RuF<sub>5</sub> and AF (A = K, Rb, NH<sub>4</sub>) at -196°C and the systems were left to warm to room temperature. Reactions occurred rapidly at ambient temperatures and were complete within 30 minutes. The solvent was slowly removed over a period of several hours by vacuum distillation, leaving behind pale pinkish/cream, highly air-sensitive non-volatile solids.

The solids were shown by mass balance, IR spectroscopy, chemical analysis and X-ray powder photography to be hexafluororuthenate(V) salts, i.e.



#### 8.5.2.1 Vibrational Spectroscopy

Only a single band at ~640 cm<sup>-1</sup> was observed in the IR spectra of both KRuF<sub>6</sub> and RbRuF<sub>6</sub> which is characteristic of ν<sub>3</sub>[RuF<sub>6</sub>]<sup>-</sup> [463,493]. The ammonium salt also contained this feature along with other bands at ~3300 and 1410 cm<sup>-1</sup> associated with the ammonium ion.

The combination band between ν<sub>4</sub> and ν<sub>5</sub> (rotatory lattice vibration) is observed only if the ammonium ion does not rotate freely in the crystal lattice, as in the case of NH<sub>4</sub>F. Since this band is not

observed in the IR of  $\text{NH}_4\text{RuF}_6$  even after the spectrum had been greatly expanded suggests that the  $(\text{NH}_4)^+$  ion rotates more freely in this compound than in  $\text{NH}_4\text{F}$ . Exposure of the salts briefly to the atmosphere caused not only severe discolouration, but the IR bands at  $\sim 640 \text{ cm}^{-1}$  broadened with a decrease in intensity and the development of a shoulder at  $\sim 590 \text{ cm}^{-1}$ , which is characteristic of  $\nu_3[\text{RuF}_6]^{2-}$  [493]. After approximately two minutes exposure to the atmosphere, the salts underwent irreversible hydrolysis.

#### 8.5.2.2 X-Ray Powder Photography

Comparison of  $\sin^2\theta$  values obtained from the X-ray powder diffraction photographs of the  $\text{ARuF}_6$  ( $A = \text{K, Rb, NH}_4$ ) salts with those of  $\text{KOsF}_6$  showed them to be isostructural [Table 8.10]. Small differences in the positions of the corresponding reflections are due, of course, to the different cell sizes. To improve the accuracy of the calculated  $\sin^2\theta$  values, the positions of the diffraction lines were measured several times from at least two separate powder photographs of each salt.

All observed X-ray reflections of the salts were initially indexed on trimolecular hexagonal cells, where:-

$$\sin^2\theta_{\text{hkj}} = \frac{\lambda^2}{3a^2} (h^2 + hk + k^2) + \frac{\lambda^2}{4c^2}$$

The trimolecular hexagonal cells were transformed to unimolecular rhombohedral cells, using the following equations:-

$$A_R = \frac{1}{3} \sqrt{3A_H^2 + C_H^2}$$

$$\cos \alpha = \frac{C_H^2 - \frac{3}{2} A_H^2}{9A_R^2}$$

where

$$\sin^2\theta_{\text{pqr}} = \frac{\lambda^2}{4a^2} \frac{(p^2 + q^2 + r^2)\sin^2\alpha + 2(pq + qr + pr)(\cos^2\alpha - \cos\alpha)}{1 + 2\cos^3\alpha + 3\cos^2\alpha}$$

