

SOME REACTIONS OF TUNGSTEN AND

RHENIUM HALIDES

by

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A Thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy of the University of Leicester.

November, 1970

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## STATEMENT

The accompanying thesis submitted for the degree of Doctor of Philosophy and entitled "Some Reactions of Tungsten and Rhenium Halides" is based on work conducted by the author in the Department of Chemistry of the University of Leicester during the period between October, 1967 and July, 1970.

All the work recorded in this thesis is original unless otherwise acknowledged in the text or by references. None of the work has been submitted for another degree in this or any other university.

Signed

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*14/11/70*

## ACKNOWLEDGEMENTS

I would like to thank my supervisor, Professor R. D. Peacock, for his continual help and guidance throughout the course of my research. I am also indebted to my colleagues at Leicester, particularly my husband, Dr. G. W. Fraser and Dr. J. Burgess, whose encouragement and advice I have found most useful.

I extend my thanks to Mrs. B. Randle who ran most of the nuclear resonance spectra in this thesis and to Miss J. Pollock who painstakingly typed the manuscript.

A University of Leicester scholarship during the academic years 1968 - 69 and 1969 - 70 is gratefully acknowledged.

## Summary

The preparation and some reactions of chloride fluorides of tungsten(VI) (of the type  $WCl_nF_{6-n}$ ) have been studied. Values for the heat of formation of liquid tungsten chloride pentafluoride and tungsten dichloride tetrafluoride of  $-387 \pm 5$  kcal/mole and  $-350 \pm 7$  kcal/mole respectively, have been calculated from measured values of the heat of hydrolysis of the compounds and known thermochemical data. These values have led to some discussion as to the relative strength of the W-F bond (and similarly the W-Cl bond) in tungsten(VI) chloride fluoride compounds.

Unsuccessful attempts have been made to separate the cis and trans isomers of tungsten dichloride tetrafluoride by both physical and chemical means. The  $^{19}F$  spectrum of  $WCl_2F_4$  consists of two triplets (in the ratio of 1:1) and a singlet, which indicates the presence of respectively the cis and trans isomers. In all experiments the  $^{19}F$  spectrum of the volatile products have shown the ratio of the  $WCl_2F_4$  isomers to still be the same. It has therefore been suggested that the cis and trans isomers of tungsten dichloride tetrafluoride are in dynamic equilibrium and cannot be separated.

Preliminary investigations of the low temperature exchange reactions between rhenium hexafluoride and the boron trihalides,  $BCl_3$  and  $BBr_3$ ; both in the presence and absence of free halogen, have resulted in solid products which are believed to be rhenium pentachloride and rhenium tetrabromide respectively. A value for the heat of formation of rhenium pentachloride of  $-85 \pm 5$  kcal/mole has been calculated.

The heats of formation of  $XeF_2$ ,  $SbF_5$  and  $XeF_2 \cdot 2SbF_5$

proved difficult to obtain, possibly due to the fact that though the predominant products of hydrolysis were those expected, small quantities of other compounds - obtained by secondary reactions - may also have been present.

A melting point of  $63^{\circ}\text{C}$  and a boiling point of  $220^{\circ} \pm 5^{\circ}\text{C}$ . were measured for pure  $\text{XeF}_2 \cdot 2\text{SbF}_5$ .

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PART I

DISCUSSION AND RESULTS

1. Introduction - Halides of Tungsten and Rhenium  
and Related Compounds.

1.1. High Oxidation State Transition Metal Binary Halides

The major progress in transition metal fluorine chemistry has been made since 1945; the stimulus for this work being gained from the requirements of atomic energy programmes. A considerable amount of work has been done in the preparation, purification and physical characterisation of the highly volatile fluorides of transition metals. However, because suitable experimental techniques have not been available until quite recently, there have been relatively few investigations of the chemical properties of these compounds. Some of the observations that have been made in the past are incorrect and most of the observations are fragmentary and not related to a systematic study of the elements concerned.

In comparison with the volume of work carried out in the last twenty years on the higher transition metal binary fluorides, relatively few advances in the chemistry of the other higher halides have occurred. The bonding between transition metals and the halogen atoms has not been closely studied. However it has been suggested by Colton and Canterford<sup>1</sup> that the trends in physical and chemical properties can both be rationalised on the basis of some back donation from partly filled metal  $t_{2g}$  orbitals to the empty d orbitals on the halogen.

As in the binary fluorides, the stabilities of the higher oxidation states of the other binary halides show the same trends in stability: a decrease towards the right of the Periodic Table being observed. The ability of

halogens other than fluorine to oxidise a transition metal to a high valency state decreases from chlorine to iodine, thus, for molybdenum the highest chloride is molybdenum hexachloride,  $\text{MoCl}_6$ , but the highest iodide is only molybdenum triiodide [see Table 1.3.1].

## 1.2. Mixed Halides

### 1.2.1. Introduction

Although monomeric volatile chloride fluorides of the characteristic elements are well known, knowledge of the halide fluorides of transition elements has been restricted. The pioneer work of Ruff and co-workers may well have produced chloride fluorides but this was not realised. For example, it is quite probable that the early preparation of tungsten hexafluoride by the action of antimony pentafluoride on tungsten hexachloride<sup>2</sup> produced chloride fluorides but that these were not detected. No hexavalent transitional metal mixed halide was reported until the identification of tungsten chloride pentafluoride from the exchange reaction between tungsten hexafluoride and titanium tetrachloride<sup>3</sup> but other less volatile mixed halides of transition metals in lower oxidation states were already characterised - viz. titanium dichloride difluoride,  $\text{TiCl}_2\text{F}_2$ ,<sup>4</sup> titanium chloride trifluoride,  $\text{TiClF}_3$ ,<sup>5</sup> uranium chloride trifluoride,  $\text{UClF}_3$ ,<sup>6</sup> vanadium chloride trifluoride,  $\text{VClF}_3$ ,<sup>7</sup> divanadium tetrachloride pentafluoride,  $\text{V}_2\text{Cl}_4\text{F}_5$ ,<sup>7</sup> niobium tetrachloride fluoride,  $\text{NbCl}_4\text{F}$ ,<sup>8</sup> tantalum tetrachloride fluoride,  $\text{TaCl}_4\text{F}$ <sup>9</sup> and osmium iodide tetrafluoride,  $\text{OsIF}_4$ .<sup>10</sup>

### 1.2.3 Preparation of Chloride and Bromide - Pentafluoride Compounds

The first chloride pentafluoride, of the type  $MClF_5$ , to have been reported was sulphur chloride pentafluoride.<sup>11</sup> With the recent discovery of the corresponding tungsten, rhenium and tellurium compounds some comparisons of the physical and chemical properties of these compounds may be made.

All the  $MClF_5$  compounds may be made by the slow fluorination of the appropriate chloride:  $SClF_5$ <sup>11</sup> from sulphur dichloride at  $-10^\circ$  (though the yield obtained by this method is very small),  $TeClF_5$ <sup>12</sup> from tellurium tetrachloride,  $WClF_5$ <sup>13</sup> from tungsten hexachloride and  $ReClF_5$ <sup>14</sup> from rhenium pentachloride.

In all cases large proportions of the corresponding hexafluoride are also formed as further substitution of fluorine for chlorine takes place. The chloride pentafluoride may then be separated from most of the hexafluoride by fractional distillation under vacuum.

In contrast with the  $MClF_5$  compounds the corresponding bromide pentafluorides,  $MBrF_5$ , are less stable. Attempts have been made to prepare tungsten bromide pentafluoride both by the action of bromine on tungsten pentafluoride [this thesis Part II section 2.1.6] and by passing a mixture of bromine trifluoride and bromine monofluoride [made by bubbling fluorine through liquid bromine] over tungsten hexacarbonyl.<sup>15</sup> The  $^{19}F$  spectra of compounds obtained from both these preparations show a large signal

due to tungsten hexafluoride and a weak doublet which was attributed to the bromide pentafluoride - the doublet reported by this writer was to lower field of tungsten hexafluoride while that reported by I. Haigh was further upfield than tungsten hexafluoride. It is thought more likely that the  $^{19}\text{F}$  spectroscopy signal of tungsten bromide pentafluoride, if it exists, would be upfield from tungsten hexafluoride.

In contrast with the uncertainty over the preparation of tungsten bromide pentafluoride the evidence for the corresponding sulphur and tellurium compound is well documented. Tellurium bromide pentafluoride may be prepared by the action of fluorine, diluted with nitrogen, on tellurium tetrabromide (cf. the corresponding chloride pentafluoride)- large proportions of tellurium hexafluoride and free bromine also resulting from this reaction.<sup>12</sup> Sulphur bromide pentafluoride may be prepared by the action of bromine on disulphur decafluoride at  $150^{\circ}$ <sup>16</sup> or bromine and bromine pentafluoride on sulphur tetrafluoride at  $100^{\circ}$ .<sup>17</sup>

No iodine pentafluoride compound, of the type  $\text{MIF}_5$ , where  $\text{M} = \text{S}, \text{Te}, \text{W}$  or  $\text{Re}$ , have, as yet, been reported.

### 1.2.3. Some Properties of Chloride and Bromide Pentafluoride Compounds

Of the four  $\text{MClF}_5$  compounds only sulphur chloride pentafluoride appears to be a completely stable entity at room temperature; tungsten chloride pentafluoride decomposes slowly at room temperature (a large proportion

decomposing within twenty-four hours) but is stable for several weeks at  $-10^{\circ}$  [see section 2.2.2] rhenium chloride pentafluoride decomposes rapidly at room temperature and slowly even at  $-30^{\circ}$  (the composition products being mainly rhenium hexafluoride and rhenium chlorides),<sup>14</sup> whilst chlorine-free samples of tellurium chloride pentafluoride have not been isolated.

Chemically all the  $MClF_5$  compounds appear to be more reactive than the corresponding hexafluoride: sulphur chloride pentafluoride and tellurium chloride pentafluoride are hydrolysed by water although sulphur hexafluoride is inert and tellurium hexafluoride reacts only slowly. Tungsten chloride pentafluoride undergoes halogen exchange reactions with phosphorus oxychloride within half an hour at room temperature, although tungsten hexafluoride remains unreacted even when allowed to stand at room temperature for several days.

A few chemical observations have been made which enable some contrasts to be drawn between tellurium chloride pentafluoride and tungsten chloride pentafluoride; the latter does not react with ethylene or phosphorus trifluoride at room temperature while the former reacts with phosphorus trifluoride to produce phosphorus chloride tetrafluoride and phosphorus dichloride trifluoride.<sup>12</sup> The reaction of tellurium chloride pentafluoride with ethylene is complex but the corresponding reaction of tellurium bromide pentafluoride produces 1, 2 bromo-fluoroethane.<sup>12</sup> In both the reactions tellurium chloride pentafluoride is reduced to tellurium tetrachloride;

indeed, in none of its reactions with a wide range of olefins can tellurium pentafluoride fragments be identified in the reaction products - this is in sharp contrast with reactions of sulphur chloride pentafluoride and olefins in which the  $SF_5$  entity is retained [e.g.  $SClF_5 + C_2H_2 \rightarrow SF_5CH_2.CH_2Cl$ ].

No comparison can be made between compounds of the type  $MBrF_5$ ; as no chemical properties of tungsten bromide pentafluoride are known. As could be expected sulphur and tellurium bromide pentafluoride undergo analogous reactions to that of the corresponding chloride pentafluoride; chemical attack of the bromide being more rapid.

#### 1.2.4. Dichloride Tetrafluorides and Other Mixed Chloride Fluorides of Transition Metals

Substitution of a second fluorine atom by a chlorine in a hexafluoride has so far been accomplished only with tungsten<sup>13,18</sup> though an unsuccessful attempt has been made to try and make the corresponding tellurium compound,  $TeCl_2F_4$ .<sup>19</sup> In this thesis is reported the identification and some of the properties of all the chloride fluorides of tungsten(VI),  $WCl_nF_{6-n}$ , where  $n = 1 \rightarrow 5$ .

The dichloride tetrafluoride,  $WCl_2F_4$ , has been made by the reaction between tungsten hexachloride and fluorine using different temperature conditions from those required in the preparation of tungsten chloride pentafluoride [this thesis Part II section 2.1.3.]. The remaining compounds of the type  $WCl_nF_{6-n}$ , have been

identified from exchange and disproportionation reactions; certain of the properties of some of them have been reported previously.<sup>13,20</sup>

#### 1.2.5. The Possible Existence of Mixed Halides of Hexavalent Transition Metal Compounds with Metals other than Tungsten and Rhenium

The most likely remaining elements which might be expected to form mixed chloride fluorides are osmium and molybdenum; especially as molybdenum forms a hexachloride.<sup>21</sup> However from the exchange reaction between osmium hexafluoride and boron trichloride<sup>22</sup> only a binary chloride (possibly osmium tetrachloride) has been isolated and it is evident that any mixed compound, of the type  $\text{OsCl}_n\text{F}_{6-n}$ , which may be formed as an intermediate readily decomposes with reduction of osmium(VI) to a lower oxidation state. The exchange reaction between excess molybdenum hexafluoride and non-metal chlorides such as carbon tetrachloride, silicon tetrachloride and boron trichloride is said to result in the reduction of molybdenum(VI) to molybdenum(V) and in the formation of  $\text{Mo}_2\text{Cl}_3\text{F}_6$  and the respective non-metal fluoride (e.g. carbon tetrafluoride, silicon tetrafluoride and boron trifluoride.<sup>20,23</sup> The room temperature exchange reaction between molybdenum hexafluoride and excess boron trichloride yields molybdenum pentachloride<sup>20</sup>, but it seems that this experiment requires repetition under milder conditions and using lower temperatures [ $\text{MoCl}_6$  loses chlorine readily below  $100^\circ$ <sup>21</sup> and it may be that compounds

of the type  $\text{MoCl}_n\text{F}_{6-n}$  may also lose halogen readily]. It should be noted that rhenium chloride pentafluoride is extremely difficult to prepare and is thermally unstable, even in a moisture and oxygen free atmosphere, giving rhenium hexafluoride and lower rhenium chlorides,<sup>14</sup> hence it would be expected that osmium chloride pentafluoride, if it did exist, would be even less thermally stable.

The key to the lack of mixed halide compounds probably lies in the oxidising power of the transition metal hexafluorides. From a comparative study of the chemical reactions of the third row transition series, Bartlett has shown that the electron affinity increases regularly in the sequence  $\text{WF}_6 < \text{ReF}_6 < \text{OsF}_6 < \text{IrF}_6 < \text{PtF}_6$ . The increase in electron affinity with unit increase in atomic number appears to be  $-20$  kcal/mole.<sup>24</sup> The oxidising ability of the hexafluorides is well illustrated by their reaction with halogens. Gibler<sup>25</sup> showed that osmium hexafluoride spontaneously oxidises iodine while tungsten hexafluoride does not. Chlorine has been shown to react immediately at room temperature with platinum hexafluoride:<sup>26</sup> the product possibly being a mixture containing  $\text{PtF}_5$  and  $\text{ClF}_2\text{PtF}_6$ .<sup>27</sup> Iridium hexafluoride has also been shown to oxidise chlorine.<sup>26</sup> Although osmium hexafluoride itself does not react with chlorine, it seems likely that the electron affinity of the substitution products,  $\text{OsCl}_n\text{F}_{6-n}$ , (and hence their oxidising power) will increase as more fluorine is replaced by chlorine so that the likelihood of a stable compound,  $\text{OsClF}_5$ , is probably remote. It should be noted that  $\text{ReClF}_5$  decomposes slowly

even at  $-30^{\circ}\text{C}$ . However, the most likely effective experiment, viz. the reaction of osmium tetrachloride with fluorine in a flow system designed to sweep the volatile products quickly from the reaction zone has not yet been attempted (cf. preparation of  $\text{WClF}_5$  and  $\text{WCl}_2\text{F}_4$ ).

### 1.3. High Oxidation State Technetium and Rhenium Chlorides and Bromides

The binary halides of the 2nd and 3rd row transition metal groups VI(a) VII(a) and VII in their highest oxidation states are listed in Table 1.3.1.

#### 1.3.1. The Reported Preparation of Rhenium and Technetium Hexachlorides

Early reports in the literature of a volatile green chloride of rhenium which was thought to be the hexa- or heptachloride,<sup>28,29</sup> but which was never characterised, were neglected after the subsequent preparation and characterisation of rhenium pentachloride. The differences between technetium and rhenium are of degree rather than of kind: though all the isotopes of the former, being radioactive, result in instability which may influence chemical kinetics particularly in the solid state.<sup>30</sup> Hence the reported discovery of technetium hexachloride<sup>31</sup> led to further attempts to prepare the corresponding rhenium compound.

Crystalline rhenium hexachloride is reported by Colton to be produced by passing a chlorine-nitrogen mixture at  $650^{\circ}$  over a rhenium film, specially prepared by absorbing ammonium perrhenate into dry porous brick and reducing to the metal at  $600^{\circ}\text{C}$  with hydrogen;<sup>31</sup> though Geilmann and co-workers had previously shown rhenium pentachloride to be the major

product of the chlorination of rhenium powder (previously heated in hydrogen to reduce oxide films) at 500 - 700°C.<sup>32</sup> This apparent contradiction has been attributed by Colton to the fact that the rhenium, used by Geilmann, was commercial rhenium, obtained by reduction of potassium

Table 1.3.1.

Highest Oxidation States of 2nd and 3rd Row Transition

Metal Binary Halides

		Fluoride	Chloride	Bromide	Iodide
Group VI a	2nd row	MoF <sub>6</sub>	MoCl <sub>6</sub>	MoBr <sub>4</sub>	MoI <sub>3</sub>
	3rd row	WF <sub>6</sub>	WCl <sub>6</sub>	WBr <sub>6</sub>	WI <sub>3</sub>
Group VIIa	2nd row	TcF <sub>6</sub>	(TcCl <sub>6</sub> ), TcCl <sub>4</sub>	TcBr <sub>4</sub>	*
	3rd row	ReF <sub>7</sub>	(ReCl <sub>6</sub> )ReCl <sub>5</sub>	ReBr <sub>5</sub>	ReI <sub>4</sub>
Group VIII	2nd row	RuF <sub>6</sub>	(RuCl <sub>4</sub> ) <sup>**</sup>	RuBr <sub>3</sub>	RuI <sub>3</sub>
	3rd row	OsF <sub>7</sub>	OsCl <sub>4</sub>	OsBr <sub>4</sub>	OsI <sub>3</sub>

There is still some doubt about the correct formulation of the compounds in parenthesis.

\* no technetium iodide has, as yet, been reported.

\*\* ruthenium tetrachloride has not been isolated but vapour-pressure measurements of the reaction between ruthenium and chlorine suggest that ruthenium tetrachloride exists in the vapour.

perrhenate and that the presence of large quantities of potassium would inhibit the formation of rhenium hexachloride. The latter maintains that some rhenium hexachloride is also prepared even when commercial rhenium is chlorinated.<sup>33</sup> More recently rhenium hexachloride has been reported to have been produced in five gramme quantities by halogen exchange reactions with rhenium hexafluoride and/or rhenium heptafluoride.<sup>34</sup> The most suitable reagent is reported to be boron trichloride: reaction proceeding below room temperature without any apparent complication from any oxidation-reduction reaction.

The first reported study of technetium chlorides was made by Nelson, Boyd and Smith.<sup>35</sup> They found that technetium did not react with chlorine in a static system, even after heating the system for considerable periods of time. However, it has since been shown that pure technetium metal reacts readily with chlorine at moderate temperatures if a flow system is utilised.<sup>31</sup> The flow of chlorine sweeps the products of the reaction away, allowing further attack of the metal. Chlorination of technetium metal by this method yields two products predominantly technetium tetrachloride and small amounts of a green volatile material said, on analytical evidence, to be technetium hexachloride.

### 1.3.2. Comparison of Some Physical and Chemical Properties Reported for $TcCl_6$ and $ReCl_6$ with those of $MoCl_6$ and $WCl_6$

Rhenium hexachloride is reported by both Colton and

Canterford and co-workers to form long needle crystals which are dichroic, appearing red-brown by transmitted light and dark green by reflected light. The physical properties of the compound measured by these two groups give its melting point as respectively  $25^{\circ}$  and  $19^{\circ} \pm 5^{\circ}$  [a dark liquid resulting which volatilises on gentle heating to give a green vapour] and a magnetic moment of 2.07 B.M.<sup>36</sup> and 1.88 B.M.<sup>37</sup> at  $297^{\circ}\text{K}$ . Both groups found that the compound obeyed the Curie-Weiss law a  $\theta$  of  $28^{\circ}$  being reported by Colton and of  $75^{\circ}$  by Canterford and Waugh. Rhenium hexachloride was shown to be free of rhenium oxide tetrachloride by infra-red spectroscopy.

Few comparisons of the properties reported for rhenium and tungsten hexachloride are possible since the data for the rhenium compound are so fragmentary. However, the little evidence available shows that the rhenium compound is surprisingly more stable than its tungsten analogue. Rhenium hexachloride is said to be thermally stable in both nitrogen and chlorine, no decomposition to the tetrachloride occurring even at  $300^{\circ}$ <sup>38</sup> where as tungsten hexachloride is known to readily dissociate to give initially tungsten pentachloride and finally the tetrachloride and free chlorine at a temperature well below  $300^{\circ}$ .<sup>39</sup> The melting point and volatility of rhenium hexachloride are very much lower than for the corresponding tungsten compound.

Very little is known about the properties of either molybdenum hexachloride<sup>21</sup> or technetium hexa-

chloride.<sup>31</sup> Both may be separated from the corresponding pentachloride by fractional sublimation and both are very unstable decomposing to the more stable lower chloride ( $\text{MoCl}_5$  and  $\text{TcCl}_4$ ) on standing at room temperature. The melting point and volatility of technetium hexachloride are very much lower than for the corresponding molybdenum compound.

### 1.3.3. Evidence against the Existence of Rhenium and Technetium Hexachloride

Cause for doubt on the correct formation of the compound purported to be rhenium hexachloride has arisen because the thermal stability reported for it<sup>38</sup> is so surprisingly high. However, evidence for this formulation seems conclusive; the analysis is consistent with this formula, no rhenium oxygen stretch is present (as detected by infra-red spectroscopy) and the colour is said to be distinct from that of rhenium oxide tetrachloride ~~but~~<sup>though</sup> the melting point is near that of rhenium oxide tetrachloride (~~though~~  $\text{ReOCl}_4$  gives a distinct rhenium-oxygen stretch at  $1030 \text{ cm}^{-1}$  in the infra-red spectrum<sup>40</sup>) and both its melting point and volatility are very much lower than those of tungsten hexachloride.

The magnetic moment of rhenium hexachloride supports it having one unpaired electron. The magnetic moment of  $\text{ReCl}_6$  of 1.88 B.M.<sup>37</sup> at  $297^\circ\text{K}$  is slightly higher than that of the ideal (spin only) moment of 1.73 B.M. The factors which affect the deviation of the magnetic moment of a compound from the spin only value are complex but the value for the magnetic moment of  $\text{ReCl}_6$  seems rather high

in comparison with the value for  $\text{ReF}_6$  of 0.25 B.M.<sup>41</sup> and that of  $\text{ReClF}_5$  of 1.11 B.M.<sup>14</sup> The magnetic moment of  $\text{ReF}_6$  is low, due to spin orbital coupling. Some delocalisation of electrons out of the rhenium  $t_{2(g)}$  orbitals into the chloride ligands will reduce the orbital angular momentum of the metal d electrons and hence the magnetic moment of  $\text{ReCl}_6$  would be expected to be greater than that of  $\text{ReF}_6$  - i.e. the effect of  $t_{2(g)}$  electron delocalisation usually brings the magnetic moment closer to the spin-only value since it corresponds to an additional quenching of orbital angular momentum.<sup>42</sup> Similarly the magnetic moment of  $\text{ReClF}_5$  is higher than that of  $\text{ReF}_6$  but lower than the ideal spin-only value, because the low symmetry ligand field component partially quenches the orbital angular momentum by destroying the degeneracy of the  $t_{2(g)}$  orbital set.

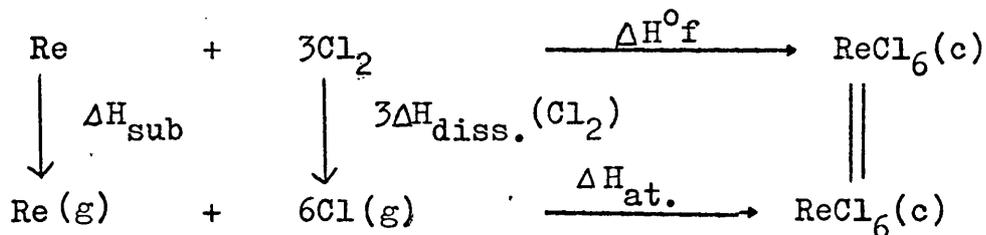
It is also possible that a value for the magnetic moment of a rhenium(V) compound could be as low as that reported for  $\text{ReCl}_6$ ; all rhenium(V) complexes seem to have magnetic properties which deviate markedly from ideal behaviour. Spin orbital coupling could reduce the magnetic moment of a rhenium(V) compound to about 1.2 to 1.5 B.M. as occurs in the octahedral  $\text{ReF}_6^-$  ion which has a magnetic moment of 1.55 B.M.<sup>30</sup>

Consideration of the possible existence of a hexavalent rhenium chloride by methods similar to those used by Dassel to explain the absence of arsenic(V) halides,<sup>43</sup> other than arsenic pentafluoride would seem to be useful. Attempts to stabilise  $\text{AsCl}_5$  as the anion,  $\text{AsCl}_6^-$ , have failed; the addition of  $\text{KCl}$  or  $(\text{CH}_3)_4\text{NCl}$  to  $\text{AsCl}_3/\text{Cl}_2$

mixtures does not produce a product  $M^+AsCl_6^-$ . Similarly no product containing the  $ReCl_7^-$  anion is known though the anion  $WCl_7^-$  has been shown to exist in a solution of tungsten hexachloride in phosphoryl chloride, provided the solvent is in excess.<sup>44,45</sup> No studies similar to the phase studies of the freezing points of  $AsCl_3/Cl_2$ <sup>46,47</sup> and  $AsBr_3/Br_2$ <sup>48,49</sup> mixtures, to see whether or not smooth curves could be obtained indicating no compound formation, have been tried using  $ReCl_4/Cl_2$  or  $ReBr_4/Br_2$  mixtures.

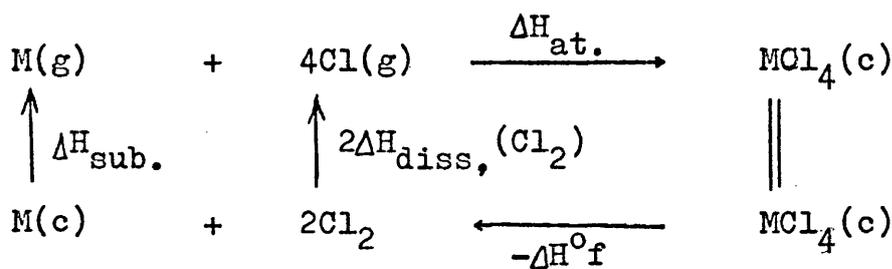
Thermochemical data on the high oxidation state transition metal halides is limited, hence predictions as to whether or not a compound rhenium hexachloride exists can only be made from theoretical calculations with known data.