TABLE 8.10

X-ray powder diffraction patterns of  $\text{KRuF}_6$ ,  $\text{NH}_4\text{RuF}_6$  and  $\text{KOsF}_6$ 

hkl	$\text{KOsF}_6$ [464] $\sin^2\theta$ d-values *	$\text{NH}_4\text{RuF}_6$ $\sin^2\theta$ d-values *	$\text{KRuF}_6$ $\sin^2\theta$ d-values *	$\text{RbRuF}_6$ $\sin^2\theta$ d-values *
100	0.0249 4.8854 54	0.02401 4.9751 45	0.02496 4.8795 50	0.02379 4.9981 55
101	0.0428 3.7262 65	0.0418 3.771 70	0.04254 3.7377 60	0.04111 3.8021 55
110	0.0568 3.2346 66	0.05424 3.3101 70	0.0573 3.2205 60	0.05404 3.3162 55
111	0.0674 2.9694 31	0.0658 3.0053 30	0.0675 2.9672 25	0.0649 3.0261 30
111	0.0956 2.4933 vwv		0.09586 2.4899 w	
200	0.0993 2.4464 25		0.09984 2.4398 25	0.0952 2.4992 30
201	0.10976 2.3269 13	0.10758 2.3504 vw	0.1104 2.32014 w	0.106012 2.3677 w
021				
211	0.1275 2.15895 24	0.12541 2.1769 15	0.1276 2.1581 20	0.1233 2.1951 15
210				
120	0.13812 2.0743 35	0.1355 2.0943 45	0.1378 2.0767 30	0.1334 2.1105 40
211	0.1417 2.04792 100	0.1378 2.0764 100	0.14238 2.04302 100	0.1363 2.0883 100
121				
202	0.1699 1.87025 31	0.16721 1.8852 40	0.17016 1.8688 30	0.16445 1.901 25
211	0.184 1.79717 21	0.1796 1.8191 20	0.1838 1.79815 20	0.1838 1.79815 20
212	0.1946 1.74754 34	0.19122 1.76292 35	0.19512 1.74521 40	0.18824 1.7768 35
122				
221	0.2288 1.61165 37	0.2215 1.6382 br 70	0.2275 1.61625 br 75	0.2185 br 1.6492 70
300				
301	0.2264 1.62017 64			
031				
220	0.2264 1.62017 23	0.23302 1.59699 15	0.23766 20	0.2294 1.60954 20
311	0.23698 1.5836 21	0.2578 1.5183 15	0.2672 1.4914 20	0.2552 1.52601 20
311	0.2652 1.4969 21			
131				
310	0.2688 1.4869 90	0.2648 1.4981 75	0.2694 1.4855 70	0.2604 1.5107 85
130				
222	0.2688 1.4869 49	0.2748 1.4706 45		
302	0.2794 1.4585 49			
032				

\* Estimated intensity values

Table 8.11 gives the lattice dimensions for both the trimolecular hexagonal and unimolecular rhombohedral cells for the hexafluororuthenate(V) salts.

### 8.5.2.3 KOsF<sub>6</sub> Structure

The structure of KOsF<sub>6</sub> is most simply described as a CsCl arrangement of K atoms and OsF<sub>6</sub> groups with a rhombohedral angle near 97° instead of 90°. Each OsF<sub>6</sub> complex consists of 6 fluorine atoms each at a distance of 1.82 Å from the central Os atom and forming around it an irregular octahedron. The fluorine atom octahedra are not stretched but are compressed along their 3-fold axes.

The OsF<sub>6</sub> octahedra are orientated in such a way that 6 fluorine atoms from 6 different groups surround each K atom to form a puckered ring. In addition, the potassium is coordinated by 6 more fluorine atoms; 3 from an OsF<sub>6</sub> octahedral unit above it and 3 from the corresponding unit below it. Thus each alkali metal is coordinated by a total of 12 fluorine atoms [464].

The structures of KRuF<sub>6</sub>, RbRuF<sub>6</sub> and NH<sub>4</sub>RuF<sub>6</sub> will thus be very similar to that described above for KOsF<sub>6</sub>, since they are isostructural.

### 8.5.3 RuF<sub>5</sub> with BF<sub>2</sub> (B = Ca, Mg) in Anhydrous Hydrogen Fluoride

The alkaline earth metal fluorides were dried in the same way as described earlier for alkali metal fluorides. Anhydrous hydrogen fluoride was distilled onto a 2:1 molar ratio of ruthenium pentafluoride and BF<sub>2</sub> (B = Ca, Mg) at -196°C and the systems were allowed to warm up to room temperature. No reactions were observed even after 6 hours, which was confirmed by IR and mass spectroscopy. Similarly, no reactions occurred when the fluorides were heated directly up to 80°C for several hours.