By considering the heats of atomisation of a given series of transition metal halides a rough estimate of the corresponding value for other compounds in the series may be determined [see Table 1.3.2. and fig. 1.3.1. and fig. 1.3.2.]. A value for the heat of atomisation of solid  $ReCl_6$  of -445 kcal/mole is then obtained. From the thermochemical cycle:



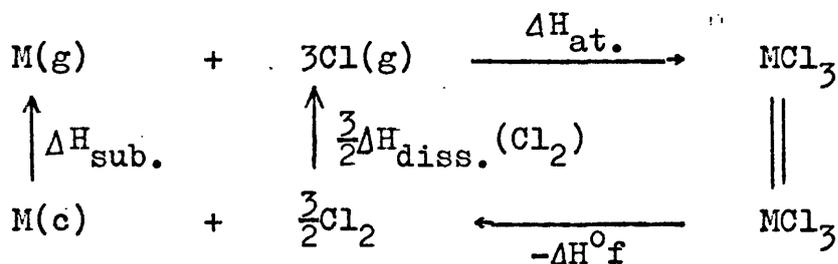
$$\begin{aligned}
 \Delta H^{\circ}f &= 3\Delta H_{diss.}(Cl_2) + \Delta H_{sub} + \Delta H_{at.} \\
 &= + [171 + 189 - 445] \text{ kcal/mole} \\
 &= - 85 \text{ kcal/mole}
 \end{aligned}$$

Heats of Atomisation of 3rd Row Transition Metal Tetra-  
chlorides



	Hf	Ta	W	Re	Os
$\Delta H_{\text{sub.}}$	-168	-186	-200	-189	-174
$2\Delta H_{\text{diss.}}$	-114	-114	-114	-114	-114
$\Delta H^{\circ}\text{f}$	<u>-234</u>	<u>-169</u>	<u>-121</u>	<u>x</u>	<u>-61</u>
$\Delta H_{\text{at.}}(\text{MCl}_4)$	-516	-469	-435	-303 + x	-349 kcal/mole

Heat of Atomisation of Rhenium Trichloride and Penta-  
chloride



$$\begin{aligned}
 \Delta H_{(\text{at.})}(\text{MCl}_3)(\text{c}) &= \Delta H_{\text{sub.}} + \frac{3}{2}\Delta H_{\text{diss.}}(\text{Cl}_2) + \Delta H^{\circ}\text{f} \\
 &= -189 + (-86) + (-63) =
 \end{aligned}$$

-338 kcal/gm. formula at.

[Where  $\Delta H^{\circ}\text{fReCl}_3(\text{c}) = -63$  kcal/mole<sup>50</sup>.]

Similarly

$$\begin{aligned}
 \Delta H_{\text{at.}}(\text{MCl}_5)(\text{c}) &= \Delta H_{\text{sub.}} + \frac{5}{2}\Delta H_{\text{diss.}}(\text{Cl}_2) + \Delta H^{\circ}\text{f} \\
 &= -189 + (-143) + (-85) \\
 &= -417 \text{ kcal/gm. formula at.}
 \end{aligned}$$

[Where  $\Delta H^{\circ}\text{fReCl}_5 = -85$  kcal/mole (this thesis 3.3.2.).]

Figure 1.3.1.

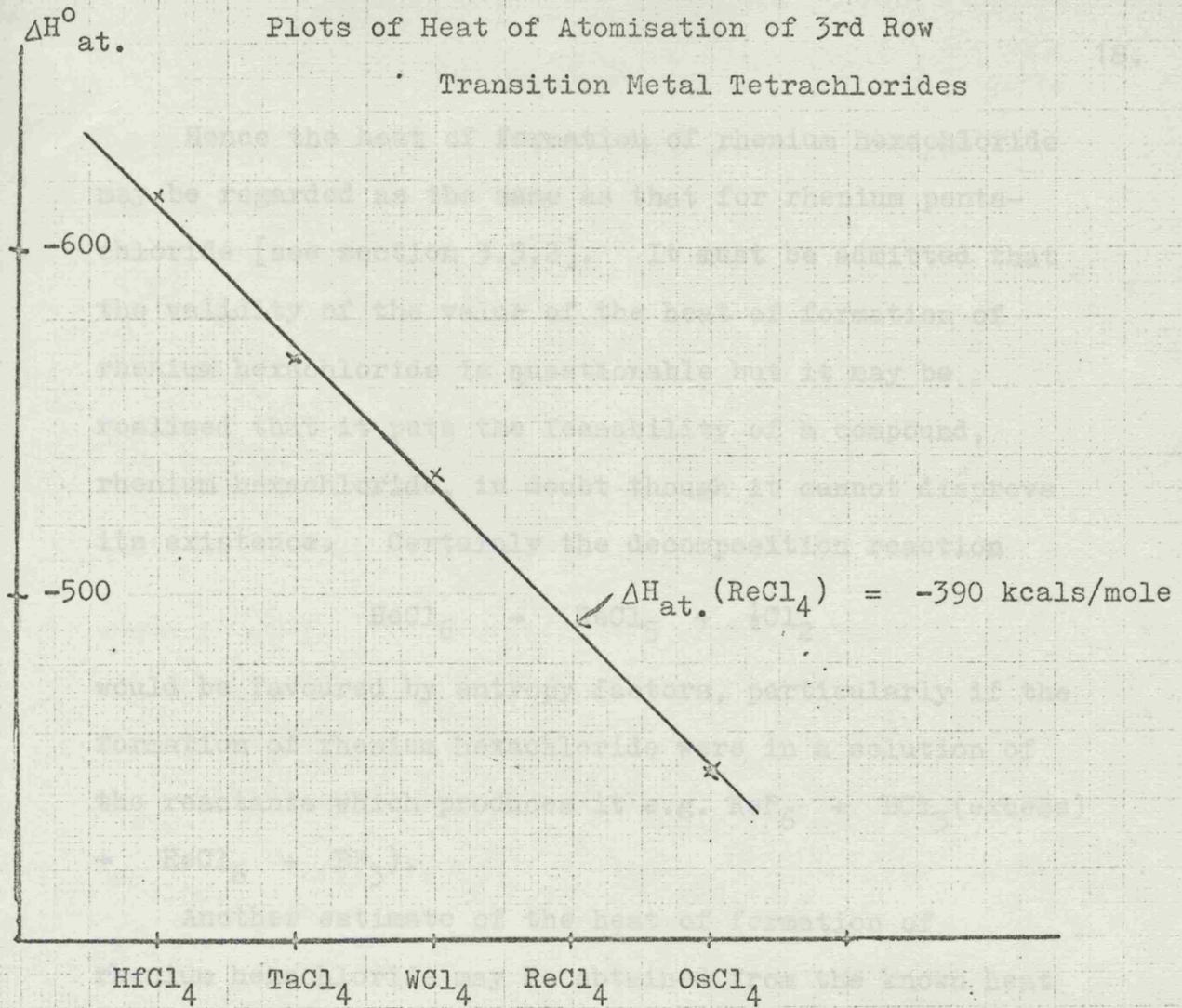
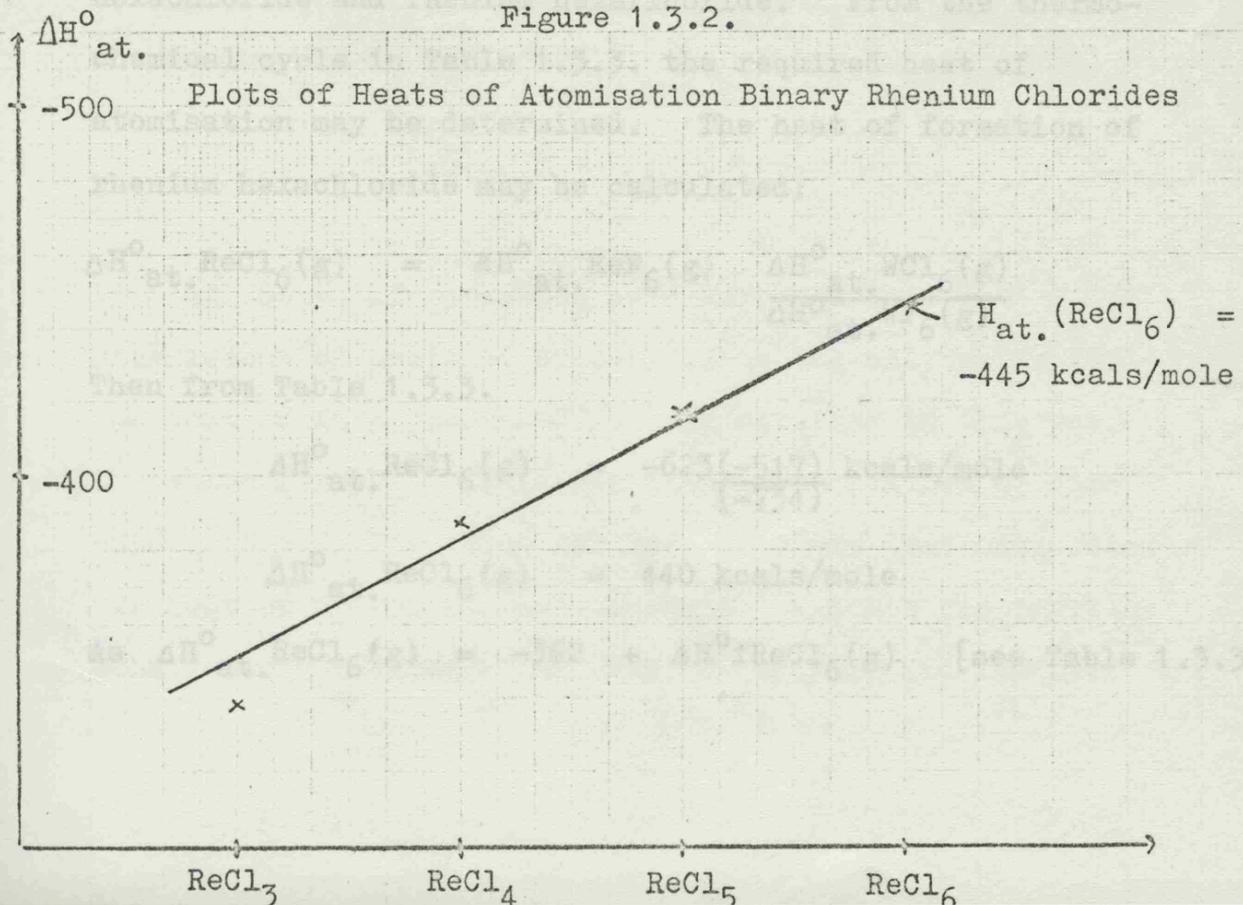
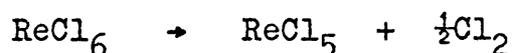


Figure 1.3.2.



Hence the heat of formation of rhenium hexachloride may be regarded as the same as that for rhenium pentachloride [see section 3.3.2]. It must be admitted that the validity of the value of the heat of formation of rhenium hexachloride is questionable but it may be realised that it puts the feasibility of a compound, rhenium hexachloride, in doubt though it cannot disprove its existence. Certainly the decomposition reaction



would be favoured by entropy factors, particularly if the formation of rhenium hexachloride were in a solution of the reactants which produces it e.g.  $\text{ReF}_6 + \text{BCl}_3(\text{excess}) \rightarrow \text{ReCl}_6 + \text{BF}_3$ ).

Another estimate of the heat of formation of rhenium hexachloride may be obtained from the known heat of atomisation of gaseous tungsten hexafluoride, tungsten hexachloride and rhenium hexafluoride. From the thermochemical cycle in Table 1.3.3. the required heat of atomisation may be determined. The heat of formation of rhenium hexachloride may be calculated:

$$\Delta H^\circ_{\text{at. ReCl}_6(g)} = \Delta H^\circ_{\text{at. ReF}_6(g)} \frac{\Delta H^\circ_{\text{at. WCl}_6(g)}}{\Delta H^\circ_{\text{at. WF}_6(g)}}$$

Then from Table 1.3.3.

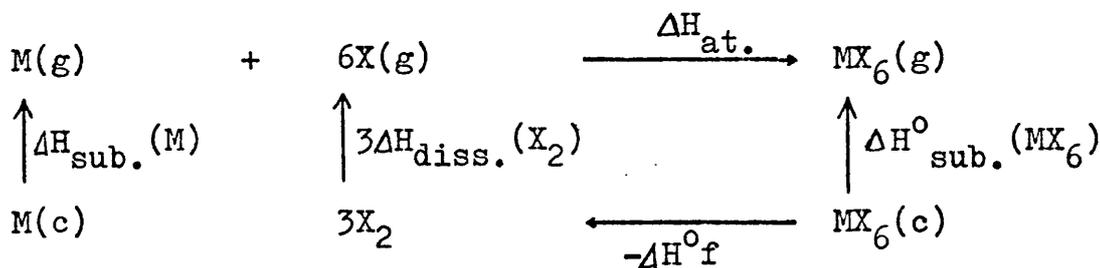
$$\Delta H^\circ_{\text{at. ReCl}_6(g)} = \frac{-623(-517)}{(-734)} \text{ kcal/mole}$$

$$\Delta H^\circ_{\text{at. ReCl}_6(g)} = 440 \text{ kcal/mole}$$

$$\text{As } \Delta H^\circ_{\text{at. ReCl}_6(g)} = -362 + \Delta H^\circ_{\text{fReCl}_6(g)} \quad [\text{see Table 1.3.3.}]$$

Heats of Atomisation of Rhenium and Tungsten Binary

Hexachlorides



where M = W or Re and X = F or Cl

where X = F

For X = Cl

	Re	W		W	Re
$\Delta H_{\text{sub.}}$	-187	-200	$\Delta H_{\text{sub.}}$	-200	-187
$3\Delta H_{\text{diss.}}$	-113	-113	$3\Delta H_{\text{diss.}}$	-175	-175
$\Delta H_{\text{f}}^\circ$	<u>-323</u>	<u>-421</u>	$\Delta H_{\text{f}}^\circ$	<u>-163</u>	<u>x</u>
$\Delta H_{\text{at.}}^{\text{MF}_6}(\text{g})$	-623	-734		-538	-362 + x
			$-\Delta H_{\text{sub.}}^{\text{MCl}_6}$	<u>-21</u>	
				-517	

Note

All heats of formation used were obtained via measurement of heats of hydrolysis as the only value for the heat of formation of  $\text{WCl}_6$ <sup>51</sup> is obtained in this way. The value for  $\text{WF}_6$ <sup>52</sup> is larger than that obtained by bomb calorimetry. The value for  $\text{ReF}_6$  used was that calculated via heat of hydrolysis measurements<sup>22</sup> and not the previous considerably smaller value obtained by Ruff and Kwasnik.<sup>53</sup>

$$\text{Then } \Delta H_f^\circ \text{ ReCl}_6(\text{g}) = -78 \text{ kcal/mole}$$

$$\text{or } \Delta H_f^\circ \text{ ReCl}_6(\text{c}) = -99 \text{ kcal/mole}$$

(If the heats of sublimation of the hexachlorides of both rhenium and tungsten are assumed to be the same.)

An estimate for the degree of error in determining the heat of formation of solid  $\text{ReCl}_6$  by this method will be large and cannot be calculated. However the value of the heat of formation may be ~~reported~~ <sup>regarded</sup> as the largest value possible as both the heat of formation of  $\text{WCl}_6$  [see section 2.10.5.] and the heat of sublimation of  $\text{ReCl}_6$  may be considerably too large.

From this calculated heat of formation of solid  $\text{ReCl}_6$  it would seem that  $\text{ReCl}_6$  is thermally stable with respect to rhenium pentachloride from thermal considerations alone, but the calculated  $T\Delta S$  term causes the Gibbs free energy of decomposition of  $\text{ReCl}_6 \rightarrow \text{ReCl}_5 + \frac{1}{2}\text{Cl}_2$  to be positive but very small.

viz. The entropy of solids may be calculated approximately by means of a formula proposed by Latimer.<sup>54</sup>

$$S^\circ = \frac{3}{2}R \cdot \ln M - 0.94$$

where  $M$  = atomic weight of solid

hence  $\Delta S^\circ$  for  $\text{ReCl}_6 \rightarrow \text{ReCl}_5 + \frac{1}{2}\text{Cl}_2$

$$\begin{aligned} \text{is } \Delta S^\circ &= -\frac{3}{2} \cdot 1.98 \cdot 2.303 [\log(363.5) - \log(398.9)] \\ &= 0.276 \text{ cal/deg.mole.} \end{aligned}$$

$$S^\circ \text{ for } \text{Cl}_2(\text{g}) = 53.29 \text{ cal/deg.mole}$$

Then for  $\text{ReCl}_6(\text{c}) \rightarrow \text{ReCl}_5(\text{c}) + \frac{1}{2}\text{Cl}_2(\text{g})$

$$\Delta S^\circ = -0.2764 + 26.65 \simeq 26.37 \text{ cal/deg.mole}$$

$T\Delta S \simeq 8$  kcal/mole at  $25^\circ$ .

$$\begin{aligned} \text{and } \Delta G(\text{ReCl}_6 \rightarrow \text{ReCl}_5 + \frac{1}{2}\text{Cl}_2) &= \Delta H - T\Delta S \\ &= [(+ 99 - 85) - 8] \text{ kcal/mole} \end{aligned}$$

$$\Delta G^\circ(\text{ReCl}_6 \rightarrow \text{ReCl}_5 + \frac{1}{2}\text{Cl}_2) = +6 \text{ kcal/mole}$$

It has been suggested that the electron affinity of  $\text{ReCl}_6^{55}$  might be of the same order as that of platinum hexafluoride and that rhenium hexachloride would be a sufficiently strong oxidising agent to oxidise any oxygen present to  $\text{O}_2^+$ . If this were the case then  $\text{O}_2^+\text{ReCl}_6^-$ , or possibly  $\text{Cl}_2^+\text{ReCl}_6^-$  (if the reaction were carried out in liquid chlorine or if decomposition of products caused chlorine to be liberated) might be formed by the halogen exchange reaction between  $\text{ReF}_6$  and  $\text{BCl}_3$  and the properties of such compounds might be consistent with some of those stated for rhenium hexachloride; however, the feasibility of either of these suggested compounds existing seems to pose greater problems than those of rhenium hexachloride itself.

The possibility of a hexachloride of technetium existing seems even less likely than that of the rhenium analogue. It has been stated that it is unstable but the degree of instability appears to be less than would be intuitively expected. Indeed its reported properties are very similar to those of technetium oxide tetrachloride. Characterisation of the reported hexachloride was by analysis, which showed a ratio of technetium to chlorine of 1:6 and also by demonstrating that the compound was hydrolysed in the manner expected for a compound of technetium(VI). No infra-red spectroscopic data has as

yet been reported.

Predicting the existence of technetium hexachloride from thermochemical considerations is not possible since data are not available for any technetium chloride or fluoride or for molybdenum hexachloride.

#### 1.3.4. The Reported Preparation of the Highest Oxidation State Technetium and Rhenium Bromide.

Colton reported rhenium pentabromide to be the major product when bromine vapour is carried in a stream of nitrogen over rhenium at  $650^{\circ}$ .<sup>56</sup> Although a previous report claimed that the tribromide only was formed at  $450^{\circ}$ .<sup>57</sup> According to Colton rhenium pentabromide is a dark blue solid which melts a little above room temperature to give a greenish-blue liquid and, on further heating, a blue vapour. However, this compound seems to have properties which might be expected for an oxide bromide.

More recently Canterford, O'Donnell and Waugh have isolated a dark brown solid from the exchange reaction between boron tribromide and rhenium hexafluoride.<sup>34</sup> This compound begins to decompose to the tribromide and free bromine at  $110^{\circ}$  in vacuo, but may be sublimed carefully in a stream of bromine.<sup>37</sup> In contrast to their findings preliminary work, done independently by this writer [see section 3.2.] on the halogen exchange reaction between rhenium hexafluoride and excess boron tribromide both in the presence and absence of large proportions of liquid bromine solvent resulted in a dark brown product whose magnetic moment was consistent with a  $d^3$  compound.

The preparation of rhenium tetrabromide by reduction

of perrhenic acid with hydrobromic acid has been questioned because of the difficulty of removing all traces of moisture from the compound, even by the use of a vacuum desiccator containing phosphorus pentoxide and potassium hydroxide. However, further evidence and characterisation of the compound obtained by the action of excess boron tribromide on rhenium hexafluoride in liquid bromine is required before any further profitable speculation can be made.

The highest oxidation state of technetium achieved for a binary bromide has recently been reported as four in technetium tetrabromide.<sup>58</sup>  $TcBr_4$  is made by oxidising technetium, suspended in water, with 130 vol. hydrogen peroxide. The solution is evaporated to dryness, water added and then the process repeated. On successive additions of 48% hydrobromic acid, followed by evaporation to dryness in vacuum, an unstable brown-red compound is obtained which is reported to analyse to technetium tetrabromide.

#### 1.3.5. Discussion on the Reported Properties of Rhenium Pentabromide

Very little is known about the properties of the compound formulated by Canterford and co-workers as rhenium pentabromide.<sup>34,37</sup> It is said to begin to decompose to rhenium tribromide and bromine at  $110^\circ$  in vacuum.<sup>37</sup> Its magnetic moment falls from 1.28 B.M. to 1.00 B.M. over the temperature range  $295 - 105^\circ K$  - the Curie Weiss law is not obeyed.<sup>37</sup>

Preliminary work done by this writer on the exchange reaction between rhenium hexafluoride and boron tribromide

seemed to indicate that rhenium tetrabromide was formed (even when excess bromine was added as a solvent). One of the reaction products appeared to be bromine - indicating possible decomposition of a higher bromide formed initially, but as the temperature of the reactants was kept below 0°C this would seem to indicate that if rhenium pentabromide was formed, then its thermal stability is less than that previously reported.

Thermochemical data on 3rd row transition metal pentabromides is sparse and the only known heat of formation of a rhenium bromide is that for rhenium tribromide: hence, calculations, to determine whether or not rhenium pentabromide would be theoretically thermochemically stable (with respect to any mode of decomposition), would require too many assumptions and approximations to give results from which meaningful conclusions could be drawn.

## 2. Halogen Compounds of Tungsten(VI)

### 2.1. Introduction

Although tungsten hexachloride and tungsten hexafluoride have been known for many years it is only recently that mixed chloride fluorides have been reported. Tungsten chloride pentafluoride has been synthesised by the reaction of tungsten hexafluoride with titanium tetrachloride.<sup>13</sup> Tungsten chloride pentafluoride and tungsten dichloride tetra fluoride may be synthesised by fluorination of tungsten hexachloride in a flow system;<sup>13,18</sup> the yield of each compound obtained depending mainly on the temperature of reaction. The reaction of tungsten hexafluoride and boron trichloride has been reported to give tungsten trichloride trifluoride.<sup>20</sup>

Studies of chemical reactions of higher fluorides of molybdenum and tungsten with a range of compounds - mostly non-metal chlorides - have indicated that molybdenum hexafluoride is more easily reduced than tungsten hexafluoride; this being in accordance with increase in stability of higher oxidation states down a given group of the periodic table.

### 2.2. Physical and <sup>19</sup>F Nuclear Magnetic Resonance Data

#### 2.2.1. The Use of Nuclear Magnetic Resonance Techniques for the Identification of Transition Metal Fluorides

The utilisation of <sup>19</sup>F nuclear magnetic resonance (n.m.r.) has proved a convenient technique for the study of liquid and soluble solid fluorides; in many cases

enabling the components of mixtures to be determined without need for separation. In the case of compounds of the type  $WCl_nF_{6-n}$  an  $^{19}F$  spectrum could be obtained which shows signals due to all compounds of this type, where  $n = 0, 1, 2, 3, 4$  or  $5$ . The ranges of observed coupling constants and chemical shifts in  $^{19}F$  resonance studies are large compared with those found in  $^1H$  spectra, because each effect is controlled by a different factor for each nucleus. Compounds containing several differently shielded nuclei, coupled by indirect spin-spin interactions, often show simple first order type spectra (cf.  $^{19}F$  spectrum of the  $WCl_nF_{6-n}$  compounds) because the chemical shift differences are large compared with the coupling constants involved. With tungsten compounds one isotope of tungsten,  $^{183}W$ , is observable as it has a half integral spin and couples to the fluorine - hence its presence can be seen indirectly by  $^{19}F$  spectroscopy in terms of the  $J_{^{183}W - ^{19}F}$  coupling constants associated with many tungsten compounds.

A further use of  $^{19}F$  n.m.r. spectroscopy is in the structural determination of fluorine compounds. From their  $^{19}F$  spectrum it appears that all the compounds of the type  $WCl_nF_{6-n}$  have  $O_h$  symmetry.

### 2.2.2. Physical and $^{19}F$ N.M.R. Studies

[For experimental details on  $^{19}F$  n.m.r. studies see Part II section 1.3.]

The physical and  $^{19}F$  n.m.r. data on tungsten chloride pentafluoride have already been reported by other workers<sup>13</sup> but are stated here for clarity and are pertinent to con-

Table 2.2.1. $^{19}\text{F}$  n.m.r. Data for Tungsten Chloride Fluorides.

	$J_{\text{W-F}}$	$J_{\text{F-F}}$	$\delta_{\text{F}_c}^*$	$\delta_{\text{F}_a}^*$
$\text{WF}_6$	44		0	
$\text{WF}_5\text{Cl}$	25	73	-16 (4)	+39 (1)
$\text{WCl}_2\text{F}_4(\underline{t})$	20	-	-25	
$\text{WCl}_2\text{F}_4(\underline{\text{cis}})$	30	66	-33	+30
$\text{WCl}_3\text{F}_3(\underline{\text{mer}})$	††	62	-43	+27
$\text{WCl}_3\text{F}_3(\underline{\text{fac}})$	††	-		+22
$\text{WCl}_4\text{F}_2(\underline{t})$	††	-	-54	
$\text{WCl}_4\text{F}_2(\underline{c})$	††	-		+14
$\text{WCl}_5\text{F}$	††	-		+8

\* Chemical shifts are mixture dependent within the range  $\pm 5$  p.p.m.

†† Not observable.

siderations of the data now available on other mixed chloride fluorides of the type  $WCl_nF_{6-n}$ .

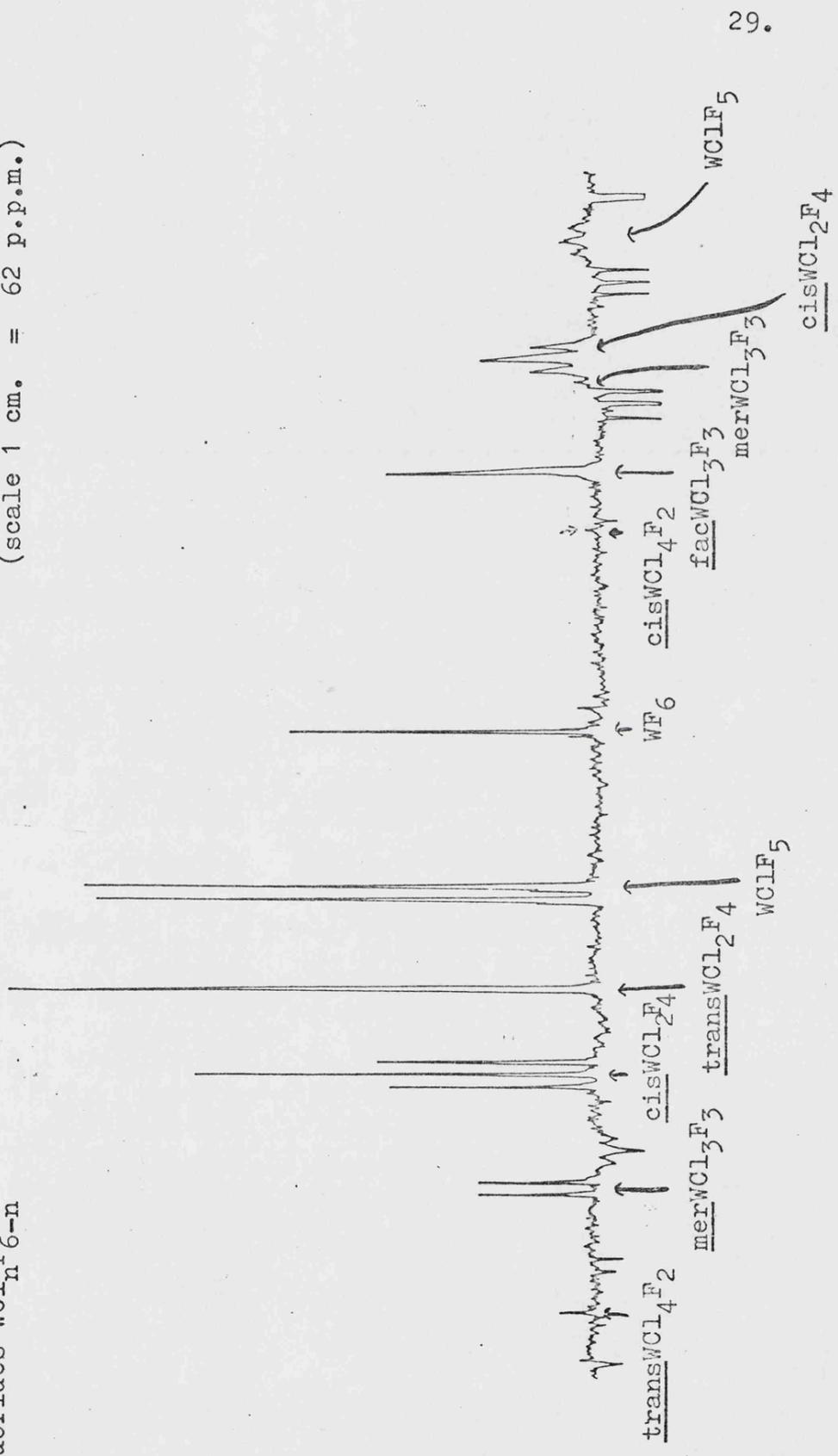
Tungsten chloride pentafluoride forms a yellow solid, a yellow liquid and a yellow vapour. The melting point determined by Stock's method is  $-33.7^\circ\text{C}$  and the vapour pressure of the liquid at  $20^\circ$  is 25 mms. The compound is stable at  $-10^\circ$  for several weeks, but at  $25^\circ$  a large proportion has decomposed after 24 hours. The  $^{19}\text{F}$  spectrum of the liquid at  $-30^\circ$  shows the expected doublet-quintet fine structure in the ratio 4:1 at 182 and 126 p.p.m. downfield from acetone <sup>(CF<sub>4</sub>)</sup> as external standard [see also Table 2.2.1.]. At higher temperatures the fine structure disappears.

Tungsten dichloride tetrafluoride is a deep yellow solid which melts at approximately  $-30^\circ\text{C}$  to a yellow liquid. ~~and~~ it is less volatile than tungsten chloride pentafluoride. The  $^{19}\text{F}$  n.m.r. spectrum at  $-20^\circ$  consists of two triplets in the ratio of 1:1 and a single line which indicates the presence of both cis and trans isomers. Above this temperature the lines broaden and collapse into three broad signals. The coupling constants and chemical shifts are given in Table 2.2.1.

Tungsten dichloride tetrafluoride may be stored for long periods at  $-30^\circ$  but is unstable at room temperature and decomposes slowly into other tungsten(VI) chloride fluorides. The decomposition has been followed by  $^{19}\text{F}$  spectroscopy. An  $^{19}\text{F}$  spectrum may be obtained, either by decomposition of  $WCl_2F_4$  or from the reaction of  $WCl_2F_4$  with  $POCl_3$ , which shows signals due to all the chloride fluorides of tungsten(VI) (fig. 2.2.1. and Table 2.2.1.). From such

Figure 2.2.1.

Diagrammatic Representation of the Complete  $^{19}\text{F}$  n.m.r. Spectrum of Tungsten Chloride Fluorides  $\text{WCl}_n\text{F}_{6-n}$   
(scale 1 cm. = 62 p.p.m.)



a spectrum the following may be noted.

1. Signals of F atoms trans to Cl atoms in the chloride fluoride molecule always occur at a higher field than those of F atoms trans to F atoms in the same molecule.
2. Signals of F atoms trans to Cl atoms in the chloride fluoride molecule occur upfield from the tungsten hexafluoride signal, whereas signals in the same molecule of F atoms trans to F atoms occur downfield.
3. As chlorine is substituted for fluorine the signals of both axial and equatorial fluorine nuclei move downfield.
4. Signals of F atoms trans to Cl atoms are much broader than signals of F atoms trans to F atoms.

Factors contributing to  $^{19}\text{F}$  chemical shifts are complex and very few comparisons with similar compounds are possible. The  $^{19}\text{F}$  chemical shifts of most of the methoxyfluorotungsten(VI) series,  $^{59,60} (\text{MeO})_n \text{WF}_{6-n}$  where  $n = 1 - 5$ , have recently been reported. From this  $^{19}\text{F}$  spectroscopic data, similar observation to these found for the chloride fluoride series can also be observed:

1. Signals of F atoms trans to MeO groups in the methoxy-fluoride molecule always occur at higher field than those of F atoms trans to F atoms in the same molecule.

2. All signals are upfield of tungsten hexafluoride.

This would be expected as the methoxy group pushes electrons into the MeO-metal bond; making the metal less electro-positive. An increase in electronegativity of the atom attached directly to the F atom causes a decrease in the  $^{19}\text{F}$  shielding and, hence, the signals in the  $^{19}\text{F}$  spectrum move upfield. For a given methoxyfluoride molecule this decrease in  $^{19}\text{F}$  nuclear shielding is greater when the

methoxy group is trans to an F atom, hence the F atom trans to a methoxy group moves further upfield than that in which the F atom is trans to an F atom [see observation 1.].

3. As methoxy groups are substituted for F atoms, the signals move upfield - with the exception of the signal due to the F atom in  $(\text{MeO})_5\text{WF}$ . Again, this is caused by increase in methoxy groups resulting in decrease in the electropositive nature of the bonded tungsten atom and with a corresponding decrease in the  $^{19}\text{F}$  nuclear shielding of all F atoms.

In the  $^{19}\text{F}$  spectrum of the chloride fluorides of tungsten(VI) the chloride atom is an electron withdrawing group and it may be that  $d\pi - d\pi$  back-bonding from filled 6d orbitals on the tungsten to empty 3d orbitals on the chlorine occurs which effectively increases the  $^{19}\text{F}$  shielding of all F atoms when one replaces F atoms by Cl atoms; hence, causing the signals to move downfield. For a given chloride fluoride molecule, the electron withdrawing effect of a chlorine atom is less than that of a fluorine atom, hence an F atom trans to a Cl atom experiences greater  $^{19}\text{F}$  nuclear shielding than an F atom trans to an F atom - thus causing the latter to be at lower field than the former.

4. Signals of fluorine atoms trans to methoxy groups are no broader than signals of fluorine atoms trans to fluorine atoms.

Dean and Evans<sup>64</sup> have investigated the  $^{19}\text{F}$  n.m.r. spectrum of a large number of fluoro-tin complexes and found that the chemical shifts could be represented by the single equation

$$\delta(\text{F}) = pC + qT$$

where  $\delta(F)$  is the chemical shift of the fluorine atom in question (relative to  $[\text{SnF}_6]^{2-}$ ),  $p$  is the number of constituents  $X$  in positions cis to fluorine atoms and  $q$  is the number of substituents trans to the fluorine atom.  $C$  and  $T$  are constants characteristic of the substance  $X$ . The chemical shifts of the tungsten chloride fluorides can also be fairly well represented by this equation if  $C = 11.7$  and  $T = -52.2$ .

The unusual feature of the  $^{19}\text{F}$  spectra of the chloride fluorides of tungsten is the width of the signals of fluorine nuclei trans to chlorine. Compared with those trans to fluorine. This broadening has not been observed in the chloride fluorides of tin, sulphur or tellurium, nor in the methoxy fluorides of tungsten and may be due to the chlorine quadrupole moment.

The coupling constants  $J_{\text{F}_a - \text{F}_e}$  and  $J_{^{183}\text{W} - \text{F}_e}$  for the tungsten chloride fluorides are given in Table 2.2.1. The fluorine-fluorine coupling constants are similar to those reported for methoxy pentafluorotungsten and phenoxy pentafluorotungsten.<sup>62</sup> However the tungsten-fluorine coupling constants (20 - 25 Hz.) are appreciably lower than other tungsten(VI) compounds. Tungsten coupling with the axial fluorine nuclei is not observed due to broad signals.

### 2.3. Separation of the Isomers of Tungsten Dichloride Tetrafluoride

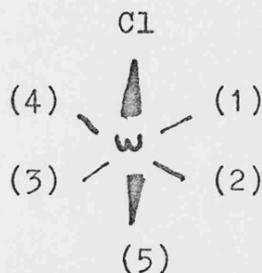
Chemical methods for separating the isomers of tungsten dichloride tetrafluoride have been attempted: these included thermal decomposition and reaction with non-metal

chlorides (ability to form other tungsten(VI) chloride fluorides), phosphorus trifluoride (oxidation and complexing properties), sulphur dioxide (formation of tungsten oxide chloride fluorides) and nitrogen dioxide and pyridine (complex formation). In all cases, examination of the product by  $^{19}\text{F}$  spectroscopy shows that either both isomers are still present in the usual 1:1 ratio or that complete decomposition of the tungsten dichloride tetrafluoride has occurred.

The melting points of the  $\text{WCl}_2\text{F}_4$  isomers would be expected to differ by several degrees, but attempts at preferential melting and solidifying one of the isomers have not succeeded [see Part II section 2.2.]. This may be because the isomers form mixed crystals, but this would not explain why ~~no~~ no chemical reaction succeeded in altering the 1:1 cis:trans ratio. It is therefore suggested that the cis and trans isomers of tungsten dichloride tetrafluoride are in dynamic equilibrium and cannot be separated.

From statistical probability considerations one would expect the ratio of cis:trans  $\text{WCl}_2\text{F}_4$  to be 4:1 but from measurement of many  $^{19}\text{F}$  spectra the isomer ratio found in practice is (1.2):1 with a deviation of  $\pm 10\%$ . Similarly, from consideration of the isomers of  $\text{WCl}_3\text{F}_3$  one would expect a mer:fac ratio of 3:2. This ratio is obtained by interchanging a chlorine atom for one of the equivalent fluorine atoms in the  $\text{WF}_6$  molecule and then calculating the probability of randomly exchanging two more chlorine atoms for fluorine atoms.

i.e.



By "fixing" the 2nd chlorine atom in positions (1) to (5) successively one can consider where on the molecule it is possible to replace a third fluorine atom by a chlorine atom.

If the 2nd Cl atom is in positions (1), (2), (3) or (4) then 2mer and 2fac  $WCl_3F_3$  positions are possible. If the 2nd Cl atom is in position (5), then 4 mer  $WCl_3F_3$  positions are possible. Hence if the 2nd Cl atom is in any position then 12 mer and 8 fac  $WCl_3F_3$  positions are possible. Therefore the total probability of obtaining mer and fac  $WCl_3F_3$  by randomly replacing any three fluorine atoms by chlorine atoms in the octahedral sites around the tungsten atom would be mer:fac = 72:48 = 3:2, but the ratio found from measurement of the proportion of each isomer from  $^{19}F$  spectra is mer:fac  $\sim$  5:1 with a deviation of  $\pm 10\%$ .

The deviation in the cis:trans ratio in  $WCl_2F_4$  and in the mer:fac ratio in  $WCl_3F_3$  (obtained from many  $^{19}F$  spectra of the compounds) seems significantly high and implies the influence of many other factors: steric considerations and whether or not a fluorine atom is more stable trans to a fluorine atom than trans to a chlorine atom must obviously be two predominant considerations.

#### 2.4. Stability of the Tungsten Halides

The tungsten dichloride tetrafluoride isomers are thermodynamically unstable and decompose into the other

chloride fluorides. It therefore appears that their existence depends, at least partly, on kinetic factors. The slow fluorination of tungsten hexachloride produces the volatile tungsten dichloride tetrafluoride which is swept away from the reaction zone and is then stabilised by being stored at low temperatures. The reaction of non-metal chlorides, e.g. trimethyl chlorosilane with tungsten hexafluoride - does not produce tungsten dichloride tetrafluoride; in most cases either the solid chloride fluorides are deposited or tungsten hexachloride is formed. However, the reaction of trimethyl chlorosilane with tungsten hexafluoride and a trace of dry hydrogen chloride at  $-30^{\circ}$  over a period of three weeks produces first tungsten chloride pentafluoride, then cis and trans tungsten dichloride tetrafluoride, mer and fac tungsten trichloride trifluoride and cis and trans tungsten tetrachloride difluoride. Eventually the solid chloride fluorides and tungsten hexachloride are deposited [see Part II section 2.9.3.]. It may well be that the  $H^{\oplus}$  ion catalyses some part of these halogen exchange reactions. By the room temperature reaction of trimethyl chlorosilane and tungsten hexafluoride only solid tungsten hexachloride is produced: no volatile chloride fluoride is observed by  $^{19}F$  spectroscopy at any stage in the reaction. One could explain this in terms of the reaction being a step-wise chlorine-fluorine exchange in which, either the first fluorine is exchanged very slowly and the others very fast, or that the solubility of  $WF_6$  in  $Me_3SiCl$  is small and that all exchange steps are fast. In the presence of a trace of  $H^{\oplus}$  the reaction rates might well alter: hence, if the exchange of the first fluorine atom occurs at a comparable rate to other exchange

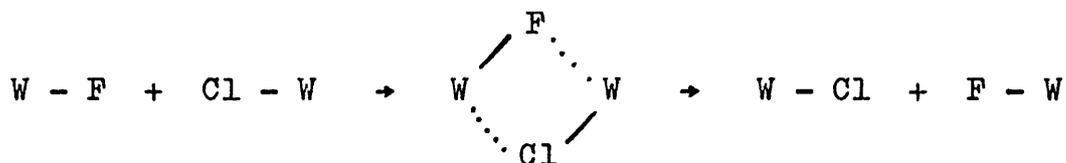
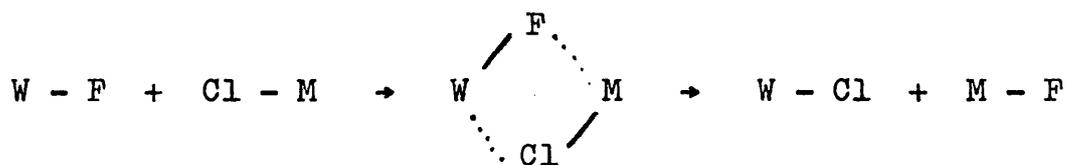
steps - either by the  $H^{\oplus}$  speeding up the exchange of the first fluorine atom or slowly down the rate of exchange of the other fluorine atoms - or if the  $H^{\oplus}$  increases the solubility of the  $WF_6$  in  $Me_3SiCl$  then the intermediate chloride fluorides would have been detected.

One further possible explanation as to why intermediate chloride fluorides of tungsten(VI) are observed only if traces of  $H^{\oplus}$  are present, during the reaction of excess  $BCl_3$  or  $Me_3SiCl$  with  $WF_6$ , would be in terms of a solution effect: it is possible that intermediate tungsten(VI) chloride fluorides are more stable in the presence of  $H^{\oplus}$  ions than in  $Me_3SiCl$  or  $BCl_3$  alone - in the latter case the intermediate chloride fluorides might decompose to  $WF_6$  and  $WCl_6$  immediately on being formed.

#### 2.5. Scheme of Decomposition of $WCl_2F_4$ and Halogen Exchange with Tungsten Chloride Fluorides

The scheme of decomposition of tungsten dichloride tetrafluoride appears to be similar to that of the other chloride fluorides and is related to that of the low temperature exchange reaction between tungsten hexafluoride and trimethyl chlorosilane. Chlorine-fluorine exchange in all these cases could occur via a transition state in which a fluorine and a chlorine bridge is formed: the tungsten atom increases its coordination number to seven. Tebbe and Muetterties have recently recorded the  $^{19}F$  n.m.r. spectrum of the tungsten hexafluoride - trimethylphosphine complex and conclude that the tungsten atom is seven coordinate.<sup>63,64</sup> A coordinate number higher than six is also believed to occur in the complex heptafluoro tungsten(VI),  $KWF_7$ . The chlorine-

fluorine bridge may then break down as follows:



The formation of a transition state will be favoured if M is a Lewis acid and can also increase its coordination number. Thus, tungsten hexachloride reacts with boron trichloride and titanium tetrachloride but not with carbon tetrachloride and phosphorus trichloride. It will also be increased if the electron density on both the chlorine and the fluorine atom is large. Trimethyl chlorosilane reacts with tungsten hexafluoride at room temperature whereas silicon tetrachloride does not react with tungsten hexafluoride even at 150° in a sealed tube. The inductive effect of the methyl group increases the electron density on the chlorine atom and therefore favours the bridged transition state by lowering its activation energy of formation. The difficulty in obtaining the liquid chloride fluorides with non-metal chlorides suggest they have similar or greater reactivity than tungsten hexafluoride and therefore react further to produce the solid chloride fluorides or tungsten hexachloride.

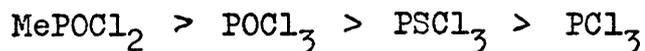
## 2.6. Exchange Reactions with $WCl_2F_4$

O'Donnell and Stewart have compared the reactivity of molybdenum and tungsten hexafluoride with non-metal chlorides<sup>20</sup> and found that, while  $MoF_6$  is highly reactive,

$WF_6$  is comparatively inert. Halogen exchange between non-metal chlorides and molybdenum hexafluoride appears to result in reduction as well as halogen exchange,<sup>20,65</sup> but by comparable reactions with tungsten hexafluoride either no reaction or halogen exchange with tungsten still remaining in a +6 oxidation state results.

Tungsten dichloride tetrafluoride is less chemically inert than tungsten hexafluoride to reaction with non-metal chlorides but halogen exchange still occurs without reduction of the oxidation state of the tungsten. The instability of the tungsten dichloride tetrafluoride presents some difficulty in drawing conclusions from the  $^{19}F$  spectrum of the volatile products obtained from room temperature reactions - since decomposition of the dichloride tetrafluoride alone would result in similar halogen exchange - hence we must consider the rate at which halogen exchange occurs at room temperature, relative to that which occurs through decomposition of tungsten dichloride tetrafluoride alone and whether or not the fluoride of the second reactant is also formed.

Reaction of  $WCl_2F_4$  with a series of phosphorus chlorides [see Table 2.6.1.] has been observed and found to be in decreasing order of reactivity:



Observation of the  $^{19}F$  spectrum of the components of the reaction mixture of  $POCl_3$  and  $WClF_5$  have shown that initially the doublet of  $WClF_5$  broadens enormously and then as the reaction proceeds, this broad peak declines in size [see Part II section 2.4.2.]. The fact that the  $WClF_5$  peak broadens but does not alter its position [i.e. its chemical shift with respect to  $WF_6$  remains constant] seems to

Table 2.6.1.

Reaction of Excess  $WCl_2F_4$  with Some Phosphorus  
Compounds at Room Temperature

Reagent	Product	Duration of Reaction
$MePOCl_2$	$WCl_6$ , $WClF_5$ , $WCl_2F_4$ $WCl_3F_3$ , $WClF_5$ , $WCl_6$	2 hours
$POCl_3$	$WCl_6$ , $WClF_5$ , $WCl_2F_4$ , $WCl_3F_3$ , $WCl_4F_2$ , $WF_6$ , $POF_3$	several hours
$PSCl_3$	mainly $WCl_3F_3$ and $WClF_5$	one day
$PCl_3$	$WCl_6$ , $WClF_5$ , $WF_6$ $PF_3$	several days
$P_2O_5$	$WOF_4$ , $WF_6$ , $POF_3$	several hours

imply that  $POCl_3$  forms a weak bond with  $WClF_5$  which is strong enough to cause the doublet to broaden substantially, but not strong enough to cause chemical shift of the signal. It was further noted that no other signal, due to a tungsten(VI) chloride fluoride, is seen to broaden in this way, either by reaction with  $POCl_3$  or with any of the other phosphorus chloride compounds used.

Oxychlorides show donor properties (coordinating properties) by means of the 'free' electron pairs on the oxygen atoms. The donor strength depends on the group attached to the oxygen. The reaction between  $WCl_2F_4$  and  $MePOCl_2$  is

Figure 2.6.1.

$^{19}\text{F}$  Spectrum of the Reaction Mixture of  $\text{WClF}_5$  and  $(\text{Me}_3\text{Si})_2\text{O}$

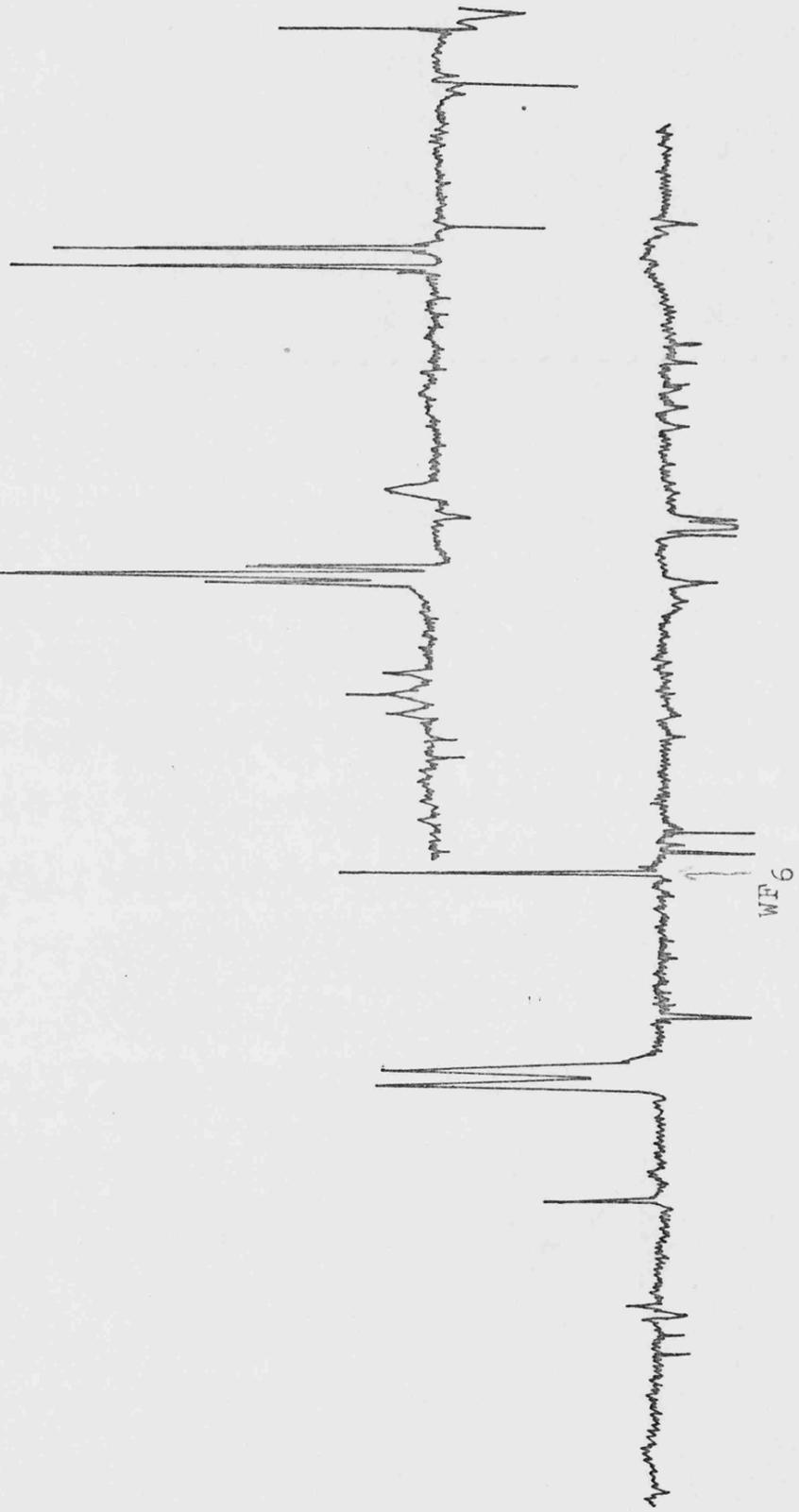


Table 2.6.2.

$^{19}\text{F}$  n.m.r. data for reaction of  $\text{WClF}_5$  with  $\text{POCl}_3$ .

Chemical Shifts ( $\delta\text{F}$ )* (in p.p.m.)	$J_{\text{F-F}}$ # (in Hz.)	$J_{\text{W-F}}$ # (in Hz.)	Description of Signal
-47			singlet
-31			doublet
-21	82		singlet
0		63	large singlet
+18			broad band

\* chemical shifts were dependent on concentration of  $\text{POCl}_3$ : the deviation being  $\pm 5$  p.p.m.

# coupling constants were estimated at  $\pm 2$  Hz.

Table 2.6.3.

$^{19}\text{F}$  n.m.r. data for reaction of  $\text{WClF}_5$  with  $(\text{Me}_3\text{Si})_2\text{O}$

Chemical Shift (in p.p.m.)	$J_{\text{F-F}}$ # (in Hz.)	$J_{\text{W-F}}$ (in Hz.)	Description of Signal
-35			singlet
-22	75	40	doublet
-6			singlet
0		63	large singlet
+9	75		triplet

# coupling constants were estimated to  $\pm 2$  Hz.

faster than that between  $WCl_2F_4$  and  $POCl_3$  and tends to indicate that the reaction might proceed via a step (already discussed in section 2.5.) which involves the tungsten atom increasing its coordination number to seven. Further evidence for this suggested reaction mechanism can be seen from the fact that heating many of these reaction mixtures to  $60^\circ$  for about half an hour causes  $^{19}F$  spectrum to be obtained which show peaks upfield of tungsten hexafluoride in the region normally associated with tungsten oxide fluorides [see Part II sections 2.4.2. and 2.4.5.].

The reaction of  $PSCl_3$  with excess  $WCl_2F_4$  [see Part II section 2.4.4.] is slower than that with the phosphorus oxychlorides, which would be expected if reaction occurs by a step which involves initially a tungsten-sulphur or a tungsten-oxygen bond since the former would be sterically unfavourable.