TABLE 8.11

Lattice Parameters of the Hexafluororuthenates (V) prepared in the present study

	Experimental		Literature Rhombohedral
	Trimolecular Hexagonal	Rhombohedral	
$\text{KOSF}_6$			$a = 4.991 \text{ \AA}; \alpha = 97.18^\circ$
$\text{KRuF}_6$	$a = 7.476 \text{ \AA}; c = 7.426 \text{ \AA}$	$a = 4.98 \text{ \AA}; \alpha = 97.4^\circ$	$a = 4.97 \text{ \AA}; \alpha = 97.4^\circ$
$\text{NH}_4\text{RuF}_6$	$a = 7.541 \text{ \AA}; c = 7.680 \text{ \AA}$	$a = 5.05 \text{ \AA}; \alpha = 96.6^\circ$	
$\text{RbRuF}_6$	$a = 7.604 \text{ \AA}; c = 7.677 \text{ \AA}$	$a = 5.08 \text{ \AA}; \alpha = 96.87^\circ$	$a = 5.07 \text{ \AA}; \alpha = 96.9^\circ$

Chemical Analysis ( $\text{NH}_4\text{RuF}_6$ )

	<u>Theoretical</u>	<u>Experimental</u> (%)
N	6.006	5.98
H	1.73	1.70
Ru	43.36	
F	48.91	47.71

#### 8.5.4 RuF<sub>5</sub> with KF in liquid uranium hexafluoride

The reaction between potassium fluoride and ruthenium pentafluoride was repeated in a seasoned FEP tube using uranium hexafluoride as a solvent. It was hoped that liquid uranium hexafluoride was sufficiently polar to initiate the formation of potassium hexafluororuthenate(V).

Uranium hexafluoride was distilled onto a 1:1 molar ratio of ruthenium pentafluoride to potassium fluoride at -196°C and allowed to warm to room temperature. The reaction mixture was heated to 80°C by means of a heating tape to ensure that liquid uranium hexafluoride was present. The pentafluoride dissolved in the hexafluoride forming a pale green solution.

No reaction was observed to take place even after 6 hours when the solvent was removed leaving behind the unreacted mixture of fluorides. However, there was a measurable weight change (~1%) in the reactants. Infrared spectra of the potassium fluoride which had been carefully separated from ruthenium pentafluoride showed a broad adsorption band at 525 cm<sup>-1</sup> which is characteristic of the  $\nu_3$  vibration of the hexafluorouranate(V) anion, presumably due to the sorption of liquid uranium hexafluoride by potassium fluoride. It is worth noting that there was no evidence to suggest that any liquid ruthenium pentafluoride was sorbed.

#### 8.5.5 Discussion

It can be concluded that the salts, ARuF<sub>6</sub> can be prepared from reactions between AF and RuF<sub>5</sub> in anhydrous hydrogen fluoride, but no equivalent reactions occur with alkaline earth metal fluorides. No reactions occurred from direct interactions between the appropriate alkali or alkaline earth group metal fluorides and ruthenium pentafluoride even at elevated temperatures. Thus it appears that the only

successful reactions required the presence of a polar solvent. The anhydrous hydrogen fluoride which is polar may, however, have acted as a catalyst.

When mixtures of alkali metal or alkaline earth fluorides and ruthenium pentafluoride were briefly exposed to the atmosphere, the IR spectra showed intense bands at  $\sim 640\text{ cm}^{-1}$  and  $590\text{ cm}^{-1}$  which are characteristic of  $\nu_3[\text{RuF}_6]^-$  and  $\nu_3[\text{RuF}_6]^{2-}$  respectively [463,493]. Thus, the presence of moisture in the atmosphere appears to cause salt formation, i.e.  $\text{ARuF}_6$ ,  $\text{A}_2\text{RuF}_6$  or  $\text{B}(\text{RuF}_6)_2$ ,  $\text{BRuF}_6$ , which again suggests that for reactions to occur a polar solvent is required. Ruthenium tetroxide was evolved and discolouration of the solid fluorides also occurred, presumably due to the formation of ruthenium oxides and hydroxides.