The series of signals in the  $^{19}F$  spectrum, obtained by heating mixtures of  $POCl_3$  and excess  $WCl_2F_4$  to  $60^\circ C$  for half an hour [Table 2.6.2.], could be attributed to oxychloride fluorides of tungsten(VI). A similar series [see Table 2.6.3. and Figure 2.6.1.] has been obtained from preliminary investigations of the reaction of  $WClF_5$  with  $(Me_3Si)_2O$ ,<sup>66</sup> but the chemical shifts relative to the predominant singlet do not correspond with those which have been obtained from the phosphorus oxychloride reaction - though the ordered description of peaks would be considered the same. No further work has been done on either series: fractional distillation would have probably been a useful mode of separation. One further point remains: that being that the predominant singlet is not tungsten oxytetrafluoride,  $WOF_4$ ,

since it always appears  $\sim 21$  p.p.m. upfield from the position normally expected for a  $WOF_4$  signal.

Boron trichloride reacts instantaneously with  $WCl_2F_4$  to give the solid chloride fluorides of tungsten(VI). It had been hoped that dimethyl dichlorosilane would have reacted more slowly so that solid intermediate chloride fluorides could have been isolated but reaction has been found to be still too fast to prevent a mixture of solid products from being formed.

## 2.7. Attempts at Reduction of $WCl_2F_4$

The chemical reactivity of the tungsten(VI) chloride fluorides in halogen exchange reactions (see previous section) demonstrates that they are more reactive than tungsten hexafluoride but less reactive than molybdenum hexafluoride. No similar pattern of results has been observed when  $WCl_2F_4$  is treated with mild reducing agents [see Part II section 2.5.] - the +6 oxidation state of the tungsten is maintained when both  $WCl_2F_4$  and  $WF_6$  are treated with mild reducing agents.

Tungsten hexafluoride has been reported to form strongly coloured solutions with donor solvents<sup>67</sup> - e.g. benzene and carbon tetrachloride - but the extent of charge transfer is small and the octahedral symmetry of  $WF_6$  is maintained. No reaction occurs between  $WCl_2F_4$  and benzene, carbon disulphide, carbon tetrachloride or silicon tetrachloride but strongly coloured solutions are formed.

It is reported that ~~the~~ red-brown tungsten tetrafluoride is obtained by heating tungsten hexafluoride in a nickel bomb at  $110^{\circ 68}$  but since Schröder's studies of tungsten penta-

fluoride<sup>69</sup> this work has been suspect. Heating  $WCl_2F_4$  and benzene to  $40^\circ$  [Part II section 2.5.1.] gives no reaction - save that of decomposition of the  $WCl_2F_4$  into other chloride fluorides of tungsten(VI) - but more vigorous conditions have not been investigated.

Attempted reduction of  $WCl_2F_4$  with hydrogen [see Part II section 2.5.5.] has also failed, even when the reaction temperature was raised to  $80^\circ C$ , but no more vigorous reducing agents have been used. Tungsten hexafluoride is reported to be reduced by hydrogen at  $600^\circ$ .<sup>70</sup>

## 2.8. Attempted Preparation of Transition Metal Complexes

Most of the preparative work on oxygen-free complexes has involved the use of non-aqueous solvents, such as bromine trifluoride and iodine pentafluoride. These solvents cannot be used with  $WClF_5$  as both immediately react with the chloride pentafluoride to give  $WF_6$  [see Part II section 2.7.]. Sulphur dioxide, however, has been reported to be a useful solvent in the preparation of lower valency fluorides.<sup>71</sup>

Very few complex fluorides of hexavalent transition metals are known. Hargreaves and Peacock<sup>72,73</sup> found that reaction of molybdenum, tungsten, <sup>and</sup> rhenium hexafluoride in iodine pentafluoride gave rise to compounds of the general formula:  $K_2XF_8$  or  $MXF_7$  [M = Rb, Cs]. The fluorotungstates may also be prepared by the reaction of alkali iodides under the same conditions.<sup>72</sup>

Reaction of caesium fluoride and  $WClF_5$  without solvent has proved unsuccessful [see Part II section 2.8.2.]. This finding is consistent with that of Clark and Eméleus<sup>74</sup> and of Hargreaves and Peacock<sup>71,72</sup> who found that dry tungsten hexafluoride would not combine with alkali metal fluorides.

Using sulphur dioxide as a solvent, a yellow solid is precipitated by the reaction of  $WClF_5$  and  $CsF$ . A white solid also obtained is probably unreacted  $CsF$  and ~~a~~ the blue solid, a hydrolysis product from reaction with traces of moisture still in the system. It is possible that this yellow solid is  $CsWClF_6$  or  $CsWClF_5$  but analysis of it could not be undertaken as attempts to separate it from impurities have failed.

Complex fluorides of rhenium, molybdenum and tungsten involving the  $ReF_6^-$ ,  $MoF_6^-$  and  $WF_6^-$  ion have been obtained by the action of the hexafluoride on the alkali iodides in sulphur dioxide. In all cases when solutions of the reactants are brought together iodine is immediately liberated even at  $-60^\circ$ . In excess of hexafluoride, all the alkali iodide is used and the complex salt can be obtained pure, merely by gradually warming the solid product to  $200^\circ$  in a good vacuum.

An orange/brown solid is obtained by the reaction of potassium iodide on excess  $WClF_5$  in the presence, or absence, of sulphur dioxide as a solvent [see Part II section 2.8.1.]. On heating this solid product to  $80^\circ$  iodine is liberated, possibly as a result of decomposition giving tungsten(IV) compounds. The amount of orange solid obtained was inadequate for further work to be continued. It may be that this product is  $KWClF_5$  and that the stability of this product is considerably less than that of  $KWF_6$ . The impure orange/brown solid gives an intense blue colour when hydrolysed, showing decomposition by a similar route to that of  $KWF_6$ .

## 2.9. Reaction of Trimethyl Chlorosilane and Tungsten Hexafluoride

O'Donnell and Stuart<sup>20</sup> have reported that the action of boron trichloride on excess tungsten hexafluoride yields tungsten trichloride trifluoride, they do not, unfortunately, state its colour. Reaction of an approximately 2:1 mole ratio of trimethylchlorosilane:tungsten hexafluoride ~~gives~~ ~~only~~ an orange solid [see Part II section 2.9.1.]; no volatile tungsten(VI) chloride fluoride ~~has been~~ <sup>was</sup> isolated and no other solid chloride fluoride was seen to precipitate. Infra-red, X-ray and analysis data ~~have~~ <sup>were</sup> not been obtained for this orange solid. Attempts at repeating this experiment have all failed.

The reaction of tungsten hexafluoride and titanium tetrachloride in an approximate 3:1 mole ratio<sup>13</sup> has been reported to give  $WCl_6$ ,  $WCl_5F$ ,  $WCl_4F_2$ ,  $WClF_5$  and  $WF_6$ . Isolation of these products has shown  $WCl_4F_2$  as an orange crystalline product which sublimes at  $60^\circ$  under vacuum and  $WCl_5F$  as red needle crystals which may be recrystallised from carbon tetrachloride. From this physical description of  $WCl_4F_2$  it seems likely that the product which has been obtained from reaction of a 2:1 mole ratio of  $Me_3SiCl:WF_6$  is in fact  $WCl_4F_2$ .

As already discussed in sections 2.4. and 2.5. the products obtained from reaction of  $WF_6$  with either  $BCl_3$  or  $Me_3SiCl$  appear to depend on the presence of  $H^+$  ions in the reaction mixture. It is difficult to remove the last traces of moisture from  $Me_3SiCl$  and it may be that a sufficient trace of  $H^+$  has been present in this particular reaction to stop the reaction at this intermediate.

Some preliminary studies of the room temperature reaction

of trimethyl chlorosilane and tungsten hexafluoride have indicated that the initial rate of disappearance of  $WF_6$  may show linear dependence on time, but further studies have not substantiated this initial conclusion. It appears that the reaction of excess  $Me_3SiCl$  with  $WF_6$  does not depend entirely on simple kinetic factors [see Part II section 2.9.2.].

## 2.10. Heats of Formation of $WCl_2F_4$ and $WClF_5$

### 2.10.1. General Introduction

In principle, the best method of determining the heat of formation of a compound is by measuring the heat of reaction of the elements from which it is formed. Often this is difficult with inorganic compounds and, hence, one must apply Hess's law and use indirect methods: one such being via the heat of hydrolysis of the compound. It is necessary, however, to ensure that the hydrolysis of the compound is stoichiometric and also to know the heat of formation of the reaction products.

To determine heats of hydrolysis all one would require, in theory would be a receptacle to contain reactants, a means of stirring to ensure thorough mixing, a system for measuring the heat evolved when the given sample is hydrolysed and a mechanism by which a known amount of heat - could be introduced into the system.

The fact that one is using a liquid has the advantage of ensuring that a uniform temperature would rapidly be attained in the system. One must, however, consider problems of thermal leakage, the heating effects of stirring and the accurate measurement of temperature.

When heat is liberated in a calorimeter a part of it remains in the calorimeter, where a resultant temperature change is produced, while part of it flows away by the process of convection and conduction. The heat loss depends on the difference in temperature between the calorimeter and its surroundings. In these experiments heat losses have been minimised by using a Dewar vessel fitted with a tightly fitting teflon lid and accounted for by plotting cooling curves and extrapolating back to give the correct deflection reading.

The error in measurement of heats of hydrolysis using this experimental apparatus is relatively large ( of the order of  $\pm 1$  to  $\pm 2\%$  of the measured heat), compared to that obtained using more sophisticated apparatus, but a greater degree of accuracy is unnecessary, as the main error factors involved in calculating these particular heats of hydrolysis (and hence estimating the heats of formation of the given compounds) are due to lack of knowledge as to whether the hydrolysis reactions are stoichiometric and to the degree of error in the thermochemical data required to calculate the heats of hydrolysis and formation of the desired compounds.

#### Accuracy of Values.

The reasonably large error in determining the heat of formation of various components, via their heat of hydrolysis accrue from factors, all of which play small but significant parts:

##### (a) Consistency of Stirring.

Stirring of the solution in the calorimeter was achieved using a glass rod attached to a mechanical stirring device; the speed of stirring being governed by a variable

rheostat which was set at the beginning of each experiment.

Too slow a speed of stirring increased the length of time for temperature equilibrium to be attained after mixing - hence increasing the risk of heat losses, which could only be partially compensated for by the corresponding heat losses occurring with heater calibration measurements. Too fast a speed of stirring lead to inconsistencies due to heat generated by stirring.

Alterations in the current supplied to the stirrer over a period could conceivably lead to errors; however, such changes would be unlikely to occur in the time of the experiment.

#### (b) Timing of Heating

The method used for the heater calibrations was to start a stop watch at the same time as the current was switched on to the heater. A finite time elapsed ( $\sim \frac{1}{2}$  min.) before a deflection in the recorder reading was noted. This delay was caused by the time required for heat to pass through the glass tube surrounding the heater into the solution. Hence, it was found precise enough merely to time the period over which the given current was allowed to pass through the heater and to determine the resulting deflection of the recorder from observation of the deflection pattern obtained.

The potential across a standard ten ohm. resistance in series with a heater was taken half way through the heating. This current was normally of the order of 0.17 amp. and varied less than 0.0005 amp. over the period in which it was passed.

### (c) Measurement of Correct Deflection

The initial reading of the recorder was always taken when the temperature of the solution in the calorimeter had been noted to be constant for at least five minutes. After mixing the recorder deflection sometimes continued to rise for several minutes, before leveling out to a constant value. The height of the deflection was obtained by extrapolating back this level value to the time of mixing. Strictly speaking one should draw the deflection line where the two areas under the curve (made by the deflection of the recorder) are the same but this is not possible using this form of measurement. However, since the deflection was purposely large the error in deflection measurement should be small (of the order of  $\pm\frac{1}{2}\%$  of the value of the heat of hydrolysis measured).

### (d) The Use of Frangible Bulbs

Other workers have used frangible bulbs when determining the heats of formation of various inorganic compounds from their heats of hydrolysis,<sup>76</sup> but none has used them for moisture sensitive, higher transition metal fluorides. Work on such compounds has been done using slightly more sophisticated apparatus; justification for this being that the use of frangible bulbs with higher fluorides leads to error:<sup>76</sup> firstly, that moisture released during the sealing off process may start a cyclical reaction with the glass and secondly that momentary high concentrations of fluoride in the presence of an appreciable glass surface area might lead to a side reaction which would substantially alter the heat of hydrolysis values obtained. However, measurements of the heat of hydrolysis of liquid tungsten hexafluoride gave consistent values for the

heat of formation of liquid  $WF_6$  which agreed with literature values obtained by several different methods. Also leaving a frangible bulb containing about 1 ml. of liquid  $WF_6$  at room temperature for a week resulted in no etching of the glass bulb and no precipitation of any tungsten oxide tetrafluoride.

Preliminary testing of the experimental procedure showed that the heat evolved, (even when the most sensitive scales of the recorder were used) when an evacuated bulb containing no sample was broken into sodium hydroxide, was negligible in comparison with the magnitude of the heat evolved during the hydrolysis of any sample. The heat evolved for bulbs of different sizes (varying in size from 4 ml. capacity to 10 ml.) was always less than 0.1 kcals.

The method used to determine the volume of air in the bulb was rather inaccurate but as the volume of the bulb was small (between 5 and 7 ml. implying a weight of air of the order of 0.008 g.), the volume reading error also small ( $\pm 0.1$  ml.) and the weight of sample used was large (between 0.1 g. and 0.4 gm.), then <sup>the resulting error</sup> ~~this inaccuracy~~ would be very small indeed.

#### (e) Temperature Measurement

The water bath used in these experiments was kept at a constant temperature using a heating coil whose operation was governed by a relay system connected to a Beckmann thermometer. A cooling coil could also be used if the temperature were only slightly above  $25^\circ C$ , but experiments were not continued if the air temperature, above the bath, rose more than a few degrees above  $25^\circ C$ . Temperature changes during hydrolysis were measured using a thermistor which is a very sensitive

resistance thermometer. A thermistor is particularly suitable for calorimetric measurements on account of its compactness and low heat capacity: its sensitivity is far greater than that of a platinum resistance thermometer. The error resulting from use of a thermistor would be small, but the circuit which incorporates the thermistor was considered to cause an error of the order of  $\pm 1\%$  of the given hydrolysis value obtained.

(f) Accuracy of Calorimetry Work in General

The errors described above are basically due to the operation of the apparatus and independent of the particular hydrolysis reaction considered. Hence, one would expect an inherent error in any heat of hydrolysis obtained by this method of between  $\pm 1$  and  $\pm 2\%$ .

The sodium hydroxide in all cases was well in excess of that required for complete hydrolysis - the strength of both the 0.1 M and 1 M solutions varying less than 2% from the beginning to the end of the hydrolysis reaction - hence the heat of formation of the aqueous hydroxyl ion throughout the experiment could be considered constant: thus, implying, that the consumption of  $\text{OH}^-$  ion during the experiment would have no effect on the heat of formation value.

The major source of error in hydrolysis reactions results from the fact that all reactions may not be stoichiometric. Though the hydrolysis reaction may well proceed via the reaction path indicated and give predominantly the expected products, side reactions may also occur which result in inconsistent values over several runs. An estimate of the heat of formation error which includes both that from the heat of solution measurements and that from the use of heats of

formation at infinite dilution was  $\pm 5$  kcal/mole for compounds such as liquid  $WClF_5$  and solid  $ReCl_5$  but larger errors may result for compounds such as liquid  $WCl_2F_4$  where slight decomposition may occur during the equilibration period.

#### 2.10.2. Bond Strengths in $WCl_2F_4$ and $WClF_5$

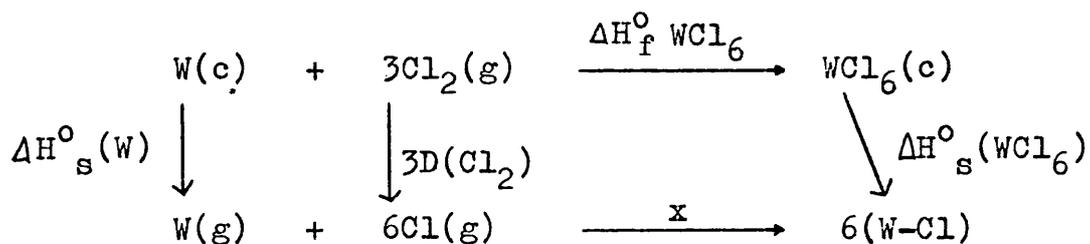
The determination of the heat of formation of  $WCl_2F_4$  and  $WClF_5$  is of interest for two reasons; firstly, because these values would help to explain from a thermodynamic standpoint why certain reactions of these compounds were possible and others not and secondly it might be a route, via which, the bond energies of the W-F and the W-Cl bond in all compounds of the type  $WCl_nF_{6-n}$  [where  $n = 0 \rightarrow 6$ ] could be calculated.

The microwave spectrum of tungsten chloride pentafluoride has been reported.<sup>77</sup> The W-Cl bond length was determined directly from the data as  $r(W-Cl) = 2.252 \pm 0.002 \text{ \AA}$ . The W-F bond length was determined in terms of a model of  $C_{4v}$  symmetry<sup>78</sup> and if all five W-F bonds are assumed equal in length the result is  $r(W-F) = 1.836 \pm 0.001 \text{ \AA}$  (where angle F-W-F axial =  $88^\circ 41' \pm 10'$ ). The uniquely determined  $r(W-Cl) = 2.252 \text{ \AA}$  is close to the electron diffraction value of  $2.26 \pm 0.002 \text{ \AA}$  for the W-Cl bond in  $WCl_6$ .<sup>79</sup> Similarly, if all W-F bond distances are assumed equal  $r(W-F) = 1.836 \text{ \AA}$  is close to the good electron diffraction value of  $1.833 \pm 0.008 \text{ \AA}$  for the W-F bond in  $WF_6$ .<sup>80</sup>

It is difficult to comment on the nature of chemical bonds from small changes, in a given bond length, from compound to compound, but determination of the heat of

formation of  $WClF_5$  and  $WCl_2F_4$  and consideration of known heats of formation of  $WF_6$  and  $WCl_6$  could lead to a similar correlation of the bond strength [i.e. the W-F bond strength could be compared in  $WF_6$ ,  $WClF_5$  and  $WCl_2F_4$  and the W-Cl bond strength could be compared in  $WCl_6$ ,  $WClF_5$  and  $WCl_2F_4$ ]. Consideration of the following thermodynamic reaction cycles for the formation of gaseous  $WF_6$  and  $WCl_6$  from their elements enables an approximate value for the bond strength of the W-F and W-Cl bond in respectively  $WF_6$  and  $WCl_6$  to be calculated.

The reaction cycle for tungsten hexachloride is:



where  $\Delta H_s^\circ$  = enthalpy of sublimation

$\Delta H_f^\circ$  = enthalpy of formation

D = bond dissociation energy

$\frac{x}{6}$  = average intrinsic bond energy for a W-Cl bond in  $WCl_6$ .

then  $\Delta H_s^\circ(W) + 3D(Cl_2) + x = \Delta H_s^\circ(WCl_6) + \Delta H_f^\circ WCl_6$

$$201.6 + (3 \times 57.1) + x = 22.9 + (-163)$$

$$x = -513 \text{ kcal/mole}$$

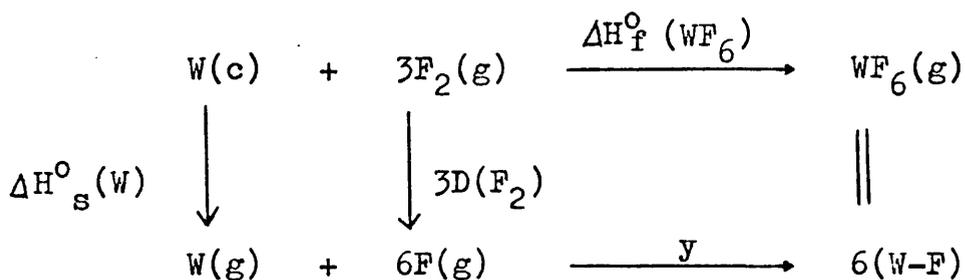
### Note

The heat of formation of solid tungsten hexachloride was determined via the heat of alkaline hydrolysis of solid tungsten hexachloride in 0.7 M. sodium hydroxide.<sup>51</sup> The tungsten hexachloride for this experiment was produced by a stepwise chlorination of tungsten trioxide.

Hydrolysis of tungsten hexachloride, prepared by the halogen exchange reaction between boron trichloride and tungsten hexafluoride, in 0.1 M, 1 M and 2 M sodium hydroxide proved too slow for the heat of hydrolysis to be determined using the experimental procedure described in this thesis [see Part II section 4.6.2.]. Even with 2 M alkali the crystalline tungsten hexachloride had not completely hydrolysed even after several hours. The tungsten hexachloride was in the form of large crystals, but grinding it down to a fine powder, under anhydrous oxygen-free conditions in a dry box, failed to speed up the hydrolysis reaction.

Analysis and Debye X-ray powder photography showed the compound to be pure tungsten hexachloride; therefore one would have expected a similar hydrolysis reaction to that obtained by the Russian workers.<sup>51</sup> It may be that  $WCl_6$  prepared by this writer was of a different crystalline form. If this were the case, the difference in the heat of formation of the two forms of  $WCl_6$  would be small, but the rate of hydrolysis could be markedly different.

The reaction cycle for tungsten hexafluoride is:



where  $\frac{y}{6}$  = the average intrinsic bond energy of a W-F bond in  $WF_6$ .

$$\text{Then } \Delta H^{\circ}_s(\text{W}) + 3D(\text{F}_2) + y = \Delta H^{\circ}_f(\text{WF}_6)$$

$$201.6 + (3 \times 38) + y = -421$$

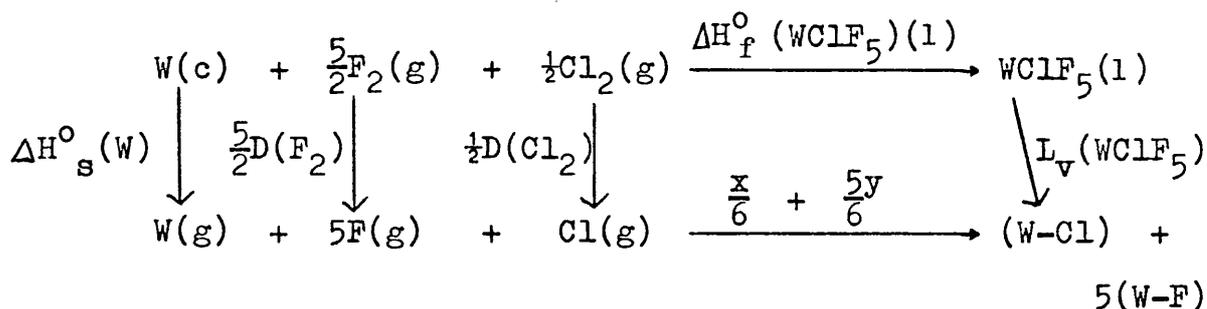
$$y = -737.6 \text{ kcal/mole}$$

### Note

The heat of formation of  $\text{WF}_6(\text{g})$  was taken to be  $-421 \text{ kcal/mole}^{52}$  as this value was obtained via the measured heat of hydrolysis of  $\text{WF}_6(\text{g})$  and this method had been used to obtain the heat of formation of  $\text{WCl}_6$ ,  $\text{WClF}_5$  and  $\text{WCl}_2\text{F}_4$  [see also section 2.10.5.].

If one assumes that the intrinsic energy in a gaseous  $\text{MX}_6$  molecule is six times the individual M-X bond energy, then the bond energy of a W-Cl bond, in gaseous  $\text{WCl}_6$ , is  $-\left(\frac{513}{6}\right) \text{ kcal.}$  and that of a W-F bond, in gaseous  $\text{WF}_6$ , is  $-\left(\frac{737.6}{6}\right) \text{ kcal.}$

As the W-F and W-Cl bond lengths in  $\text{WClF}_5$  have been shown<sup>77</sup> to be the same as the corresponding bond lengths in respectively  $\text{WF}_6$  and  $\text{WCl}_6$ , then it is possible that the W-F and W-Cl bond strengths are also the same as the corresponding bond strengths in respectively  $\text{WF}_6$  and  $\text{WCl}_6$ . Given this assumption, one could postulate a heat of formation of  $\text{WClF}_5$  by consideration of the following thermodynamic reaction cycle:



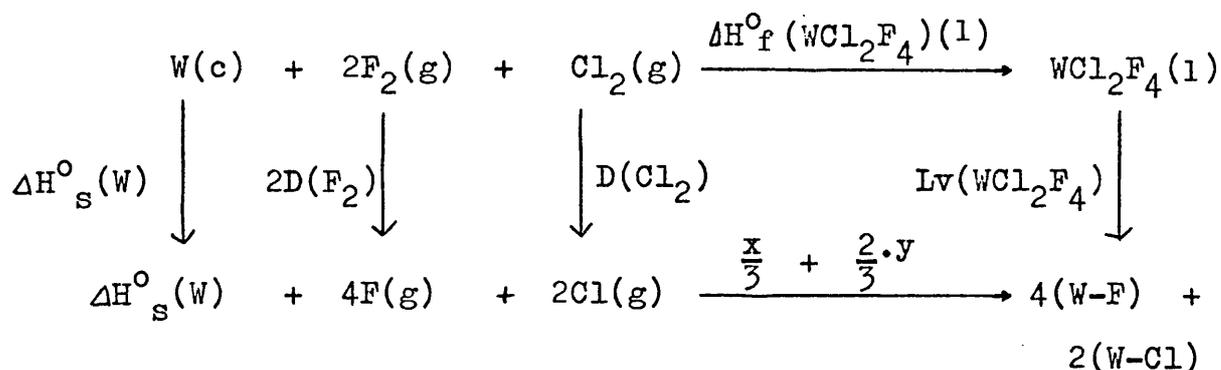
where  $L_v(WClF_5)$  = latent heat a vapourisation of  $WClF_5$ .

$$\text{Then } \Delta H_s^\circ + \frac{5}{2}D(F_2) + \frac{1}{2}D(Cl_2) + \frac{1}{6}x + \frac{5}{6}y =$$

$$\Delta H_f^\circ(WClF_5(l)) + L_v(WClF_5)$$

$$\text{i.e. } \Delta H_f^\circ(WClF_5)(l) = -375 \text{ kcal/mole} - L_v(WClF_5)$$

Similarly, if one assumes that the (W-F) and (W-Cl) bond strengths in  $WCl_2F_4$  would be the same as the corresponding (W-F) and (W-Cl) bond strengths in  $WF_6$  and  $WCl_6$  respectively. Then, from a similar reaction cycle, one could obtain a value for the heat of formation of liquid  $WCl_2F_4$ :



$$\Delta H_s^\circ(W) + 2D(F_2) + D(Cl_2) + \frac{x}{3} + \frac{2}{3}y = \Delta H_f^\circ(WCl_2F_4)(l) + L_v(WCl_2F_4)$$

$$\text{Then } \Delta H_f^\circ(WCl_2F_4)(l) = -328 \text{ kcal/mole} - L_v(WCl_2F_4)$$

Shortage of time prevented a value for the latent heat of vaporisation of  $WClF_5$  and  $WCl_2F_4$  from being ~~calculated~~ <sup>measured</sup>. However, an approximate value of  $L_v(WClF_5)$  and  $L_v(WCl_2F_4)$  may be calculated from consideration of the known latent heat of vaporisation of  $WF_6$  of 6.3 kcal/mole<sup>81</sup> and the latent heat of vaporisation of  $WCl_6$  of 14.5 kcal/mole.<sup>51</sup>

$$\text{i.e. } L_v(WClF_5) \simeq 7.7 \text{ kcal/mole and } L_v(WCl_2F_4) \simeq 9.1 \text{ kcal/mole.}$$

From this:

$$\Delta H_f^\circ (\text{WClF}_5)(\text{l}) = -375 - 7.7 = -383 \text{ kcal/mole}$$

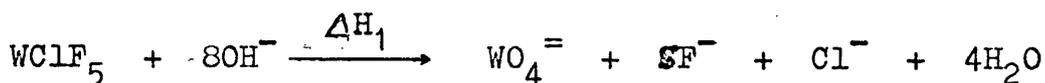
$$\Delta H_f^\circ (\text{WCl}_2\text{F}_4)(\text{l}) = -328 - 9.1 = -337 \text{ kcal/mole}$$

### 2.10.3. Calculated Heats of Formation of $\text{WCl}_2\text{F}_4$ and $\text{WClF}_5$

#### (a) Heat of formation of $\text{WClF}_5$

From consideration of the hydrolysis reaction of  $\text{WClF}_5$  and known thermochemical data, the heat of formation of this chloride fluoride may be determined.