It appears that if a suitable polar solvent is found, then the salts  $\text{B}(\text{RuF}_6)_2$  should be synthesised from interactions between  $\text{BF}_2$  and  $\text{RuF}_5$ .

#### 8.5.6 Partial Hydrolysis of $\text{ARuF}_6$ Salts (A = K, $\text{NH}_4$ )

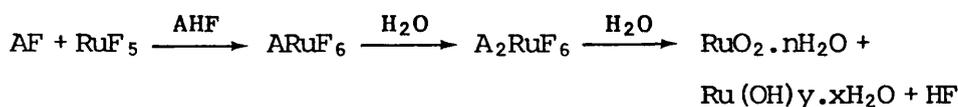
It has been reported that the partial hydrolysis of  $\text{ARuF}_6$  salts leads to the formation of hexafluororuthenates(IV),  $\text{A}_2\text{RuF}_6$ . In this study, a similar procedure was adopted to that stated in the literature [438].

Both  $\text{KRuF}_6$ , and  $\text{NH}_4\text{RuF}_6$  were treated with a minimum amount of water (approximately 15 ml per g of the salt) and warmed gently until effervescence had ceased. The gas liberated had the distinctive colour of  $\text{RuO}_4$  and, in both cases, yellow solutions were obtained. It is essential that the solutions are kept below  $\sim 60^\circ\text{C}$ , since above this temperature irreversible hydrolysis occurs. Immediately dissolution was complete, the solutions were cooled to  $0^\circ\text{C}$ , whereupon the potassium

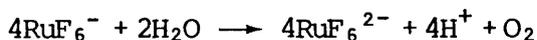
salt yielded yellow plates while reddish-yellow crystals were obtained from the ammonium salt.

The crystals were collected on sintered glass crucibles, washed with cold water, carbon tetrachloride (which removes any traces of ruthenium tetroxide) and dried under dynamic vacuum. A further crop of less pure crystals were obtained by adding a concentrated solution of AF (A = K, NH<sub>4</sub>) to the appropriate mother liquor. The crystals obtained from the ammonium salt, which presumably are (NH<sub>4</sub>)<sub>2</sub>RuF<sub>6</sub>, were unstable and underwent irreversible complete hydrolysis before they could be dried. Thus, as a consequence, no data on (NH<sub>4</sub>)<sub>2</sub>RuF<sub>6</sub> crystals was obtained.

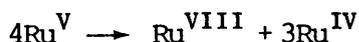
The yellow plates obtained from the partial hydrolysis of KRuF<sub>6</sub> were identified as K<sub>2</sub>RuF<sub>6</sub> by IR spectroscopy and X-ray powder photography [469], i.e.



It has been proposed by Peacock et al. [438,469] that the partial hydrolysis of the salts can be represented by one of the following equations:-



but since a small amount of RuO<sub>4</sub> is formed, the side reaction:-



may also take place.

## 8.6 CONCLUSIONS

Since both RuF<sub>3</sub> and RuF<sub>4</sub> are non-volatile under ordinary conditions and RuF<sub>6</sub> decomposes rather readily to give RuF<sub>5</sub>, the only ruthenium

fluoride likely to be present in impure  $\text{UF}_6$  is the pentafluoride.

The method most likely to be effective in removing  $\text{RuF}_5$  from a mixture with other volatile fluorides is to complex it as a low-volatility salt. Salts such as  $\text{ARuF}_6$  ( $\text{A}=\text{K}, \text{Rb}, \text{NH}_4$ ) and  $\text{B}[\text{RuF}_6]_2$  ( $\text{B}=\text{Mg}, \text{Ca}$ ) are known but we have shown that neither can be obtained by the reaction of  $\text{AF}$  or  $\text{BF}_2$  with  $\text{RuF}_5$  directly or in solution in  $\text{UF}_6$ , and it is clear, certainly in the case of the  $\text{ARuF}_6$  species, that anhydrous  $\text{HF}$  or some other polar solvent is necessary. Thus,  $\text{ARuF}_6$  ( $\text{A}=\text{K}, \text{Rb}, \text{NH}_4$ ) can be prepared by the reaction between  $\text{AF}$  and  $\text{RuF}_5$  in anhydrous  $\text{HF}$ .

One method which may be effective, however, is the introduction of trace quantities of water. Ruthenium pentafluoride is highly susceptible to hydrolysis but  $\text{UF}_6$  is not. For example, 'dried'  $\text{HF}$  (which contains water at the  $<0.02\%$  level) will hydrolyse  $\text{RuF}_5$  but has no obvious effect on  $\text{UF}_6$ . Similarly, during study of the direct interaction of  $\text{AF}$  and  $\text{RuF}_5$  at elevated temperatures discolouration of the pentafluorides was evident, presumably due to hydrolysis, whereas  $\text{UF}_6$  was apparently unaffected under similar conditions. It is also worth noting that the preparation of  $\text{UOF}_4$ , by reaction of  $\text{UF}_6$  with traces of  $\text{H}_2\text{O}$  in hydrogen fluoride solution is not easily effected [79-82]. Thus the introduction of trace amounts of water or moist air may be effective in depositing ruthenium from mixtures of  $\text{RuF}_5$  in  $\text{UF}_6$  and this may warrant further investigation.

❧  
CHAPTER  
9

Experimental Techniques

## 9.1 GENERAL PREPARATIVE TECHNIQUES

Many of the starting materials and majority of the products described in this thesis are sensitive to air and/or moisture and required handling in either vacuo or inert atmospheres to prevent decomposition. Metal, glass or fluoroplastic containers provided vessels for reactions and storage. Metal reactors were pumped to high vacuum ( $\sim 10^{-4}$  torr), seasoned with fluorine, flamed, and re-evacuated before use. Glass and fluoroplastic containers were evacuated with heating, seasoned with fluorine or chlorine trifluoride and pumped to high vacuum.

Volatile, air-sensitive materials were transferred using either static or dynamic vacuum conditions by the application of a suitable temperature gradient. Non-volatile materials were manipulated under a dry nitrogen atmosphere in an auto-recirculating positive pressure dry box [Vacuum Atmospheres Co., VAC HE 42-2 Dri Lab]. The atmosphere of the box is circulated through columns of manganous oxide and molecular sieves to remove oxygen and water. Static electricity caused difficulties when transferring or weighing small quantities of finely divided solids in the dry box. In order to alleviate this problem a 4m Ci  $^{210}\text{Po}$   $\alpha$ -emitting source [type PDV 1, Radiochemical Centre, Amersham, Bucks.] was employed. Weighings were recorded using a Sartorius microbalance which was situated inside the dry box.

## 9.2 VACUUM SYSTEMS AND REACTION VESSELS

Vacuum line techniques were used in the preparation of all the compounds studied. A metal manifold with high and low vacuum facilities formed the basic system [Fig. 9.1] which was constructed from  $\frac{3}{8}$ " o.d.,  $\frac{1}{8}$ " i.d. nickel tubing [H. Wiggins & Co., Hereford] and



argon arc welded nickel "U" traps. The manifold was completed with AE-30 series hard drawn stainless steel needle valves, crosses and tees [Autoclave Engineers Ind., Erie, Pennsylvania, USA] and connected to the vacuum systems through diaphragm valves [Hoke International (UK) Ltd., Barnet, Herts.].