The hydrolysis reaction equation of  $\text{WClF}_5$  in 0.1 M NaOH is:



where  $\Delta H_f^\circ \text{OH}^-(\text{aq.}) = -54.96 \text{ kcal/mole}$

$$\Delta H_f^\circ \text{WO}_4^{=}(\text{aq.}) = -266.6 \text{ "}$$

$$\Delta H_f^\circ \text{F}^-(\text{aq.}) = -78.66 \text{ "}$$

$$\Delta H_f^\circ \text{Cl}^-(\text{aq.}) = -40.023 \text{ "}$$

$$\Delta H_f^\circ \text{H}_2\text{O} = -68.32 \text{ "}$$

Then

$$\begin{aligned} \Delta H_f^\circ \text{WClF}_5(\text{l}) &= \Delta H_f^\circ (\text{WO}_4^{=})(\text{aq.}) + 5\Delta H_f^\circ (\text{F}^-(\text{aq.})) + \\ &\quad \Delta H_f^\circ (\text{Cl}^-(\text{aq.})) + 4\Delta H_f^\circ (\text{H}_2\text{O}) \\ &\quad - [\Delta H_1 + 8\Delta H_f^\circ (\text{OH}^-(\text{aq.}))] \end{aligned}$$

$$\Delta H_f^\circ \text{WClF}_5(\text{l}) = -[534 + \Delta H] \text{ kcal/mole}$$

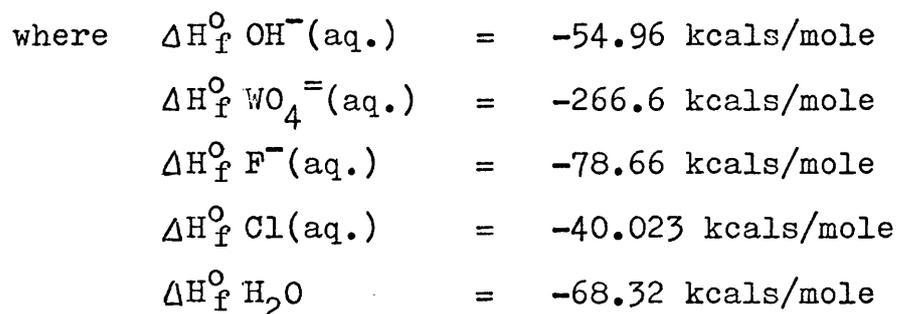
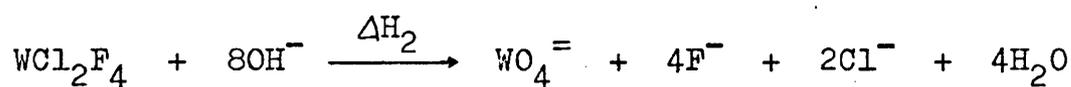
The heat of hydrolysis of  $\text{WClF}_5$  was obtained for a liquid sample [see Part II Table 4.5.1.] and the normal inherent experimental error was increased to accommodate for the gaseous tungsten chloride pentafluoride in the sample.

The heat of hydrolysis of  $\text{WClF}_5$  (liquid) was measured as

-147  $\pm$  2 kcal/mole [see Part II section 4.5.], from which the heat of formation of liquid  $WClF_5$  could be calculated as -387  $\pm$  5 kcal/mole. This value is slightly greater than that predicted from calculations described in the previous section [section 2.10.2.].

(b) Heat of formation of  $WCl_2F_4$

From consideration of the hydrolysis reaction of  $WCl_2F_4$  and known thermochemical data the heat of formation of this chloride fluoride may be determined. The hydrolysis reaction for  $WCl_2F_4$  in 0.1 M NaOH is:



Then

$$\Delta H_f^\circ WClF_5(l) = \Delta H_f^\circ WO_4^{=}(aq.) + 4\Delta H_f^\circ F^-(aq.) + 2\Delta H_f^\circ Cl^-(aq.) + 4\Delta H_f^\circ H_2O - [\Delta H_2 + 8\Delta H_f^\circ OH^-(aq.)].$$

$$\Delta H_f^\circ WCl_2F_4(l) = -[495 + \Delta H_2] \text{ kcal/mole}$$

Errors in the heat of hydrolysis of  $WCl_2F_4$  were due to three factors: firstly, inherent errors caused by the experimental procedure and apparatus; secondly, errors due to the presence of a small quantity of gaseous chloride fluoride in a predominantly liquid sample; and thirdly, errors caused by decomposition of the sample while it was equilibrating at room temperature. The heat of alkaline hydrolysis of liquid  $WCl_2F_4$  was measured as -145  $\pm$  4 kcal/

mole [see Part II section 4.4.], from which a heat of formation of liquid  $WCl_2F_4$  of  $-350 \pm 7$  kcal/mole is obtained. This heat of formation value is not consistent with that obtained by considering that the bond strength of the W-F and W-Cl bond in  $WCl_2F_4$  is the same as the W-F bond strength in  $WF_6$  and the W-Cl bond strength in  $WCl_6$ . This may be caused by greater decomposition of the  $WCl_2F_4$  than was allowed in the error factor, lack of consideration of errors in the calculated value or to the fact that the original assumption that the W-F bond strength is the same in all  $WCl_nF_{6-n}$  compounds ( $n = 0 \rightarrow 5$ ) and that the W-Cl bond strength is the same in all  $WCl_nF_{6-n}$  compounds ( $n = 1 \rightarrow 6$ ) was incorrect.

#### 2.10.4. Factors that Affect the Bond Strength of a Given Bond in a Series of Compounds

The original assumption [in section 2.10.2.] that if the length of the W-F bond in tungsten hexafluoride, tungsten chloride pentafluoride and tungsten dichloride tetrafluoride were the same, and that the length of the W-Cl bond in tungsten hexachloride, tungsten chloride pentafluoride and tungsten dichloride tetrafluoride were the same, then the corresponding bond strengths would also be the same has been shown experimentally [in section 2.10.3.] to be incorrect.

The strength of a covalent metal- (or non-metal-) halogen bond in an octahedral complex is dependent on three main factors: the  $\sigma$  inductive effect from the group trans to the bond considered, any contribution from available d orbitals to back-bonding and any distortion of the octahedra.

In sulphur chloride pentafluoride the back-bonding from sulphur to empty d orbitals on the chlorine atom is slight,

due to lack of available d orbitals on the sulphur. The  $\sigma$  inductive effect does apply, as can be seen by  $^{19}\text{F}$  spectroscopy which shows that the fluorine signal of fluorine trans to a fluorine atom in  $\text{SClF}_5$  is to lower field than the signal for a fluorine atom trans to a chlorine atom, but the predominant influence affecting the strength of the S-F and S-Cl bond in  $\text{SClF}_5$  relative to the corresponding bonds in  $\text{SF}_6$  and  $\text{S}_2\text{Cl}_2$  appears to be controlled by factors which distort the symmetry of the molecule. This is substantiated by the fact that the S-Cl bond in  $\text{SClF}_5$  is longer than those obtained from electron diffraction measurements in other compounds involving the S-Cl bond.<sup>82</sup> Hence, one would expect the bond energy of the S-F bond in sulphur chloride pentafluoride to be weaker than that in sulphur hexafluoride and the bond energy of the S-Cl bond to be less than that in disulphur dichloride.

Craig and Magnusson<sup>83</sup> predicted from calculations for the relative bond strengths in sulphur compounds in which the sulphur atom forms six covalent bonds that the greatest bond energies could be expected when all six bonds were fluorine. They further suggested that if one of the fluorine atoms was replaced by a larger less-electronegative chlorine atom, not only would the S-Cl bond be weaker than the S-F bond, but also that the five remaining bonds would be weaker than in sulphur hexafluoride. These predictions were substantiated by Leach and Roberts,<sup>84</sup> who found that their experimentally determined value for the heat of formation of sulphur chloride pentafluoride gave an S-F bond strength which was less than that determined from the heat of formation of sulphur hexafluoride.

The relative bond strengths of tungsten-halogen bonds in tungsten hexahalogen compounds may be predicted in a similar manner to that used for consideration of the relative bond strengths of sulphur-halogen bonds in sulphur halogen compounds, but the influence of the various factors affecting bond strengths would appear to be different. Substitution of one fluorine atom by a chlorine atom in sulphur hexafluoride results in an increase in the axial sulphur-fluorine stretching frequency as seen by infra-red and Raman spectroscopy [ $\nu_1(\text{SClF}_5) = 854.6 \text{ cm}^{-1}$  <sup>85,86</sup> and  $\nu_1(\text{SF}_6) = 775 \text{ cm}^{-1}$  <sup>87</sup>] but a similar substitution in tungsten hexafluoride results in a frequency shift in the opposite sense [ $\nu_1(\text{WClF}_5) = 744 \text{ cm}^{-1}$  <sup>78</sup> and  $\nu_1(\text{WF}_6) = 769 \text{ cm}^{-1}$  <sup>88</sup>]. Hence, it would appear that factors causing the W-F and W-Cl bonds to be stronger in mixed chloride fluoride compounds, of the type  $\text{WCl}_n\text{F}_{6-n}$ , than in the corresponding binary hexahalogen compound would predominate.

The  $\sigma$  inductive effect on a chlorine atom trans to a fluorine atom in a tungsten(VI) chloride fluoride molecule would cause the W-F bond energy to be greater than in tungsten hexafluoride. This argument is supported by  $^{19}\text{F}$  spectroscopic evidence which shows that signals due to fluorine atoms trans to chlorine atoms are further upfield than signals due to fluorine atoms trans to fluorine atoms in the same chloride fluoride molecule [see section 2.2.2.]. It is further anticipated that there may be a degree of back-donation from partly filled tungsten  $t_{2g}$  orbitals to the 3d orbitals on the chlorine atom: this would increase the bond strength of the W-Cl bond in the chloride fluoride compounds relative to that of the W-Cl bond in tungsten hexachloride.

This supposition is supported by the  $^{19}\text{F}$  spectra of tungsten(VI) chloride fluoride compounds which show that replacement of fluorine atoms by chlorine atoms causes all signals to move downfield. However, the W-Cl bond strength may not necessarily be affected by  $d\pi-d\pi$  back-bonding as there will be presumably similar (though perhaps less) back-bonding in tungsten hexachloride itself. Data obtained from the microwave spectrum of tungsten chloride pentafluoride suggests that there is no appreciable distortion of the octahedral symmetry of the tungsten(VI) halide molecule.<sup>77</sup> Hence, the size of the central tungsten atom must have no significant effect on the strength of the W-Cl and W-F bonds in  $\text{WCl}_n\text{F}_{6-n}$  compounds.

The bond strength of the W-Cl and W-F bonds in the tungsten(VI) mixed halides, relative to that in respectively tungsten hexachloride and tungsten hexafluoride is obviously difficult to predict, but it is quite probable that it will be greater. Further evidence in support of this comes from the fact that though, from statistical probabilities, the cis:trans ratio in tungsten dichloride tetrafluoride would be 4:1, that found experimentally by  $^{19}\text{F}$  spectroscopy is 1:1 [see section 2.3.]; hence, implying that a fluorine trans to a chlorine is favoured more [i.e. bond energies of the W-F and W-Cl bond are greater] than a fluorine ~~cis~~<sup>trans</sup> to a fluorine atom in a given chloride fluoride molecule.

The difference in the relative bond strength in the mixed halide relative to that in the parent halide of both sulphur and tungsten may be explained in terms of d orbitals and the size of the atom to which the halides are attached

but it cannot be concluded that this explains entirely, the slightly greater strength of the W-Cl and W-F bond in tungsten chloride pentafluoride and tungsten dichloride tetrafluoride relative to that in respectively tungsten hexachloride and tungsten hexafluoride. It must not be forgotten that the mixed halides do decompose thermally  $[WCl_nF_{6-n} \rightarrow WCl_6 + WF_6]$ , hence implying a negative Gibbs free energy term-albeit that this term would be expected to be less negative than that for the corresponding mixed halide of sulphur. Thus, entropy as well as enthalpy, is obviously a significant factor in determining bond energies in tungsten mixed halide compounds.

#### 2.10.5. Choice of Values for the Heat of Formation of Tungsten Hexafluoride

The tungsten-fluorine bond strength in  $WF_6$  was calculated using the value for the heat of formation of gaseous tungsten hexafluoride obtained via the heat of hydrolysis of tungsten hexafluoride in 0.1 M sodium hydroxide<sup>76</sup> and revised by J.A.N.A.F.<sup>52</sup> This heat of formation of gaseous  $WF_6$  of  $-421 \pm 4$  kcal/mole is markedly higher than that of  $-411.5$  kcal/mole obtained by O'Hare and Hubbard<sup>89</sup> and  $411.7$  kcal/mole by Schröder and Sieben<sup>90</sup> from bomb calorimetry combustion of tungsten and fluorine. It was, however, thought better to use this value for the heat of formation of tungsten hexafluoride, obtained via the heat of alkaline hydrolysis of tungsten hexafluoride, as the value for the heat of formation of tungsten hexachloride<sup>51</sup> and those for tungsten chloride pentafluoride and tungsten dichloride tetrafluoride [see section 2.10.3.] were also obtained by this

method: hence comparison of the W-F bond strength and the W-Cl bond strength in all tungsten(VI) halide compounds would be more meaningful.

It has been noted that in both tungsten hexafluoride and molybdenum hexafluoride the value for the heat of formation, obtained from bomb calorimetry combustion of the elements, is of the order of 10 kcal/mole less than that obtained via the heat of hydrolysis reaction. The heat of formation of gaseous molybdenum hexafluoride is -372 kcal/mole from bomb calorimetry<sup>91</sup> and -382 kcal/mole from the heat of hydrolysis and solution of molybdenum hexafluoride in dilute sodium hydroxide.<sup>76</sup> Similarly, the heat of formation of gaseous tungsten hexafluoride is measured as 411.5 kcal/mole by bomb calorimetry<sup>89,90</sup> and is calculated as -416 kcal/mole from the heat of hydrolysis and solution in dilute sodium hydroxide<sup>76</sup> - this latter value being revised by J.A.N.A.F. to -421 kcal/mole.<sup>52</sup>

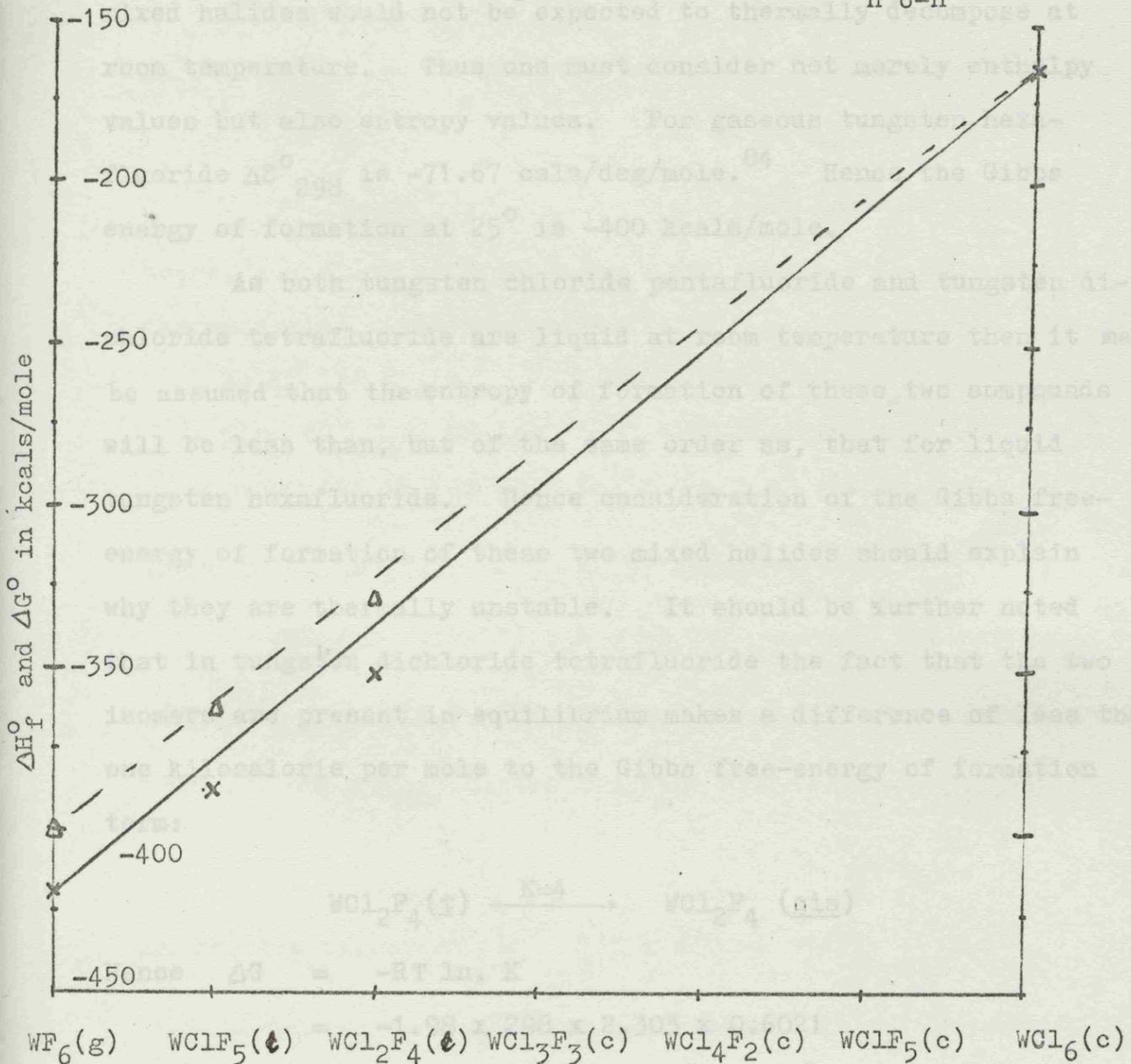
In the light of the values obtained for the heat of formation of tungsten hexafluoride and molybdenum hexafluoride it is conceivable that the values for the heat of formation of tungsten chloride pentafluoride and tungsten dichloride tetrafluoride may also be higher than expected.

#### 2.10.6. Entropy as a Factor Influencing the Thermal Stability of Tungsten Chloride Pentafluoride and Tungsten Dichloride Tetrafluoride.

A graph showing the known heat of formation of compounds of the type  $WCl_nF_{6-n}$  indicates how little the values for tungsten chloride pentafluoride and tungsten dichloride tetrafluoride differ from idealised values obtained from

consideration of entropy Figure 2.10.1. [see fig. 2.10.1.]

### Heat of Formation of Compounds of the Type $WCl_nF_{6-n}$



$$\Delta G = -RT \ln K$$

$WF_6(g)$   $WClF_5(c)$   $WCl_2F_4(l)$   $WCl_3F_3(c)$   $WCl_4F_2(c)$   $WClF_5(c)$   $WCl_6(c)$

$$\Delta G = -0.8 \text{ kcal/mole}$$

Consideration of the likely mode of dismutation of

Key

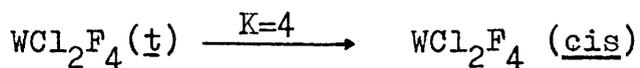
X enthalpy of formation value

Δ Gibbs free-energy value

solid chloride fluoride intermediates may precipitate before the reaction is complete.

consideration of enthalpy factors only [see fig. 2.10.1.]. However, it can also be seen that the two forementioned mixed halides would not be expected to thermally decompose at room temperature. Thus one must consider not merely enthalpy values but also entropy values. For gaseous tungsten hexafluoride  $\Delta S^{\circ}_{298}$  is  $-71.67$  cal/deg/mole.<sup>84</sup> Hence the Gibbs energy of formation at  $25^{\circ}$  is  $-400$  kcal/mole.

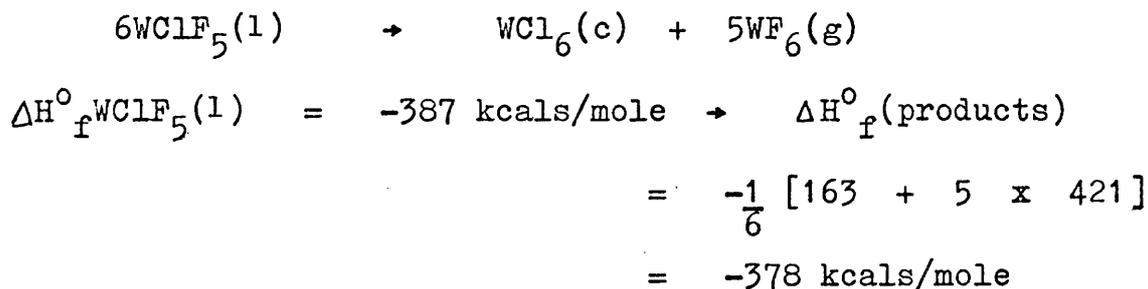
As both tungsten chloride pentafluoride and tungsten dichloride tetrafluoride are liquid at room temperature then it may be assumed that the entropy of formation of these two compounds will be less than, but of the same order as, that for liquid tungsten hexafluoride. Hence consideration of the Gibbs free-energy of formation of these two mixed halides should explain why they are thermally unstable. It should be further noted that in tungsten dichloride tetrafluoride the fact that the two isomers are present in equilibrium makes a difference of less than one kilocalorie per mole to the Gibbs free-energy of formation term:



$$\begin{aligned} \text{Hence } \Delta G &= -RT \ln. K \\ &= -1.98 \times 298 \times 2.303 \times 0.6021 \\ \Delta G &= 0.8 \text{ kcal/mole} \end{aligned}$$

Consideration of the likely mode of dismutation of tungsten dichloride tetrafluoride and tungsten chloride pentafluoride show that entropy factors may be sufficient to make the compounds unstable. The decomposition of the two mixed halides gives predominantly the two binary halides but some solid chloride fluoride intermediates may precipitate before the reaction is complete.

For tungsten chloride pentafluoride:



hence, a minimum of 9 kcal/mole are required to make the decomposition reaction favourable.

$$\text{As } \Delta S \text{ for } \text{WF}_6(g) = -71.67 \text{ kcal/mole.}^{89}$$

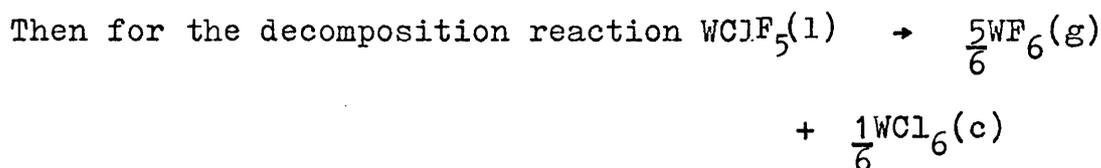
$$\text{Then } \Delta G_{298}^\circ \text{f } \text{WF}_6(g) = -400 \text{ kcal/mole.}$$

If one assumes  $\Delta S$  for  $\text{WClF}_5(c)$  to be  $\frac{5}{6}\Delta S$  for  $\text{WF}_6(c)$

$$\text{where } \Delta S \text{ for } \text{WF}_6(1) = -92.77 \text{ cal/deg/mole.}^{89}$$

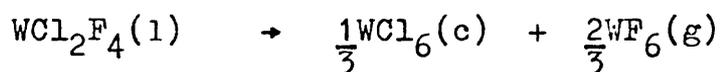
$$\text{TAS for } \text{WClF}_5(1) = -\frac{5.28}{6} = -23 \text{ kcal/mole}$$

$$\text{and } \Delta G_{298}^\circ \text{f } \text{WClF}_5(1) = -387 + 23 = -364 \text{ kcal/mole}$$



$$\begin{aligned}
 \Delta G \text{ for the reaction} &= -\frac{1}{6}[5 \times 400 + 163] + 364 \\
 &= +4 \text{ kcal/mole}
 \end{aligned}$$

This implies that  $\text{WClF}_5$  is only marginally stable towards decomposition, but the error factor predicted for  $\text{WClF}_5 = \pm 5$  kcal/mole could render this value for the Gibbs free-energy of reaction as negative. The decomposition reaction of liquid  $\text{WCl}_2\text{F}_4$  may be similarly considered:



$$\text{At } 25^\circ \text{ the T}\Delta\text{S term for } \text{WCl}_2\text{F}_4(\text{l}) = \frac{2 \cdot -28}{3} = -19 \text{ kcal/mole}$$

$$\text{Hence } \Delta G^\circ_{298} \text{ f } \text{WCl}_2\text{F}_4(\text{c}) = -350 + 19 = -331 \text{ kcal/mole}$$

$$\begin{aligned} \Delta G \text{ for the decomposition reaction of } \text{WCl}_2\text{F}_4(\text{c}) &= \frac{1}{3} \\ & [163 + 2 \times 400] + 331 \\ &= +10 \text{ kcal/mole} \end{aligned}$$

The large error factor predicted for the heat of formation value of liquid  $\text{WCl}_2\text{F}_4$  could reduce this Gibbs free-energy of reaction value to +3 kcal/mole but it would appear from calculations on known thermochemical data that  $\text{WCl}_2\text{F}_4$  should still be thermally stable; however practical studies have shown this to be incorrect. Hence one can only conclude that one, or possibly more than one, of the assumptions on which these calculations were based are in fact incorrect.

### 3. Halogen Exchange with Rhenium Hexafluoride

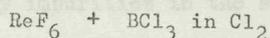
#### 3.1. The Highest Oxidation State of Rhenium as a Binary Rhenium Chloride

The reaction of boron trichloride with tungsten hexafluoride has given the expected highest chloride of tungsten, tungsten hexachloride. By a similar halogen exchange reaction, between rhenium hexafluoride and excess boron trichloride in liquid chlorine, the highest stable binary chloride of rhenium is expected - this being either rhenium hexachloride or rhenium pentachloride. Rhenium hexachloride has already been reported<sup>31,34</sup> and its claimed thermal stability seems to imply that it could easily be formed by a route which involves halogen exchange with rhenium hexafluoride.

It had been anticipated, prior to recent studies,<sup>34</sup> that if rhenium hexachloride could exist then it would be chemically very reactive and possibly thermally unstable with respect to decomposition to rhenium pentachloride and free chlorine. Hence, initial halogen exchange reactions (by this writer) between rhenium hexafluoride and boron trichloride have utilised liquid chlorine both as a solvent and to deter possible decomposition of any rhenium hexachloride produced.