The rough vacuum system (ultimate vacuum  $\sim 10^{-2}$  torr) consisted of a single-stage rotatory pump fitted with a large metal trap containing granules of soda lime (5-10 mesh) in order to trap out and neutralise fluorine and other volatile fluorides removed from the manifold. The main vacuum system (ultimate vacuum  $\sim 10^{-5}$  torr) consisted of a double-stage rotatory pump which was connected to the manifold via a mercury diffusion pump and a glass cold trap maintained at  $-196^{\circ}\text{C}$ . A facility for admitting fluorine gas was attached, allowing the gas directly into the manifold for seasoning apparatus from welded nickel cans ( $\sim 1 \text{ dm}^{-3}$ ) fitted with stainless steel needle valves.

Manifold pressures of plus or minus one atmosphere (0-1500 torr  $\pm$  5 torr) were measured using a stainless steel Bourdon-tube gauge [Type IF/66Z, Budenberg Gauge Co. Ltd., Broadheath, Greater Manchester]. The vacuum was monitored using a cold-cathode Penning ionisation gauge [Model 2A, Edwards High Vacuum Ltd., Crawley, W. Sussex] capable of measuring pressures in the range  $10^{-2}$  to  $10^{-6}$  torr.

A variety of metal, fluoroplastic or pyrex 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 precision  $\frac{1}{4}$ " o.d. glass connected to  $\frac{1}{4}$ " o.d. stainless steel tubing machined to fit Autoclave Engineers AE-30 series fittings with ChemCon connectors [types STD/4-E/P and STD/4-TP, Production Techniques Ltd., Fleet, Hampshire] using PTFE compression unions. Greaseless glass

valves [Quickfit 'Rotaflo', Dow-Corning Ltd. or 'Youngs' valves, J. Young, Scientific Glassware Ltd., Acton, London] fitted with PTFE stems were used where glass systems were employed or, alternatively, glass reaction vessels were fitted with ChemCon PTFE needle valves.

Small fluoroplastic reactors were fabricated by heating and moulding either  $\frac{1}{4}$ " o.d. or  $\frac{3}{16}$ " o.d. Teflon-FEP tubing [Trimflex Corporation, USA]. These reactors were attached to the manifold via 'ChemCon' PTFE needle valves and PTFE compression unions.

Metal reactors consisted of either stainless steel or spun nickel test tubes (volume  $\sim 30 \text{ cm}^3$ ) with a compression union sealed by a gold gasket. The reactor was attached to the manifold via an Autoclave Engineers series AE-30 high temperature stainless steel needle valves.

### 9.3 CHARACTERISATION OF PRODUCTS

#### 9.3.1 Infrared Spectroscopy

Infrared spectra in the range  $4000\text{--}180 \text{ cm}^{-1}$  were recorded on Perkin-Elmer 580B spectrometers. Solid samples were run as dry, finely ground powders pressed between KBr ( $4000\text{--}300 \text{ cm}^{-1}$ ) or polyethylene ( $700\text{--}200 \text{ cm}^{-1}$ ) windows. Gas phase spectra were obtained using 10 cm path length copper cells fitted with AgCl windows ( $4000\text{--}400 \text{ cm}^{-1}$ ). The gas cells were attached to the manifold and were equipped with side arms into which the gaseous samples could be frozen out. PTFE gaskets provided an air-tight seal between the windows and the cell body.

#### 9.3.2 Raman Spectroscopy

Raman spectra were recorded on a Codberg T800 spectrometer with either a 250 mW  $\text{Ar}^+$  laser [model 52, Coherent Radiation Labs.] or a

500 mW Kr<sup>+</sup> laser [Model 164, Spectra Physics Inc.]. The Ar<sup>+</sup> laser provided exciting lines at 5145 Å (green) and 4880 Å (blue), whilst the Kr<sup>+</sup> laser gave an exciting line at 6471 Å (red). Solid samples were contained in Pyrex capillaries or 1/4" o.d. FEP tubes.