The low temperature ( $-50^{\circ}\text{C}$ ) exchange reaction between rhenium hexafluoride, contaminated with a little rhenium heptafluoride, gives predominantly a dark brown/black crystalline product which has been identified by Debye X-ray powder photography - giving  $\sin^2\theta$  values which correspond to values obtained from single crystal studies<sup>4</sup> [see Table 3.1.1.] - as rhenium pentachloride. Analysis has proved rather difficult; consistent percentages of chloride and

Table 3.1.1.



	Sin <sup>2</sup> +	Sin <sup>2</sup> *	Intensity		hkl. *
			obs. +	calc. *	
1.	.0082	.007795	W <sup>+</sup>	W*	100
2.	.0134	.012938	W	W	11 - 1
3.	.0186	.018354	W → M	M	102
4.	.0191	.018395	VS	S	002
5.	.0224	.022449	W → M	S	021
6.	.0234	.022816	VS	M	11 - 2
7.	.0270	.026326	W + b	M	12 - 1
8.	.0321	.031182	W	W-M	200
		.032406		W-M	21 - 1
9.	.0332	.032406	W	W-M	21 - 1
		.034027		W	102
10.	.0350	.034027	W	W	102
		.035644		W-M	210
11.	.0362	.035644	W	W-M	210
		.038366			
12.	.0390	.03866	VW	W	21 - 2
13.	.0432	.041892	W → M	W-M	11 - 3
14.	.0491	.048080	W-M	W-M	211
		.048639		W	13 - 1
15.	.0568	.055280	W	W-M	12 - 3
16.	.0599	.059240	W	W-M	023
17.	.0662	.065703	W	VW	10 - 4
		.067464		W	31 - 1
18.	.0690	.068106	W	W-M	23 - 1
19.	.0800	.078790	VW	W-M	123
		.080745		W-M	31 - 3
20.	.0822	.082893	VW	W-M	32 - 2
		.083101		W-M	222
21.	.0847	.083553	S-VS	W-M	12 - 4
		.083780		W-M	231
22.	.0912	.089755		W	14 - 2
		.089796	W-M	W-M	042
		.094132		VW-W	32 - 3
23.	.0983	.097050	W-M	W-M	104
		.100544		W	213
24.	.1020	.101181	W	W	31 - 4
		.103165		W	33 - 1
25.	.1072	.105413		S	232
		.105866	S	S	13 - 4
		.107637		W	11 - 5
26.	.1385	.137104	S	MS	14 - 4
		.139507		W	25 - 1
27.	.1520	.149843	W	VW	10 - 6
28.	.1565	.155181	W	W	251
29.	.1622	.16029	W	W-M	125
30.	.1670	.166516	W-M	W-M	33 - 5
31.	.1715	.168451	W-M	M	144
		.174095		M	
32.	.1768	.176608	M	W-M	35 - 2
		.176814		W-M	252
33.	.1806	.179179	W	W-M	42 - 5
34.	.1925	.190097	VW	VW	50 - 4
		.194883		VS	500
35.		.196242		VS	40 - 0
		.196864		S	106
	.1991	.194441	VS	M	52 - 1
		.198082		M	16 - 3
36.	.2091	.208283	W-M	W-MW	35 - 4

+ Observed

\* Reported values K. Mucker, G.S. Smith and Q. Johnson,

Acta Cryst., 1968, B24, 874.

rhenum not being obtained. However, this may have been partially caused by impurities in the solid product (powder photography does not detect impurities of less than 5% of the total sample). The chloride and rhenum analysis of the brown/black product obtained from five separate reactions mixtures did seem to indicate a rhenum:chloride ratio of between 1:5 and 1:6 but the results are inconclusive. It may be that mutual interference of rhenum and chloride analysis occurs by this method [see Appendix I and III]. An infra-red spectrum of the solid has shown no band in the rhenum-oxygen stretching region - usually around  $1,000 \text{ cm}^{-1}$ .

The exchange reaction between rhenum hexafluoride and boron trichloride in liquid chlorine appears to be an equilibrium reaction (cf. corresponding reaction with tungsten hexafluoride) as further quantities of rhenum pentachloride are precipitated if the volatile components of the reaction mixture are distilled and allowed to stand at  $-50^{\circ}$ . Fractional distillation of the volatile reaction products has shown rhenum hexafluoride, boron trichloride and liquid chlorine still to be present. Equilibrium in this halogen exchange reaction, appears to be reached after about an hour at  $-50^{\circ}$ ; leaving the reactants at  $-50^{\circ}$  for several days still results in further precipitation of rhenum pentachloride when the volatile products are distilled and again left at  $-50^{\circ}$ .

Any rhenum heptafluoride present in the reaction mixture is converted either initially to rhenum hexafluoride or, perhaps, preferentially undergoes halogen exchange to form rhenum pentachloride. This is shown by the fact

that fractional distillation of the volatile products immediately after precipitation of rhenium pentachloride shows large proportions of rhenium hexafluoride still to be present but no rhenium heptafluoride. It is expected that rhenium heptafluoride would preferentially undergo halogen exchange with boron trichloride, but whether or not rhenium(VII) would be more likely to form rhenium hexachloride under these conditions is a more arguable point.

The reaction of excess trimethyl chlorosilane with tungsten hexafluoride in the presence of traces of hydrogen chloride [see section 2.4.] as followed by  $^{19}\text{F}$  spectroscopy, shows in turn the presence of all intermediate compounds of the type  $\text{WCl}_n\text{F}_{6-n}$  [ $n = 0, 1, 2, 3, 4, 5$ ]. It may well be that a similar reaction occurs with rhenium hexafluoride, but that the quantities and stabilities of the rhenium(VI) chloride fluoride compounds formed are such that their presence is both undetected and in the case of the brown and red solids, held at  $-30^\circ$  [see Part II section 3.3.] which could possibly have been rhenium chloride fluorides, uncharacterised.

The reaction of excess boron trichloride with rhenium hexafluoride without chlorine or hydrogen chloride being present has been reported to give rhenium hexachloride.<sup>34</sup> This binary chloride is said to be very soluble in excess halogenating reagent and might be the cause of the initial green solution observed by this writer [see Part II sections 3.2., 3.3. and 3.4.]. Unfortunately, no further experimental details of Canterford and co-workers studies<sup>34,37</sup> are known: it has not been stated, for example, how long the reactants were left before the mixture was fractionally

distilled.

On treating rhenium hexafluoride with excess boron trichloride (using no solvent) at both  $-30^{\circ}$  and room temperature, this writer has observed the precipitation of a dark green/brown crystalline compound which is involatile under a dynamic vacuum at room temperature. This solid product gives a Debye X-ray powder photograph which corresponds to that of rhenium pentachloride.

In all experiments carried out by this writer on the exchange reaction between rhenium hexafluoride and excess boron trichloride, no volatile dark green compound possessing characteristics similar to those reported by both Colton<sup>31</sup> and Canterford<sup>34</sup> and attributed to the compound rhenium hexachloride has been obtained. Traces of a bright green compound, which volatilised from all reaction mixtures described [see Part II section 3.2. and 3.3.] and which was held at  $-78^{\circ}\text{C}$  under vacuum, has been observed but further fractional distillation of this product appears to result in its decomposition.

It has been noted that the rhenium pentachloride precipitated in reaction solutions, containing chlorine as a solvent, is finer and less crystalline than that obtained by reaction of rhenium hexafluoride with excess boron trichloride in the absence of a solvent; this may be due to the difference in the solubility of rhenium pentachloride in solutions of boron trichloride containing, and in the absence of, liquid chlorine.

### 3.2. The Highest Oxidation State of Rhenium as a Binary Rhenium Bromide

At present rhenium tri-, tetra- and pentabromide are known, but the description of their preparation is incomplete and information on their properties is contradictory.<sup>62,93</sup> Tronev and Dovlyatshina have found that the bromination of rhenium, by passing over it bromine vapour and purified nitrogen,<sup>94</sup> is very slow; the yield of products being a mixture of bromides and oxybromides of rhenium in different oxidation states.

Preliminary experiments on the reaction of excess boron tribromide with rhenium hexafluoride in liquid bromine below 0°C have resulted in the precipitation of a dark brown solid, but comparison of data from a Debye X-ray powder photograph of this compound [see Table 3.2.1.] with data from  $\alpha$ <sup>95</sup> and  $\beta$ <sup>96</sup> rhenium tetrachloride, niobium tetrachloride<sup>97</sup> and technetium tetrachloride<sup>98</sup> did not facilitate its identification.

It has been reported<sup>99</sup> that rhenium tetrabromide may be prepared in a similar manner to that used in the preparation of rhenium tetraiodide;<sup>100</sup> whereby perrhenic acid is reduced with hydrobromic acid, evaporated to small volume and dried, under a dynamic vacuum in a desiccator containing potassium hydroxide pellets and phosphorus pentoxide. However, attempts to repeat this procedure [this thesis Part II section 3.1.4.] did not give a completely oxygen, or moisture free product. Hence, no comparison between the compound made by halogen exchange and believed to be rhenium tetrabromide and rhenium tetrabromide made by another method is possible.

In the rhenium atom the valency electrons are  $5d^5 6s^2$ ; the d electrons having parallel spins and separately occupy

Table 3.2.1.

Powder Photograph of Brown Solid obtained by the Reaction of Excess  $\text{BBr}_3$  on  $\text{ReF}_6$  in Liquid Bromine.

Intensity	d(in Å)	$\sin^2$
W-M	8.943	0.0074
W-M	7.218	0.0115
VS	5.816	0.0176
VS	5.572	0.0191
M	4.529	0.0290
VS	2.826	0.0745
W-M	2.566	0.0903
W-M	2.462	0.0981
W-M	2.344	0.1082
W-M	2.162	0.1272
W	2.119	0.1325
W	2.095	0.1350
W	1.988	0.1503
M	1.927	0.1600
M	1.895	0.1654
W-M	1.844	0.1750
W-M	1.823	0.1791
W	1.706	0.2040
VW	1.1629	0.2242

orbitals of equal energy. For a rhenium(IV) compound, a magnetic moment consistent with three unpaired electrons would be expected (i.e. a  $\mu_{\text{eff}}$  calculated for spin only of 3.88 B.M.). Cotton and Wilkinson have found that rhenium tetraiodide has a magnetic moment consistent with three unpaired electrons<sup>99</sup> but other workers have calculated the magnetic moment to be 0.9 B.M.<sup>101</sup> Rhenium tetrachloride has an anomalously low magnetic moment of 1.02 B.M.<sup>102</sup> which is explained in terms of an unusual structural feature (pairs of rhenium tetrachloride octahedra joined by a shared edge or face<sup>103</sup>). The magnetic moment of the rhenium bromide compound obtained by the reaction of rhenium hexafluoride with excess boron tribromide in liquid bromide is consistent with a compound containing three unpaired electrons thus implying that the compound might be rhenium tetrabromide.

The reaction of rhenium hexafluoride, contaminated with small proportions of rhenium heptafluoride, with excess boron tribromide in the absence of bromine as solvent at  $-30^{\circ}$  and room temperature also results in the precipitation of a dark brown involatile solid at a temperature below  $0^{\circ}$ . A Debye X-ray powder photograph of this product is identical with that obtained by the same reaction using liquid bromine as a solvent. Fractional distillation of the reaction mixture shows bromine to be one of the products, thereby indicating the possibility of decomposition of an unstable higher oxidation state binary rhenium bromide. Holding the reaction mixture at temperatures at, or below,  $-20^{\circ}$  and distilling the volatile products at  $0^{\circ}$  has still caused bromine to be detected on further fractional distillation of the volatile products.

The exchange reaction between rhenium hexafluoride and excess

boron tribromide in the absence and presence of liquid bromine appears to be an equilibrium reaction (cf. comparable reaction of rhenium hexafluoride and excess boron trichloride) as further quantities of the rhenium bromide compound are precipitated if the volatile components of the reaction mixture are distilled and allowed to stand at  $0^{\circ}$ . Fractional distillation of the volatile products has shown rhenium hexafluoride and boron tribromide still to be present even when the reaction mixture has been allowed to stand for a week at  $-20^{\circ}$ .

### 3.3. Heat of Formation of Rhenium Pentachloride

#### 3.3.1. Introduction

Very few thermochemical data on rhenium binary halides are known. It had been hoped that a heat of hydrolysis of both rhenium pentachloride and rhenium hexachloride would have been measured but the lack of success of this writer in making the hexachloride of rhenium has resulted in a heat of hydrolysis of the former, only, being obtained.

The only known heats of formation of binary rhenium halides reported in the literature are those of the trichloride<sup>50</sup> and tribromide<sup>50</sup> [ $\Delta H_f^{\circ} \text{ReCl}_3(\text{c}) = -63.0$  kcal/mole and  $\Delta H_f^{\circ} \text{ReBr}_3(\text{c}) = -39.3$  kcal/mole]. Work by I. Haigh<sup>22</sup> in this laboratory has shown the value for the heat of formation of rhenium hexafluoride of  $-275$  kcal/mole of Ruff and Kwasnik<sup>53</sup> to be incorrect, a more realistic value being  $-323$  kcal/mole.

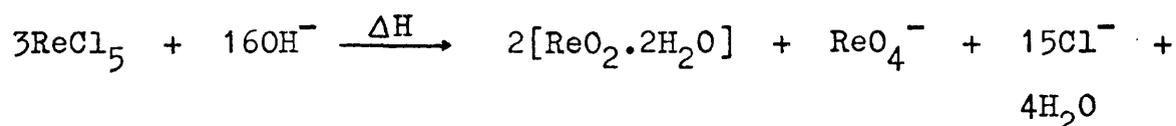
### 3.3.2. Calculation of the Heat of Formation of Rhenium Pentachloride

Since the rhenium pentahalides are largely covalent and contain the metal in a high oxidation state they have a great susceptibility to hydrolysis: due substantially, to the strength of the metal oxygen bond formed in the hydrolysis products. The hydrolysis of rhenium pentachloride has not previously been investigated thermochemically but the reaction is known to give rhenium(IV) and rhenium(VII) derivatives.<sup>32</sup>

Busey et al. have determined the heat of hydrolysis of potassium hexachlororhenate(IV),  $K_2ReCl_6$ , and have found that anaerobic conditions, for the determination of this value, are necessary, so as to ensure that the rhenium dioxide,  $ReO_2 \cdot 2H_2O$ , formed is not oxidised to the perrhenate ion,  $ReO_4^-$ .<sup>104</sup> They have further found that the speed of hydrolysis depends on the concentration of alkali used. However, the hydrolysis reaction of rhenium pentachloride in both 0.1 M and 1 M sodium hydroxide has proved to be complete in less than two minutes, hence showing that appreciable variation in reaction rate does not occur in this case over this concentration range. In the hydrolysis of rhenium pentachloride the sodium hydroxide solution to be used is initially boiled to expel any dissolved oxygen and then cooled before a sufficient quantity of boiled and cooled distilled water is added to bring back the concentration to its original value. It may be that some atmospheric oxygen did dissolve during the twelve hours in which the hydrolysis reaction system is equilibrating but the consistency of the results obtained for the heat of hydrolysis of rhenium pentachloride seems to indicate that this is not the case. After completion of each run it has been noted that quantities of

rhenium dioxide have been precipitated but no attempt has been made to weigh this solid and calculate, from this, whether or not the correct amount of the dioxide has been formed.

Hydrolysis of the rhenium pentachloride, as measured by the deflection of the recorder, is seen to be complete in less than two minutes. Six consistent values for the heat of hydrolysis of rhenium pentachloride of  $-137 \pm 2$  kcals/mole have been obtained in 0.1 M sodium hydroxide [see Part II section 4.7.2. and Table 4.7.1.]. Increasing the strength of the alkali used to 1 M [see Part II section 4.7.2. and Table 4.7.2.] did not increase the value obtained for the heat of hydrolysis, hence it can be assumed that the hydrolysis reaction has gone to completion in the 0.1 M alkali. The hydrolysis reaction is of the form:



where

$\Delta H_f^\circ[\text{ReO}_2 \cdot 2\text{H}_2\text{O}]$ (aq.)	=	-241.8 kcals/mole
$\Delta H_f^\circ[\text{ReO}_4^-]$ (aq.)	=	-189.2 kcals/mole <sup>105</sup>
$\Delta H_f^\circ[\text{Cl}^-]$ (aq.)	=	-40.023 kcals/mole
$\Delta H_f^\circ[\text{OH}^-]$ (aq.)	=	-54.96 kcals/mole
$\Delta H_f^\circ[\text{H}_2\text{O}]$	=	-68.32 kcals/mole

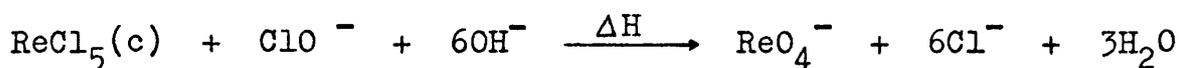
$$\Delta H = 2\Delta H_f^\circ[\text{ReO}_2 \cdot 2\text{H}_2\text{O}](\text{aq.}) + \Delta H_f^\circ[\text{ReO}_4^-](\text{aq.}) + 15\Delta H_f^\circ[\text{Cl}^-](\text{aq.}) + 4\Delta H_f^\circ[\text{H}_2\text{O}] - [3\Delta H_f^\circ[\text{ReCl}_5](\text{c}) + 16\Delta H_f^\circ[\text{OH}^-](\text{aq.})]$$

$$\text{OR } \Delta H_f^\circ[\text{ReCl}_5](\text{c}) = -\frac{1}{3}[667.16 + \Delta H]$$

$$\text{therefore } \Delta H_f^\circ[\text{ReCl}_5](\text{c}) = -85 \pm 5 \text{ kcals/mole}$$

A further check to ensure that the hydrolysis reaction is complete in M/10 alkali has been made by measuring the heat of reaction of rhenium pentachloride in alkaline hypochlorite

[see Part II section 4.7.3.]. Precautions, similar to those described previously in this section, have ensured the absence of dissolved oxygen in the M/10 alkali. A consistent value for this heat of reaction of  $-192 \pm 5$  kcal/mole of  $\text{ReCl}_5$  [see Part II section 4.7.3.] has been obtained and from this measured heat of reaction and known thermochemical data the heat of formation of solid rhenium pentachloride may be calculated.



$$\begin{aligned} \text{where } \Delta\text{H}_f^\circ[\text{ClO}_4^-] (\text{aq.}) &= -26.2 \text{ kcal/mole}^{106} \\ \Delta\text{H}_f^\circ[\text{OH}^-] (\text{aq.}) &= -54.96 \text{ kcal/mole} \\ \Delta\text{H}_f^\circ[\text{ReO}_4^-] (\text{aq.}) &= -189.2 \text{ kcal/mole}^{105} \\ \Delta\text{H}_f^\circ[\text{Cl}^-] (\text{aq.}) &= -40.023 \text{ kcal/mole} \\ \Delta\text{H}_f^\circ[\text{H}_2\text{O}] &= -68.32 \text{ kcal/mole} \end{aligned}$$

$$\begin{aligned} \text{and } \Delta\text{H} &= \Delta\text{H}_f^\circ[\text{ReO}_4^-](\text{aq.}) + 6\Delta\text{H}_f^\circ[\text{Cl}^-](\text{aq.}) + 3\Delta\text{H}_f^\circ[\text{H}_2\text{O}] \\ &\quad - [\Delta\text{H}_f^\circ[\text{ReCl}_5](\text{c}) + \Delta\text{H}_f^\circ[\text{ClO}_4^-](\text{aq.}) + 6\Delta\text{H}_f^\circ[\text{OH}^-](\text{aq.})] \end{aligned}$$

$$\text{then } \Delta\text{H}_f^\circ[\text{ReCl}_5](\text{c}) = -[278 + \Delta\text{H}] \text{ kcal/mole}$$

$$\text{i.e. } \Delta\text{H}_f^\circ[\text{ReCl}_5](\text{c}) = 86 \pm 5 \text{ kcal/mole}$$

#### 4. Properties of the Adduct of Xenon Difluoride and Antimony Pentafluoride. $\text{XeF}_2 \cdot 2\text{SbF}_5$

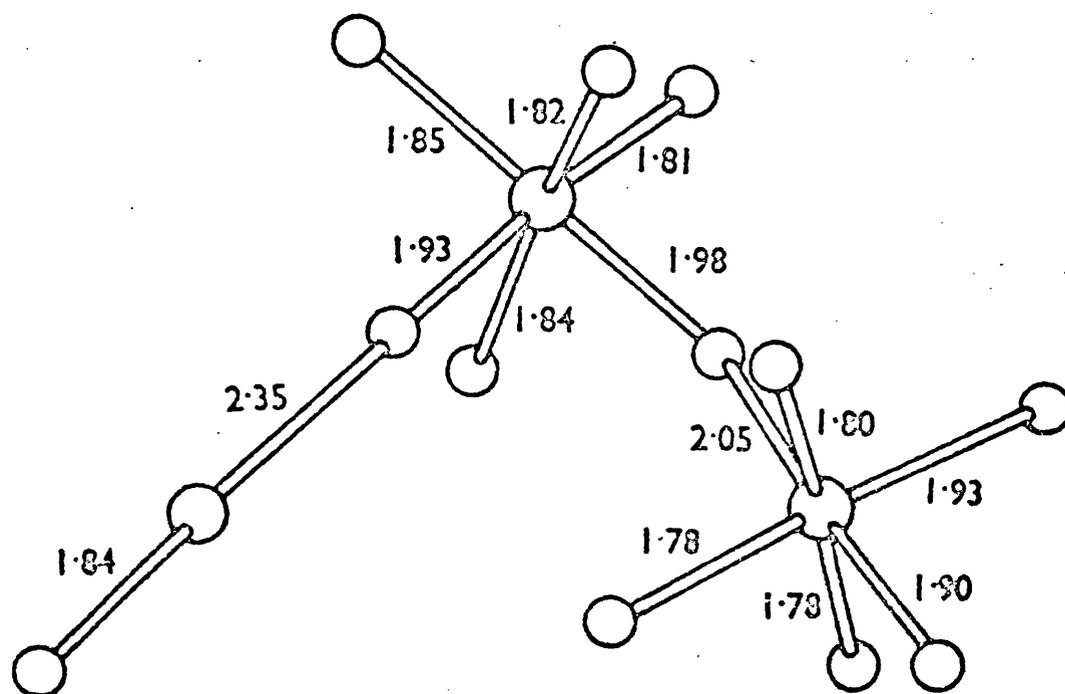
##### 4.1. Introduction

Much interest has been focused on the adducts of xenon difluoride: extensive studies being undertaken on the properties and characteristics of compounds of the type  $2\text{XeF}_2 \cdot \text{MF}_5$ ,  $\text{XeF}_2 \cdot \text{MF}_5$  and  $\text{XeF}_2 \cdot 2\text{MF}_5$  [where M = transition metal, arsenic, antimony]. Difficulty has arisen in the consideration and interpretation of the exact nature of the Xe-F-M-F bond. Neil Bartlett and co-workers have studied a number of  $\text{XeF}_2$  transition metal pentafluoride compounds.<sup>24</sup> The findings of this research have tended to show that the xenon metal pentafluoride bond is ionic. Examination of the infra-red and Raman spectra of  $\text{XeF}_2 \cdot 2\text{SbF}_5$  causes Bartlett to suggest<sup>24</sup> that this molecule could best be considered as an ion pair  $[\text{XeF}]^+ [\text{Sb}_2\text{F}_{11}]^-$ .

A single crystal study on  $\text{XeF}_2 \cdot 2\text{SbF}_5$  by Peacock et al<sup>107</sup> shows a distribution of bond lengths which could be interpreted to indicate an ion pair  $[\text{XeF}]^+ [\text{Sb}_2\text{F}_{11}]^-$ : nevertheless, these workers prefer to regard this ionic notation as purely a formalised way of defining the compound, while still regarding it as essentially a covalent molecule. Their justification for this is based mainly on the short bridging  $-\text{Xe} \cdots \text{F}-$  distance of 2.35 Å compared with the Xe-F distance of 1.84 Å in the normal Xe-F bond [see fig. 4.1.1.] and of 2.0 Å in xenon difluoride itself.<sup>108</sup>

As a result of the single crystal data on  $\text{XeF}_2 \cdot 2\text{SbF}_5$  further studies of the molecule have been undertaken and the heat of formation of the compound has been determined. In

Figure 4.1.1.

The Crystal Structure of  $\text{XeF}_2 \cdot 2\text{SbF}_5$ 

From: V. M. McRae, D. D. Peacock and D. R. Russell, Chem. Comm., 1969, 62.

some ways  $\text{XeF}_2 \cdot 2\text{SbF}_5$  is an "unfortunate" compound to choose because our Raman and infra-red studies indicate that the bonding in the compound may be more complex than in the related xenon difluoride-transition metal pentafluoride compounds.

A study of the 1:1 adduct of xenon difluoride and arsenic pentafluoride<sup>109</sup> might have proved to be less complex because unlike antimony pentafluoride, which is also a good fluoride-ion acceptor, it does not form polymeric anions so readily.

#### 4.2. Some Physical Properties of Xenon Difluoride Metal Pentafluoride Adducts

The physical characteristics of the xenon difluoride metal pentafluoride adducts known are listed in Table 4.2.1. It may be noted that the non-transition metal pentafluoride adducts have similar melting points to the corresponding metal pentafluoride adducts. A study of the adduct  $\text{XeF}_2 \cdot 2\text{SbF}_5$  [this thesis section 4.3.] has shown that the compound boils at  $220^\circ \pm 5^\circ$ ; further heating resulting in the compound being deposited on cooler parts of the reaction vessel. The low melting point and long liquid range of  $\text{XeF}_2 \cdot 2\text{SbF}_5$  would seem to indicate a considerable degree of covalent interaction within the molecule.

#### 4.3. Stability of $\text{XeF}_2 \cdot 2\text{SbF}_5$ to Decomposition

Previous work has indicated that  $\text{XeF}_2 \cdot 2\text{SbF}_5$  decomposes to give a green liquid below its boiling point. Reactions, however, were carried out in pyrex glass and decomposition may have occurred due to reaction with moisture in the glass. If silica apparatus is used, no decomposition is seen to occur at

Table 4.2.1.

Physical Properties of Xenon Difluoride Metal  
Pentafluoride Adducts.

Adduct	Colour	Melting Point (°C)	Vapour Pressure at Room Temperature
$\text{XeF}_2 \cdot \text{NbF}_5^5$	pale yellow	30 - 35	negligible
$\text{XeF}_2 \cdot 2\text{NbF}_5^5$	" "	42 - 47	"
$\text{XeF}_2 \cdot \text{TaF}_5^5$	" "	52 - 53	"
$\text{XeF}_2 \cdot 2\text{TaF}_5^5$	" "	82 - 83	"
$\text{XeF}_2 \cdot \text{RuF}_5^1$	pale green	110 - 111	"
$\text{XeF}_2 \cdot 2\text{RuF}_5^1$	bright green	49 - 50	"
$2\text{XeF}_2 \cdot \text{RuF}_5^1$	pale yellow-green	98 - 99	"
$\text{XeF}_2 \cdot \text{OsF}_5^1$	brown	decomposes slowly at 20°	"
$2\text{XeF}_2 \cdot \text{OsF}_5^1$	pale yellow-brown		"
$\text{XeF}_2 \cdot \text{IrF}_5^1$	yellow-green	152 - 153	"
$\text{XeF}_2 \cdot 2\text{IrF}_5^1$	orange-yellow	69 - 70	"
$2\text{XeF}_2 \cdot \text{IrF}_5^1$	pale yellow-green	92 - 93	"
$\text{XeF}_2 \cdot \text{PtF}_5^1$	orange-red	82 - 83	"
$\text{XeF}_2 \cdot \text{AsF}_5^6$	white	looses $\text{AsF}_5$ at 0°	
$2\text{XeF}_2 \cdot \text{AsF}_5^6$	pale yellow-green	99°	
$\text{XeF}_2 \cdot 2\text{SbF}_5^7$	pale yellow	63°	negligible

temperatures up to  $230^{\circ}$  under vacuum; the yellow liquid  $\text{XeF}_2 \cdot 2\text{SbF}_5$  boils and yellow crystals solidify on cooler parts of the reaction vessel [see Part II section 5.1.]. On heating under one atmosphere of dry nitrogen the boiling point of  $\text{XeF}_2 \cdot 2\text{SbF}_5$  has been measured as  $220 \pm 5^{\circ}\text{C}$ . It has further been noted that if the sample of  $\text{XeF}_2 \cdot 2\text{SbF}_5$  is very pure it does not decompose in pyrex glass but that any impurity in the sample causes immediate etching of the glass when the solid is heated above its melting point.

In preliminary investigations to determine the conductivity of  $\text{XeF}_2 \cdot 2\text{SbF}_5$  it has been found that the compound when liquid reacts with tungsten and with copper wire giving a decomposition reaction in which one of the products is xenon.

#### 4.4. Infra-red and Raman Studies on Liquid and Solid $\text{XeF}_2 \cdot 2\text{SbF}_5$

Raman spectra have been obtained of  $\text{XeF}_2 \cdot 2\text{SbF}_5$  as a fine crystalline solid (at room temperature), as a liquid (at  $70^{\circ}$ ) and as a solid (after allowing the liquid to cool to room temperature again). The data obtained [see Table 4.4.1.] is similar to that of Bartlett et al<sup>24</sup> [see Table 4.4.2.]. The solid cooled from the melt has the appearance of a glass and may be converted to the crystalline solid by dissolving in excess antimony pentafluoride and then distilling off the solvent under vacuum.

All Raman peaks are strong, both in the liquid and in the solid, seeming to indicate some considerable covalent interaction. It is further noted that all bands in the solid are also present in the liquid spectrum.

Table 4.4.1.

Raman Bands in  $\text{XeF}_2 \cdot 2\text{SbF}_5$  (obtained by this writer).

Crystal	Solid cooled from the melt	Liquid at 70°
689 (60)	701 (25)	
682 (25)	694 (84)	687 (48)
660 (sh.)	663 (20)	654 (90)
654 (55)	651 (95)	615 (100)
620 (100)	622 (100)	
574 (very weak)	602 (10)	
526 (25) (broad)	544 (5)	519 (14)
	520 (12)	478 (7)
480 (10)	482 (7)	
268 (15)	306 (17)	296 (12)
		274 (10)
226 (17)	231 (8)	226 (10)
	209 (6)	128 (20)

Relative intensities are given in parenthesis.

Table 4.4.2.

Raman Bands ( $\text{cm}^{-1}$ ) for  $\text{XeF}_2 \cdot 2\text{MF}_5$  Compounds and Related Salts.

Compound	X	Y	Z	A	B	C	D	other bands
					[ $\text{M}_2\text{F}_{11}$ ] $^-$ bands			
$\text{Cs}^+[\text{Sb}_2\text{F}_{11}]^-$			690(16)		653(35)			very high background only strongest lines seen
$[\text{XeF}]^+[\text{Sb}_2\text{F}_{11}]^-$	621(100)		693(55)	682(21)	662(sh)	529(18)		Low frequency bands not defined
					654(46)			
$[\text{XeF}]^+[\text{Ru}_2\text{F}_{11}]^-$	604(100)		733(18)	696(23)	650(62)			285(sh) 229(31)
	598(53)		716(97)	683(54)	645(82)			269(58)
								246(32)
$[\text{XeF}]^+[\text{Ir}_2\text{F}_{11}]^-$	612(100)		699(115)	686(120)	635(27)	527(25)		261w(72) 229(40)
	601(68)†			679(132)				253w

† May be due in part to  $[\text{XeF}]^+[\text{IrF}_6]^-$  impurity.

Relative intensities are given in parenthesis. The bands X and Y are attributed to Xe-F stretching and Z to F-XeF bending. The bands A, C and D are respectively the  $\nu_1$ ,  $\nu_2$  and  $\nu_5$ ,  $O_h$  modes, or their relatives. The bands B are attributed to derivatives of the  $O_h \nu_3$  mode, rendered Raman active by interaction of the cation and the anion.

From F.O. Sladky, B.A. Bulliner and N. Bartlett, J. Chem. Soc. (A), (1969), 2179

Bartlett has compared the Raman spectrum of  $\text{XeF}_2 \cdot 2\text{SbF}_5$  and  $\text{Cs}^+[\text{Sb}_2\text{F}_{11}]^-$  [see Table 4.4.2.]; however, the degree of polarisability of  $\text{XeF}^+$ , as shown by single crystal data [fig. 4.1.1.] would appear to indicate that comparison with such cations as  $\text{Ag}^+$  or  $\text{Tl}^+$  would be more helpful.

Peacock<sup>55</sup> has compared the infra-red data of antimony pentafluoride with that from a spectrum of  $\text{XeF}_2 \cdot 2\text{SbF}_5$  in antimony pentafluoride and has found that the only signal in the latter, which is not also in the former, is a strong band at  $618 \text{ cm}^{-1}$ .<sup>55</sup> This work is in agreement with the data obtained by Bartlett<sup>24</sup> [see Table 4.4.3.] who assigns a band at  $622 \text{ cm}^{-1}$  in  $\text{XeF}_2 \cdot 2\text{IrF}_5$  to a xenon-fluoride stretching vibration.

Fuggle has suggested from N.Q.R. measurements on the adducts of xenon difluoride and niobium pentafluoride and  $\text{XeF}_2$  and tantalum pentafluoride (viz.  $\text{XeF}_2 \cdot \text{NbF}_5$ ,  $\text{XeF}_2 \cdot 2\text{NbF}_5$ ,  $\text{XeF}_2 \cdot \text{TaF}_5$  and  $\text{XeF}_2 \cdot 2\text{TaF}_5$ ) that there is only a 30% ionic contribution in the xenon difluoride-metal pentafluoride bond,<sup>110</sup> but further information on this point is still to be published.

#### 4.5. Heat of Formation of $\text{XeF}_2 \cdot 2\text{SbF}_5$

The heat of formation of  $\text{XeF}_2 \cdot 2\text{SbF}_5$  has been estimated from measurement of the heat of hydrolysis of  $\text{XeF}_2 \cdot 2\text{SbF}_5$  and known thermochemical data.

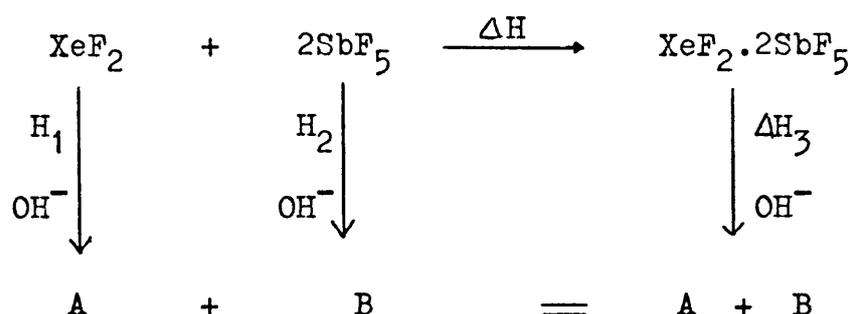


Table 4.4.3.

Infra-red Spectrum ( $\text{cm}^{-1}$ ) of Some Adducts of  $\text{XeF}_2$  and  $\text{MF}_5$ .

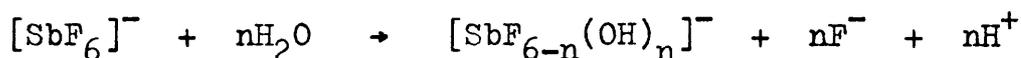
$2\text{XeF}_2 \cdot \text{AsF}_5$	$2\text{XeF}_2 \cdot \text{IrF}_5$	$\text{XeF}_2 \cdot \text{IrF}_5$	$\text{XeF}_2 \cdot 2 \cdot \text{IrF}_5$
690 (vs)	650 (sh)	625 (vs)	675 (sh)
595 (s)	625 (vs)	495 (br)	622 (vs)
400 (vs)	575 (m)		535 (br)
	540 (m)		
	ca. 400 (vs)		

Data from F.O. Sladky, B.A. Bulliner and N. Bartlett,  
J. Chem. Soc. (A), (1969), 2179.

Difficulty has arisen, however, in determining the exact nature of the hydrolysis products. In initial experiments all heat of hydrolysis measurements had been carried out using 0.1 M sodium hydroxide; giving a consistent value for the heat of hydrolysis of antimony pentafluoride of  $-72.5 \pm 4$  kcal/monomeric unit of  $\text{SbF}_5$  [see Part II section 4.8. and Table 4.8.1.] and for the hydrolysis of  $\text{XeF}_2 \cdot 2\text{SbF}_5$  of  $-219 \pm 4$  kcal/mole [see Part II section 4.11. and Table 4.11.1.]. It had been noted that the deflection of the recorder in the hydrolysis of antimony pentafluoride was sharp initially but instead of them stabilising, it had continued to increase over a period of at least ten minutes - this last deflection being of the order of one sixth of the total deflection observed - hence, implying that the last fluorine was lost very slowly. To increase the rate of hydrolysis the strength of the alkali was increased to molar concentration: with the result that the total deflection became sharp, equilibrium being obtained after no greater a time than two minutes. For this reason, all heats of hydrolysis were then measured using molar alkali.

#### 4.5.1. Heat of Formation of $\text{SbF}_5$

Mazeika and Newmann<sup>111</sup> have followed the hydrolysis reaction of  $[\text{SbF}_6]^-$  by titration of either the fluoride or the hydrogen ion liberated.



Their findings have indicated that the first fluorine atom is lost instantaneously. In acid solution only 60% of the fluoride is released after a reasonable length of time but

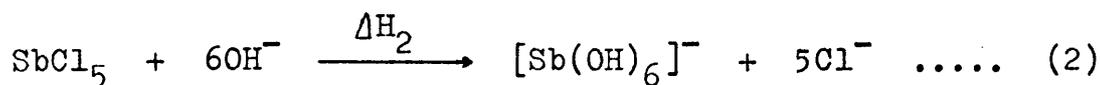
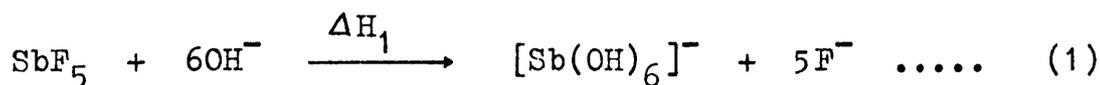
in solutions more basic than  $\text{pH} = 12$  the hydrolysis is seen to be complete, all six fluorine atoms being rapidly lost. The reaction in 1 M alkali is so fast that immediate precipitate of a fine, white crystalline solid occurs.

On mixing antimony pentafluoride in excess of 0.1 M sodium hydroxide a fine white crystalline solid is precipitated when the solution had been left standing at room temperature for six hours (the solution turned cloudy after about three hours) - with excess molar sodium hydroxide this white solid had precipitated immediately. These solids have been shown to be identical by Debye X-ray powder photography.

As the nature of the exact products of alkaline hydrolysis of antimony pentafluoride was uncertain, the hydrolysis of antimony pentachloride has also been investigated [see Part II section 4.9.]. Again, a white solid is precipitated immediately with molar sodium hydroxide but more slowly with M/10 sodium hydroxide. By X-ray powder photography both products have been shown to be identical to one another and to the white solid obtained from alkaline hydrolysis of antimony pentafluoride. The unit cell size of the crystalline white solid has been shown to be identical with that recorded in the literature for sodium antimony hydroxide,  $\text{Na}^+[\text{Sb}(\text{OH})_6]^-$ .<sup>112</sup>

The products of the alkaline hydrolysis of both antimony pentafluoride and antimony pentachloride are the same except for the fact that they liberate fluoride ion and chloride ion respectively.

From consideration of the following equations,



measured values for  $\Delta H_1$  and  $\Delta H_2$  and the known value for the heat of formation of antimony pentachloride ( $\Delta H_f^\circ \text{SbCl}_5(1) = -104.8 \text{ kcal/mole}^{113}$ ) a value for the heat of formation of antimony pentafluoride may be obtained:

$$\begin{aligned} \Delta H_1 = & 5\Delta H_f^\circ(\text{F}^-)(\text{aq.}) + \Delta H_f^\circ[\text{Sb}(\text{OH})_6]^- (\text{aq.}) - 6\Delta H_f^\circ(\text{OH})^- (\text{aq.}) \\ & - \Delta H_f^\circ \text{SbF}_5(1) \dots\dots\dots (3) \end{aligned}$$

$$\begin{aligned} \Delta H_2 = & 5\Delta H_f^\circ(\text{Cl}^-)(\text{aq.}) + \Delta H_f^\circ[\text{Sb}(\text{OH})_6]^- (\text{aq.}) - 6\Delta H_f^\circ(\text{OH})^- (\text{aq.}) \\ & - \Delta H_f^\circ \text{SbCl}_5(1) \dots\dots\dots (4) \end{aligned}$$

Then from (3) and (4)

$$\begin{aligned} \Delta H_f^\circ(\text{SbF}_5)(1) = & [\Delta H_f^\circ(\text{F}^-)(\text{aq.}) - \Delta H_f^\circ(\text{Cl}^-)(\text{aq.})] - \\ & [\Delta H_1 - \Delta H_2] + \Delta H_f^\circ \text{SbCl}_5(1) \end{aligned}$$

From measurements of the heat of hydrolysis of liquid antimony pentafluoride and antimony pentachloride [this thesis Part II sections 4.8. and 4.9.].

$$\Delta H_1 = -108 \text{ kcal/gm. formula wt.}$$

$$\Delta H_2 = -131 \text{ kcal/mole}$$

$$\text{Hence } \Delta H_f^\circ \text{SbF}_5(1) = -321 \pm 10 \text{ kcal/gm. formula wt.}$$

The necessarily large error factor brings this measurement into reasonable agreement with that obtained by Woolf<sup>114</sup> [ $\Delta H_f^\circ \text{SbF}_5 = -329.5 \text{ kcal/gm. formula wt.}$ ] from calorimetric measurement of the heat of reaction of bromine trifluoride and antimony.

The only other known value for the heat of formation of antimony pentafluoride [ $\Delta H_f^\circ \text{SbF}_5 = -308.6 \pm 1 \text{ kcal/gm.}$

formula wt.<sup>115</sup>) has been estimated by comparison of the heat of hydrolysis of antimony pentafluoride and antimony pentoxide in 10 M hydrofluoric acid. In this determination it was assumed, without evidence, that the ~~hydrolysis~~ ~~solution~~ products of  $\text{SbF}_5$  and  $\text{Sb}_2\text{O}_5$  were identical and  $\Delta H_f^{\circ}(\text{SbF}_5)$  was determined from heat of hydrolysis measurements and the known heat of formation of antimony pentoxide (cf. the heat obtained by this writer).

#### 4.5.2. Heat of Hydrolysis of Xenon Difluoride

Hydrolysis of xenon difluoride is said to liberate oxygen and xenon quantitatively,<sup>116,117</sup> hence, consistent results were expected from our measurements of the heat of hydrolysis of xenon difluoride in dilute sodium hydroxide [see Part II section 4.10.]. However, the reaction may not be fast enough to be determined by this writer's calorimetric apparatus as it requires that the reaction be complete in less than five minutes.

As little work has been done on the alkaline hydrolysis of xenon difluoride, it is possible that, though the main products are oxygen, xenon and hydrogen fluoride, small quantities of oxygen difluoride and hydrogen peroxide may be formed by side reactions. However, the presence of platinum black in the sodium hydroxide did not enable a consistent value for the heat of hydrolysis to be obtained.

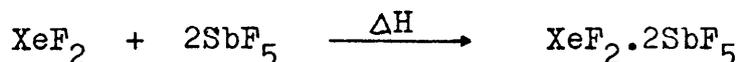
#### 4.5.3. Heat of Formation of $\text{XeF}_2 \cdot 2\text{SbF}_5$

A white solid is precipitated on addition of  $\text{XeF}_2 \cdot 2\text{SbF}_5$  to sodium hydroxide; precipitation being immediate with molar sodium hydroxide but after several hours

with 0.1 M alkali. Debye X-ray powder photography has shown these solids to be identical to each other and to the white solid product of alkaline hydrolysis of antimony pentafluoride and antimony pentachloride.

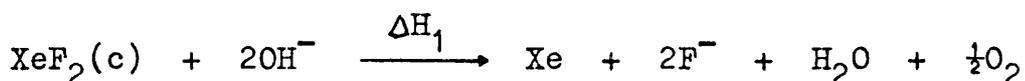
A consistent value for the heat of hydrolysis of solid  $\text{XeF}_2 \cdot 2\text{SbF}_5$  of  $-219 \pm 5$  kcal/mole has been obtained using 0.1 M sodium hydroxide and of  $-281 \pm 7$  kcal/mole using molar alkali [see Part II section 4.11.]. The error factor is larger when the reaction was in stronger alkali because the results obtained were not so consistent.

As the value for the heat of formation of crystalline xenon difluoride is now known accurately from bomb calorimetric measurements [ $\Delta H_f^\circ \text{XeF}_2(\text{c}) = -25.9$  kcal/mole<sup>118</sup>] an approximate value for the heat of reaction



may be estimated.

From the known heat of formation of crystalline xenon difluoride, the heat of hydrolysis of the compound may be deduced:



where  $\Delta H_f^\circ \text{F}^-(\text{aq.}) = -78.66$  kcal/mole

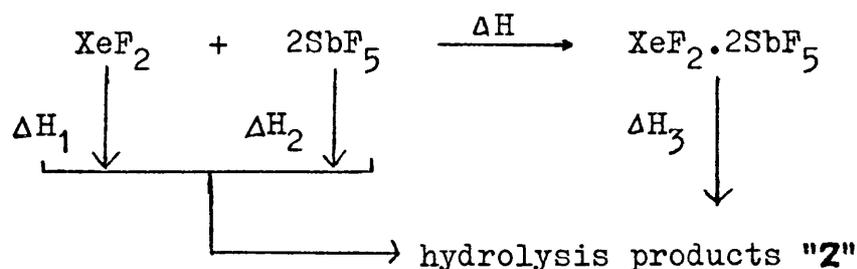
$\Delta H_f^\circ \text{H}_2\text{O} = -68.32$  kcal/mole

$\Delta H_f^\circ \text{OH}^-(\text{aq.}) = -54.96$  kcal/mole

Then  $\Delta H_1 = 2\Delta H_f^\circ \text{F}^-(\text{aq.}) + \Delta H_f^\circ \text{H}_2\text{O} - [2\Delta H_f^\circ \text{OH}^-(\text{aq.}) + \Delta H_f^\circ \text{XeF}_2(\text{c})]$

i.e.  $\Delta H_1 = -90.7$  kcal/mole

Consideration of the heat of hydrolysis in the reaction cycle



then enables  $\Delta H$  to be calculated.

For values of  $\Delta H_2$  and  $\Delta H_3$  using molar alkali:

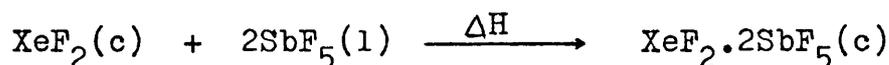
$$\Delta H = -[91 + (2 \times 108)] + 281 = -26 \pm 10 \text{ kcal/mole}$$

This value of -26 kcal/mole gives an estimate of the stability of the bonding between  $\text{XeF}_2$  and  $\text{Sb}_2\text{F}_{10}$  in the adduct  $\text{XeF}_2 \cdot 2\text{SbF}_5$ , but the degree of error in the value makes the validity of discussion as to the nature of the  $-\text{Xe} \cdots \text{F} \cdots \text{Sb}$ -bonds rather doubtful. It implies a value for

$$\Delta H_{\text{f}}^{\circ} \text{XeF}_2 \cdot 2\text{SbF}_5(\text{c}) = \Delta H + \Delta H_{\text{f}}^{\circ} \text{XeF}_2(\text{c}) + 2\Delta H_{\text{f}}^{\circ} \text{SbF}_5 = -333 \text{ kcal/mole}$$

but the degree of error in this value would be of the order of  $\pm 20$  kcal/mole.

It should be noted that if one assumes incomplete hydrolysis of antimony pentafluoride in 0.1 M sodium hydroxide, but that the proportion of the compound hydrolysed is the same in the hydrolysis of both antimony pentafluoride and the adduct  $\text{XeF}_2 \cdot 2\text{SbF}_5$  and also that the heat of hydrolysis of xenon difluoride is the same in molar and 0.1 molar alkali then a second value for  $\Delta H$  in the equation



may be calculated. Where the heat of hydrolysis in 0.1 M alkali of  $\text{SbF}_5$  and  $\text{XeF}_2 \cdot 2\text{SbF}_5$  are respectively -72.5 kcal/gm. formula unit and -219 kcal/mole [see Part II sections 4.8. 4.11.] then:

$$\Delta H = -[91 + (2 \times 72.5)] + 219 = -17 \text{ kcal/mole}$$

This value for the stability of the bonding between  $\text{XeF}_2$  and  $\text{Sb}_2\text{F}_{10}$  in the adduct  $\text{XeF}_2 \cdot 2\text{SbF}_5$  is within the value previously stated, given the necessarily large error factor.

A possible alternative route to determine the heat of formation of  $\text{XeF}_2 \cdot 2\text{SbF}_5$  might have been approached via vapour pressure measurements. However the low vapour pressure of the adducts makes the validity of ~~these values~~ <sup>such assumptions</sup> questionable.

#### 4.6. The Nature of the -Xe ... F ... Sb- Bond in $\text{XeF}_2 \cdot 2\text{SbF}_5$

##### 4.6.1. Introduction

To define what is meant by an ionic bond is not a simple task. Ideally, a substance should be called "ionic" if an analysis of the electron density distribution shows that within small well defined limits, each atom or complex radical bonded by distribution minima carries an integral net charge. Unfortunately, such an analysis is not possible with  $\text{XeF}_2 \cdot 2\text{SbF}_5$ . An ionic compound normally displays the three following characteristics: it exists as an involatile solid at normal temperatures, it conducts poorly in the solid state but well when fused, and it possesses a three dimensional lattice in which the atoms are regularly disposed.

$\text{XeF}_2 \cdot 2\text{SbF}_5$  is a solid which readily melts at  $63^\circ$  and boils at  $220^\circ$ . These physical properties would seem to indicate that the compound is predominantly covalent. However, with compounds containing complex ions, interionic reactions may occasionally cause low volatility: for example, X-ray studies of solid phosphorus pentachloride suggest the formulation  $\text{PCl}_4^+ \text{PCl}_6^-$ , but the compound sublimes to give  $\text{PCl}_5$  on mild heating.

Bartlett and co-workers have pointed out that the strong close doublet<sup>24</sup> centred at ca.  $605 \text{ cm}^{-1}$  in the Raman spectra

of solid  $\text{XeF}_2 \cdot 2\text{RuF}_5$  and  $\text{XeF}_2 \cdot 2\text{IrF}_5$  indicates the  $[\text{XeF}]^+$  ion to be present but this doublet is not present in the Raman spectrum of  $\text{XeF}_2 \cdot 2\text{SbF}_5$ . These workers point out that there is undoubtedly some interaction in the 1:1 salts between the  $[\text{XeF}]^+$  ion and the  $[\text{MF}_6]^-$  ion [where M = transition metal], but maintain that the vibrational data indicates that it is weak relative to the bonding interaction in  $[\text{XeF}]^+$  or in  $\text{XeF}_2$ <sup>119,120</sup> itself. It may be that although the noble metal  $\text{XeF}_2 \cdot 2\text{MF}_5$  compounds can best be regarded as ionic compounds of the type  $[\text{XeF}]^+[\text{M}_2\text{F}_{11}]^-$ ; nevertheless the fact that they are not isomorphous with  $\text{XeF}_2 \cdot 2\text{SbF}_5$  tends to suggest that  $\text{XeF}_2 \cdot 2\text{SbF}_5$  may still best be regarded as basically a covalent compound. It is likely that in all  $\text{XeF}_2 \cdot 2\text{MF}_5$  compounds (whether M = noble metal, antimony or arsenic) there is some ionic and some covalent interaction; certainly, the unsymmetric and dipolar nature of the  $[\text{XeF}]^+$  cation could lead to a strong interaction between the positive end of the diatomic (the xenon atom) and the fluoride ligand of the  $[\text{M}_2\text{F}_{11}]^-$  ion.

In the compounds  $\text{FXeSO}_3\text{F}$  and  $\text{FXeClO}_4$ <sup>121</sup> an ionic formulation would be inappropriate as the XeF stretch is ca.  $510 \text{ cm}^{-1}$ . In these compounds there is strong evidence for a significant interaction of xenon with oxygen. Hence it can be seen that it is quite feasible for an XeF group to bond covalently to a group such as perchlorate which is itself a good electron acceptor. Similarly, antimony pentafluoride has been reported to form adducts of the type  $\text{SbF}_5 \cdot \text{B}$  and  $(\text{SbF}_5)_2 \cdot \text{B}$  with weak bases such as  $\text{SO}_2\text{ClF}$  and  $\text{CH}_3\text{SO}_2\text{F}$ <sup>122</sup> and acids such as water, sulphuric acid and fluorosulphuric acid<sup>123</sup> in sulphur dioxide solvent. In some cases the  $\text{SbF}_5$  group

forms the bridging group in the complex in others it is the acceptor group.

#### 4.7. The Binding Energy in $\text{XeF}_2 \cdot 2\text{SbF}_5$

With compounds such as  $\text{XeF}_2 \cdot 2\text{SbF}_5$  the main experimental criteria for the presence of ions is the high symmetry of the discrete anion and a change in the geometry of the cation relative to that of the neutral radical. These two properties are usually detected by vibrational spectroscopy and X-ray analysis. However, the complexity of the Raman spectrum and the short bridging distance of the  $-\text{Xe} \cdots \text{F}-$  bond obtained by X-ray analysis seem to indicate ionic and covalent forces to both be operative in the molecule.

The binding energy of  $\text{XeF}_2 \cdot 2\text{SbF}_5$  at  $298^\circ$  ( $\Delta H_{\text{lattice}}$ ) is related to other important quantities in the Born-Haber cycle [see figure 4.7.1.]. Hence, if all the necessary thermodynamic values in this cycle are known a value for the lattice enthalpy may be calculated and compared with that for a purely ionic compound, both lattice enthalpy values being obtained via Kapustinskii's equation.<sup>124</sup>

$$\text{Lattice enthalpy} = 287.2 \cdot n \cdot \frac{Z_1 \cdot Z_2}{r_c + r_A} \left[ 1 - \frac{0.345}{r_c + r_a} \right]$$

where  $n$  is the number of ions in the molecule

$Z_1$  and  $Z_2$  are the ionic charges

$r_c + r_A$  is the sum of the radii of the cation and anion in the lattice.