### 9.3.3 X-Ray Powder Diffraction

Samples were ground into a fine powder in a dry box and loaded into seasoned Pyrex capillaries (~0.5 mm o.d.). The capillaries were plugged inside the dry box with a low melting point wax, which was melted with a soldering iron, and immediately on removal from the dry box sealed using a microtorch [Model H164/1, Jencons, Hemel Hempstead, Hertfordshire]. Photographs were taken in a Phillips 11.64 cm diameter camera, on Koldirex KD 59T film [Eastman-Kodak Limited]. Nickel filtered Cu-K $\alpha$  radiation was used with exposure times of 3 to 9 hours.

### 9.3.4 Nuclear Magnetic Resonance Spectroscopy

Both <sup>1</sup>H and <sup>19</sup>F nmr spectra were recorded on a Jeol JNM-PS-100 instrument operating at 94.08 MHz, with samples contained in sealed 3/16" o.d. preseasoned FEP tubes. Low temperature spectra (probe temperature, 0 to -130°C) were obtained by cooling the spinning sample with a stream of cold, dry nitrogen from a 5-litre Dewar vessel of liquid nitrogen. The temperature was measured using an electric thermometer [Comark, Model 1623].

The <sup>1</sup>H and <sup>19</sup>F spectra were calibrated using TMS and CFCl<sub>3</sub> respectively as external standards.

### 9.3.5 Electron Spin Resonance Spectroscopy

Esr spectra were recorded on a Bruker ER200 spectrometer with a

solution of the sample in dry acetonitrile in a sealed  $\frac{3}{16}$ " o.d. FEP tubing. Spectra were usually recorded at liquid nitrogen temperature.

#### 9.3.6 Mass Spectroscopy

Mass spectra were recorded on a VG Micromass 16B machine. Volatile samples were introduced to the ionisation chamber through a vacuum inlet system, whilst 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. In order to minimise the decomposition of the sample during the passage through the mass spectrometer the entire system was preseasoned by flushing with small amounts of fluorine.

#### 9.3.7 Elemental Analysis

Elemental analyses were performed by either CHN Analysis [Countess-thorpe Road, South Wigston, Leicester] or by BNF plc [Springfield Works, Salwick, Preston]. Samples for analysis were loaded into pre-seasoned FEP tubes in a dry box and sealed under vacuum.

### 9.4 GENERATION OF FLUORINE

Ruthenium pentafluoride was prepared in a flow system by the direct fluorination of ruthenium powder [Goodfellows Ltd.]. The fluorine was produced by a medium temperature 60 amp fluorine generator [ICI Ltd., General Chemical Division] with a maximum output of 40g per hour. The fluorine emitted from the generator was led directly to an efficient fume hood or to the reaction system through metal traps containing sodium fluoride pellets to remove hydrogen fluoride. Further impurities were removed by liquid oxygen or dry ice traps built into the glass reaction systems were attached to the metal line through

1/4" o.d. neoprene compression seals. Dry nitrogen gas was used to purge the cathode compartment and the reaction system before and after preparation and was used as a diluent during fluorination.

## 9.5 CHEMICALS, SOURCES AND PURIFICATION PROCESSES

### 9.5.1 Starting Materials

FLUORINE (99.8% purity, Matheson Gas Products); for use on the manifold was used without purification from a cylinder. For safety and convenience the gas was transferred to welded nickel cans (~1 dm<sup>3</sup> capacity).

CHLORINE TRIFLUORIDE (Fluorochem Ltd.); was used for seasoning without further purification directly from the cylinder.

URANIUM HEXAFLUORIDE (British Nuclear Fuels plc); was vacuum sublimed before use.

MOLYBDENUM HEXAFLUORIDE, TUNGSTEN HEXAFLUORIDE (Ozark Mahoning Ltd.); used straight from the cylinder after removal of two or three 'heads', to treat the manifold and remove any hydrogen fluoride from the cylinder.

NITRIC OXIDE and NITROGEN DIOXIDE/DINITROGEN TETRAOXIDE (Aldrich Chemical Co. Ltd.); were purified by vacuum distillation before use.

COPPER (Koch-Light Ltd.), ZINC (Fisons Scientific Apparatus Ltd.), MOLYBDENUM (Hopkin & Williams Ltd.) and TUNGSTEN (Fisons Scientific Apparatus Ltd.); these metal powders were cleaned with dilute acid, dried in an oven and degassed under dynamic vacuum before use.

SULPHUR and ZINC SULPHIDE (B.D.H. Ltd.); were used after pumping at elevated temperatures in dynamic vacuum.

TUNGSTEN(IV) SULPHIDE (Alfa Products Ltd.); was degassed under dynamic vacuum before use.

TRIMETHYL Silyl Methyl Sulphide and BIS-TRIMETHYL Silyl Sulphide

(Lancaster Synthesis); were vacuum distilled onto activated type 4A molecular sieves.

UREA and THIOUREA (Fisons Scientific Apparatus Ltd.); were used after drying in an oven and degassed under dynamic vacuum.

SODIUM FLUORIDE (Aldrich Chemical Co. Ltd., powder), MAGNESIUM FLUORIDE, CALCIUM FLUORIDE, BARIUM FLUORIDE, MAGNESIUM FLUORIDE (5% NICKEL FLUORIDE), and CRYOLITE (British Nuclear Fuels plc, pellets); were dried under dynamic vacuum and heated to 300°C in an atmosphere of fluorine prior to use.

RUTHENIUM (Goodfellows Ltd.); was used after being reduced at red heat in a stream of hydrogen.

POTASSIUM FLUORIDE, RUBIDIUM FLUORIDE, CALCIUM FLUORIDE (B.D.H. Ltd.), MAGNESIUM FLUORIDE and AMMONIUM FLUORIDE (Aldrich Chemical Co. Ltd.); these powders were dried under dynamic vacuum at 250°C and fluorinated several times at elevated temperatures before use.

### 9.5.2 Solvents

HYDROGEN FLUORIDE (ICI Ltd.); was vacuum distilled from a cylinder into a welded nickel storage can. To remove the traces of moisture approximately one atmosphere, at -78°C of fluorine gas was introduced into the can. The can was allowed to warm to room temperature and was agitated periodically over a period of several hours before removal of the more volatile contents of the reactor. This procedure was repeated several times before the hydrogen fluoride was distilled through a fluorine atmosphere into a 3/4" o.d. Kel-F storage tube.

ACETONITRILE (B.D.H. Ltd., Spectroscopic Grade); was repeatedly distilled onto and refluxed over phosphorus pentoxide. It was then

distilled into glass ampoules in which it was stored over activated type 4A molecular sieves.

GENETRON 113 (Fluka AG); was purified by vacuum distillation onto dry phosphorus pentoxide.

CARBON TETRACHLORIDE (B.D.H. Ltd.); was distilled and then vacuum distilled onto activated 4A molecular sieves before use.



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# PURIFICATION OF URANIUM HEXAFLUORIDE BY NON-AQUEOUS MEANS

NIGEL PHILLIP FREESTONE

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## Abstract

This work has shown that nitrogen dioxide will selectively remove uranium hexafluoride from a mixture containing the hexafluorides of uranium, molybdenum and tungsten *via* the formation of nitrylium hexafluorouranate(V).

The production of lower uranium fluorides and elemental sulphur or sulphur fluorides from many of the attempted preparations of uranium(VI) thiofluorides was predicted from a thermodynamic study of the stabilities of  $MCl_nF_{6-n}$  ( $M = U, Mo, W; n = 1-5$ ),  $MO_nF_{6-2n}$ ,  $MS_nF_{6-2n}$  ( $M = U, Mo, W; n = 1$  or  $2$ ) with respect to decomposition and disproportionation.

Sorption of the liquid hexafluorides on various potential sorbents was investigated. Encouraging results were obtained for cryolite.

Salts such as  $ARuF_6$  ( $A = K, Rb, NH_4$ ) were synthesised by direct interactions between  $AF_6$  and  $RuF_5$  in AHF. These reactions were found to require the presence of a polar solvent. It was found that ruthenium pentafluoride in liquid uranium hexafluoride could be removed by the introduction of trace quantities of water.