[Given that one can find the centre of the cation and anion - i.e. the centre of the positive and negative charge - in the ion pair.]

A value for the fluoride ion affinity of antimony penta-

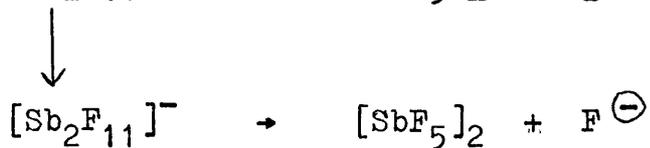
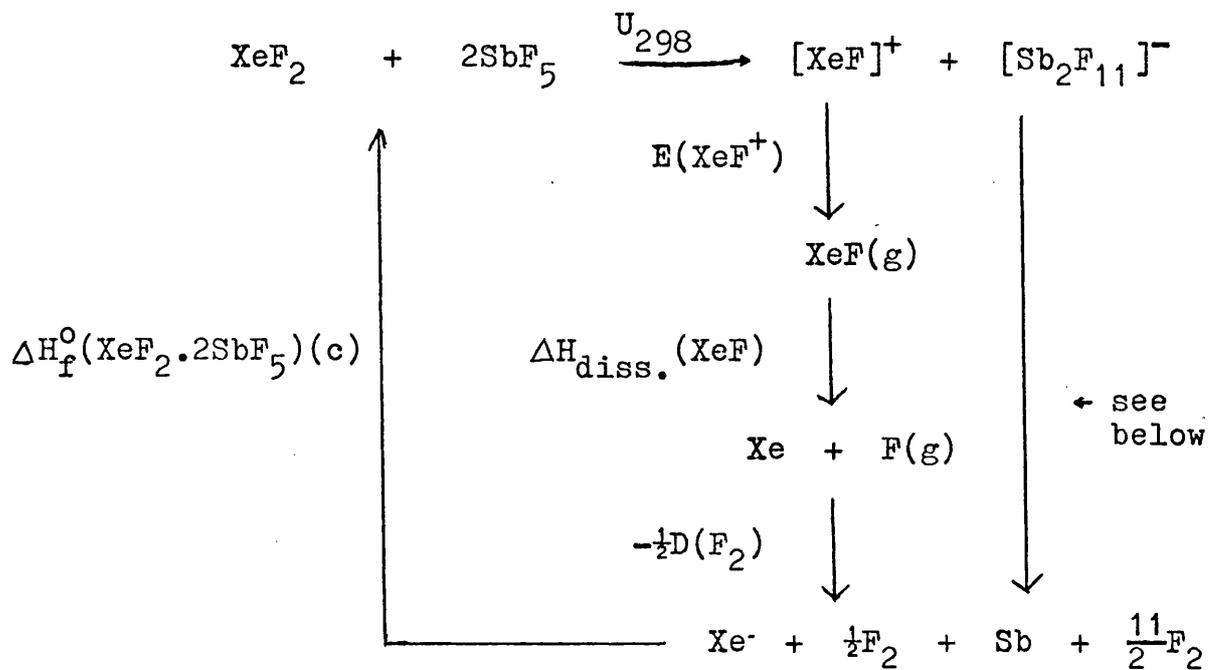
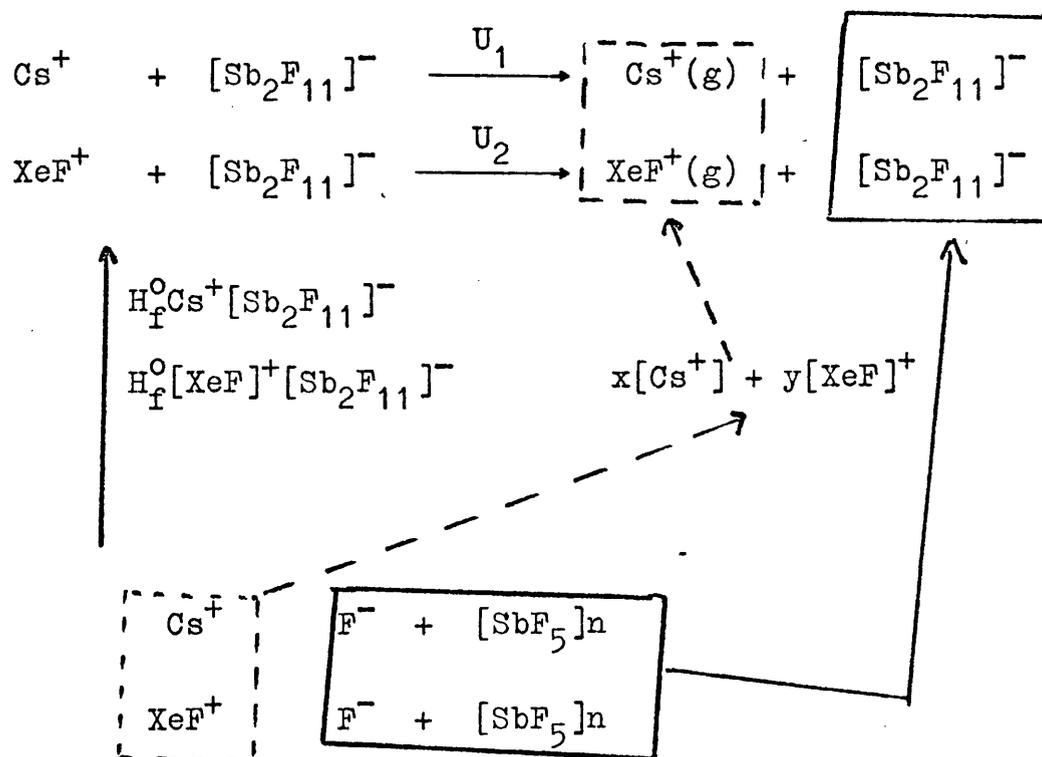
Figure 4.7.1.Thermodynamic Reaction Cycle for  $\text{XeF}_2 \cdot 2\text{SbF}_5$ 

Figure 4.7.2.

Thermochemical Reaction Cycles for  $[\text{XeF}]^+[\text{Sb}_2\text{F}_{11}]^-$   
and  $\text{Cs}^+[\text{Sb}_2\text{F}_{11}]^-$  (assuming both compounds are ionic).



fluoride could possibly be obtained by extended calculation from values of the lattice energy of some alkali and alkaline earth metal cation  $[\text{Sb}_2\text{F}_{11}]^-$  anion compounds. However, this difficulty could be eliminated by comparing the cycles for  $\text{XeF}_2 \cdot 2\text{SbF}_5$  and  $\text{Cs}^+[\text{Sb}_2\text{F}_{11}]^-$  [see figure 4.7.2.] and obtaining single crystal data on the latter.

Further difficulties arise in calculating the heat of formation of the  $[\text{XeF}]^+$  ion. This may be only estimated from calculations similar to those suggested by Bartlett<sup>24</sup> and require assumptions and approximations the validity of which is still in doubt.

From the foregone discussion it is apparent that this route will not give a quantitative value for the forces involved in bonding in the xenon difluoride-antimony pentafluoride adduct. However, prolonged research along these lines might lead to a relative ordering of the proportion of ionic bonding influences within a series of  $\text{XeF}_2 \cdot 2\text{MF}_5$  compounds.

PART II

EXPERIMENTAL

# 1. Experimental Techniques for Handling Volatile Fluorides

## 1.1. General Techniques

Standard vacuum line techniques were utilised in the manipulation of all volatile compounds. Ground glass joints and taps were kept to a minimum and were lubricated with Kelf 90" grease as ordinary high vacuum grease is attacked by transitional metal fluorides. Break-seal vessels were used to store the volatile fluorides: with binary fluorides dry sodium fluoride was also added to absorb any hydrogen fluoride formed by reaction of the fluoride with the glass. N.m.r. tubes were of thick walled, specially machined, tubing and were always sealed under vacuum.

## 1.2. Handling and Use of the Fluorine Generators

Fluorine was obtained from 10 amp. and 60 amp. I.C.I. medium temperature electrolytic cells. The 10 amp. cell was used when only partial fluorination was required [e.g. in the preparation of  $WCl_2F_4$  and  $WClF_5$ ] as better control of the fluorine supply was possible than with the larger cell. Electrolytic fluorine contains oxygen [moisture in the molten potassium hydrogen fluoride electrolyses preferentially], which was minimised by operating the cell for a period before reaction, and hydrogen fluoride: the latter is trapped out by passing the fluorine gas through sodium fluoride scrubbers - sodium fluoride absorbs hydrogen fluoride - and through a trap held at  $-180^\circ$ .

The copper fluorine-line was connected to glass apparatus with copper plumbing unions sealed with neoprene O-rings. The

fluorine having passed through the reaction mixture and product collecting traps bubbled through concentrated sulphuric acid [about  $\frac{1}{2}$  cm. of the bubbler's inner tube was immersed in the conc.  $\text{H}_2\text{SO}_4$ ] and along a copper waste pipe to a fume extractor. The purpose of the acid bubbler was two fold: firstly, to give an indication of the rate of flow of the reacting gasses and secondly, to prevent back-diffusion of moisture if the gas flow should be stopped (especially by a blockage).

### 1.3. Experimental Details of N.M.R. Studies

All samples were prepared on a vacuum line and sealed into 15 cm. long. thick walled, tubes accurately machined to 4.5 mm. diameter and supplied by Jencons Scientific Co. About a 3 cm. depth of liquid sample was required to fill the probe area. In certain cases, small samples were increased in volume by addition of arcton 11,  $\text{CFCl}_3$ , or another appropriate solvent (e.g. acetonitrile,  $\text{CH}_3\text{CN}$ ).

A Varian DA6- high resolution nuclear magnetic resonance spectrometer was used for  $^{19}\text{F}$  and  $^{31}\text{P}$  resonances and operated at 56.4 MHz. for  $^{19}\text{F}$  and 19.3 MHz. for  $^{31}\text{P}$  resonance. Proton magnetic resonances were measured on a Varian A60.

Measurements on the DA60 was by standard side band technique.<sup>125</sup> Chemical shifts were noted to vary over several parts per million according to the concentration of the compound being measured and the solvent used; so that the quoted values were always modified by a possible chemical shift error factor.

The method of recording used on the DA60 involves the generation of side bands, by the machine, of about 2 MHz. which are superimposed on all spectra. They are the result of an

electronic means of stabilising the recorder base line and did not normally interfere with spectra under study. These side-bands were found to drift in frequency with time and thus could not be put to use for calibration.

#### 1.4. Experimental Details of Magnetic Measurements

Magnetic susceptibility measurements were made by the Guoy technique. The samples were enclosed in thin walled Pyrex tubes of 5 mm. outer diameter. The sample tubes were loaded in a dry box and were sealed under vacuum.

Magnetic measurements were obtained using a single temperature Guoy balance, which consisted of an electromagnet with a field of between 5,000 and 10,000 gauss. The micro-balance had a sensitivity of  $\pm 0.01$  mg.

The sample was suspended from the balance pan by means of an aluminium chain and collar. All the sample tubes were of the order of 10 cm. long. The length of sample in the tube was usually about 6 cm. The tube containing the sample was weighed in and out of the magnetic field. Mercury cobalt tetrathiocyanate was used as the magnetic standard.<sup>126</sup> A diamagnetic correction for the container, at room temperature, was obtained by weighing the empty sample tube in and out of this field.

The gram susceptibility of the sample,  $\chi_g(s)$ , was calculated from the equation:

$$\chi_g(s) = \chi_g(st) \times \frac{W(s) + dm}{W(s)} \times \frac{W(st)}{W(st) + dm}$$

where  $\chi_g(s)$  is the g. susceptibility of sample,  $\chi_g(st)$  the g. susceptibility of standard ( $= 16.44 \times 10^{-6}$  c.g.s. units for  $\text{HgCo}(\text{CNS})_4$  at  $20^\circ$ ),<sup>127</sup>  $W(s)$  and  $W(st)$  are the changes in weights of the sample and standard respectively and  $dm.$  is the

diamagnetic correction due to the container.

The molar susceptibility,  $\chi_M$ , was corrected for the diamagnetic susceptibility of the ligands with Pascal's constants<sup>127</sup> to give the gramme atomic susceptibility  $\chi_A$ .  $\mu_{\text{eff}}$  is given by  $\mu_{\text{eff}} = 2.839 \sqrt{\chi_A T}$  where T is in degrees absolute.

### 1.5. Experimental detail for Debye X-ray Powder Photography

Pyrex capillaries, of 0.3 and 0.5 mm. diameter, were used to support X-ray powder samples. With all of the compounds studied, which were moisture sensitive, the capillaries were loaded in a dry box and sealed, either with a small hot flame or with plaster~~ercine~~, depending on the degree of moisture and air sensitivity of the sample.

X-ray powder photographs were taken by the Straumanis method with copper  $K_{\alpha}$ -radiation, using a commonly available powder camera (Philips' Debye-Scherrer, Type PW.1026). The dimensions of the camera are such that one degree of  $\theta$  (the Bragg angle) corresponds to one mm. of the developed and stretched film. A pin hole collimator was used and the exposure time was normally between three and four hours.

The diameters of the arcs of the X-ray powder patterns were measured using a light box provided with an accurate scale and vernier. Readings were obtained within an accuracy of 0.0005 cm. Bragg angles, d-spacing and  $\sin^2 \theta$  values were then obtained from the arc measurements.

## 2. Tungsten(VI) Halogen Compounds

### 2.1. Preparation of Some Tungsten(VI) Halide Compounds

#### 2.1.1. Preparation of Tungsten Hexafluoride

Tungsten hexafluoride was prepared by direct fluorination of reduced tungsten, at atmospheric pressure in a nickel reaction tube, using a flow system at a temperature of  $150^{\circ}$  -  $300^{\circ}$ . The tungsten was previously reduced in a stream of hydrogen for a further two hours: this removed any oxide impurity from the surface of the metal which would hinder fluorination and produce oxide fluoride impurities. The product of the fluorination of the tungsten powder, collected at  $-180^{\circ}$ , was fractionated in a vacuum line from  $-40^{\circ}$  to  $-180^{\circ}$  to remove traces of tungsten oxide tetrafluoride. The tungsten hexafluoride was then stored in glass break seal vessels at  $-30^{\circ}$ , or in a metal cylinder fitted with a needle valve. All such storage vessels contained dry sodium fluoride which would absorb any hydrogen fluoride present.

#### 2.1.2. Preparation of Tungsten Chloride Pentafluoride

Tungsten chloride pentafluoride was prepared by fluorination of tungsten hexachloride in a flow system [see fig. 2.1.1.]. The tungsten hexachloride, contained in a glass reaction vessel, was purged with dry nitrogen before being treated with a slow stream of fluorine ( $\sim 500$  ml./hour) diluted with an equal volume of nitrogen. Reaction took place with the evolution of heat; the dark purple hexachloride turned red, then orange, before volatilising almost completely - the trace of white crystalline residue had the appearance of tungsten oxide tetrafluoride. The volatile products, which were held at  $-180^{\circ}$  were eventually separated under vacuum, fractions being

Figure 2.1.1.

Preparation of Mixed Volatile Chlorine Fluorides of Tungsten(VI)

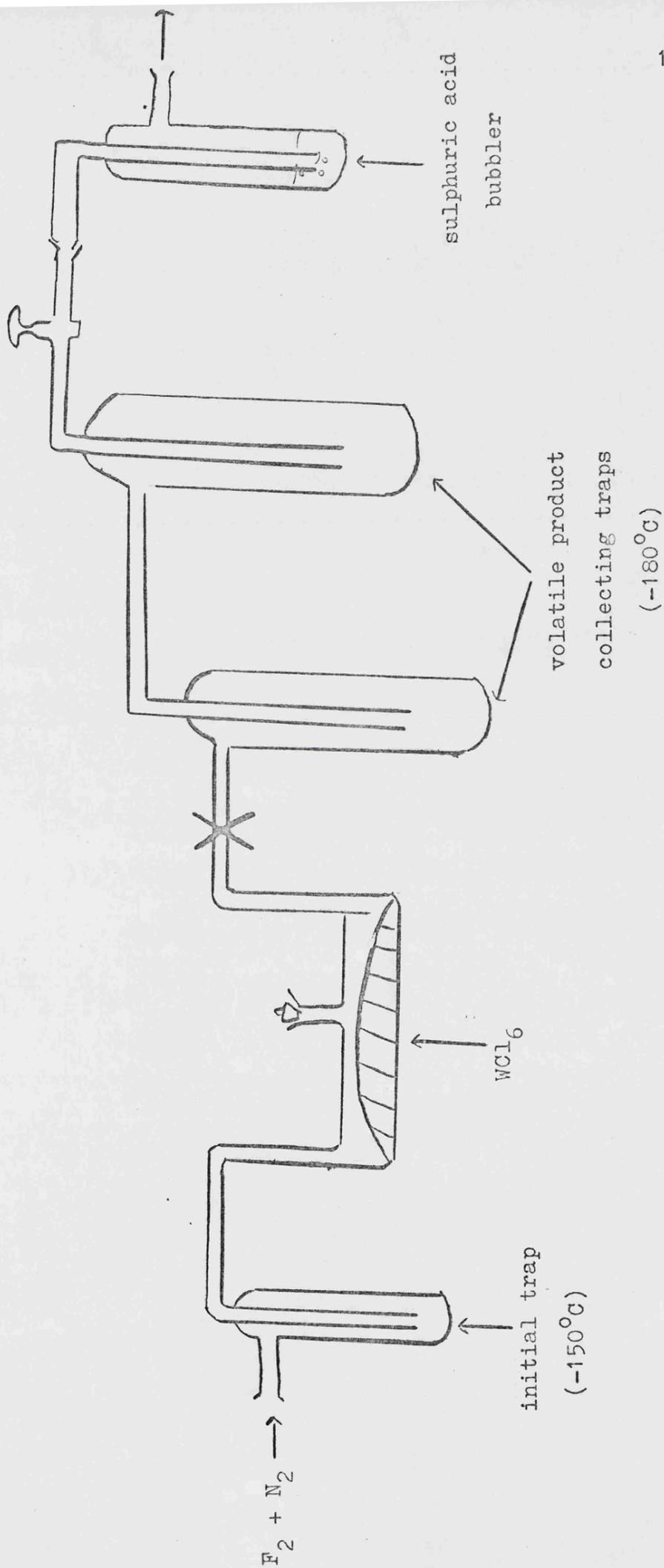
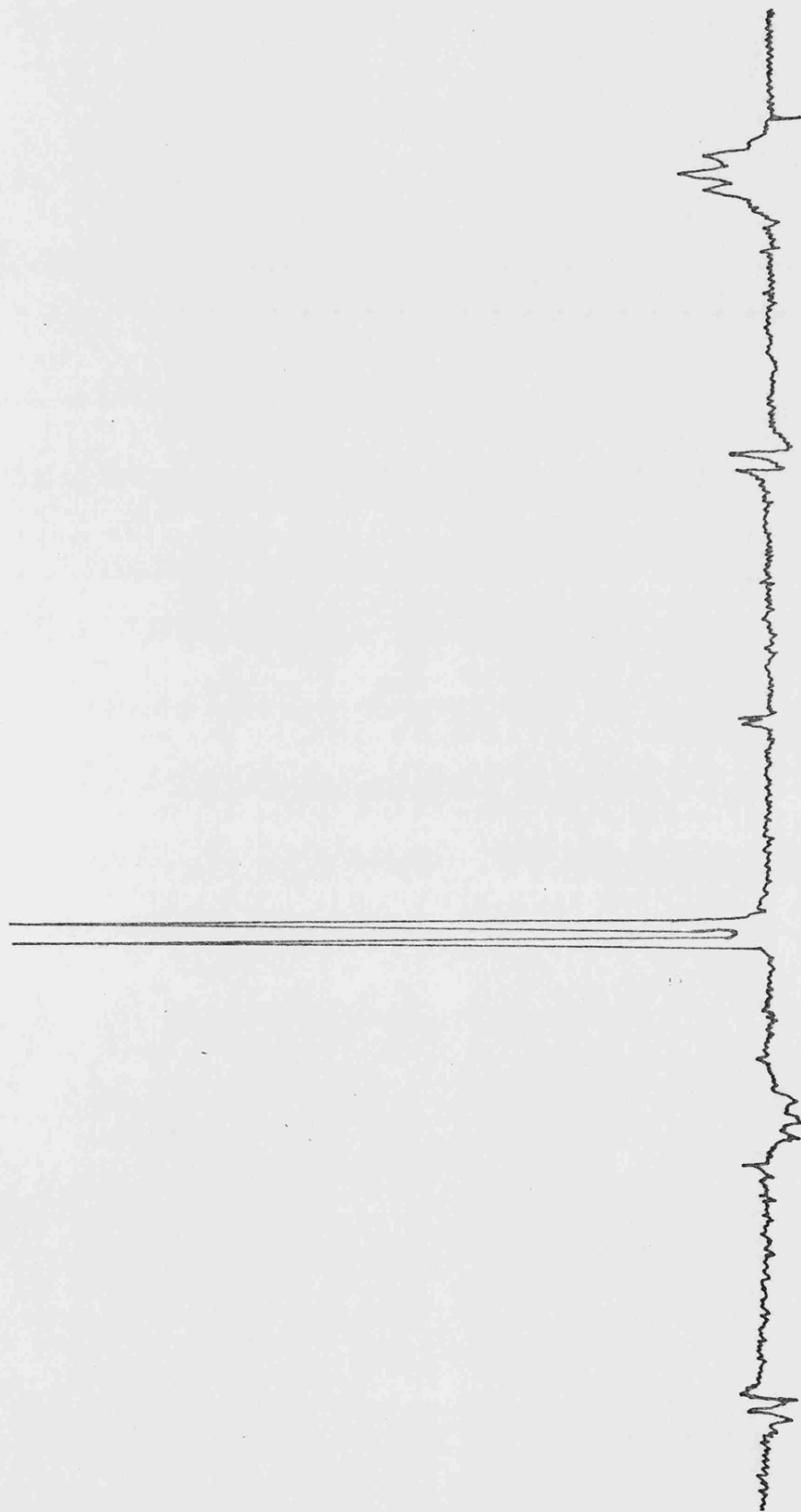


Figure 2.1.2.

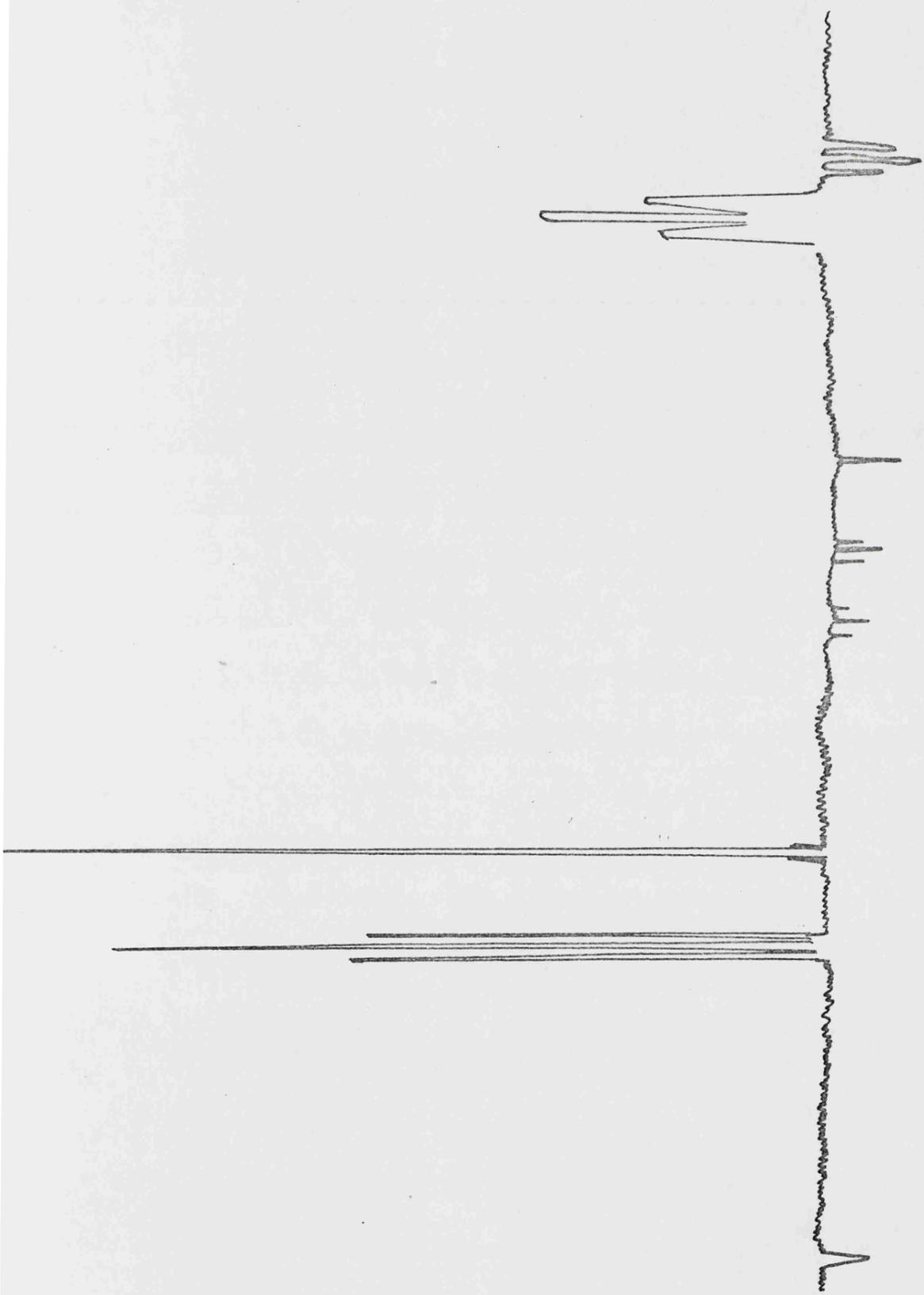
$^{19}\text{F}$  Spectrum of Pure Tungsten Chloride Pentafluoride



collected at  $-40^{\circ}$ ,  $-78^{\circ}$  and  $-180^{\circ}$  respectively. The  $-180^{\circ}$  trap contained chlorine, a little tungsten hexafluoride and impurities; chiefly silicon tetrafluoride. The  $-78^{\circ}$  trap contained mainly tungsten chloride pentafluoride contaminated with a little tungsten dichloride tetrafluoride and tungsten hexafluoride (identified by  $^{19}\text{F}$  spectroscopy). The tungsten chloride pentafluoride proved difficult to purify; further fractionation through  $-50^{\circ}$  and  $-60^{\circ}$  traps being ineffective but pumping on the mixture at  $-78^{\circ}$  for several weeks caused first the  $\text{WF}_6$  to be removed and then the  $\text{WClF}_5$ . This was a slow and rather wasteful method of obtaining pure  $\text{WClF}_5$ ; however, it did enable  $\text{WClF}_5$  to be obtained in 99% purity with  $\text{WF}_6$  as the only contaminant. The product thus obtained gave an  $^{19}\text{F}$  spectrum of the liquid at  $-30^{\circ}$  showing the expected doublet-quintet fine structure ( $J_{\text{F}_a - \text{F}_e} = 73$  cycles/sec.) in the ratio 4:1 at 182 and 126 p.p.m. downfield from arcton as external standard [see figure 2.1.2.]. Analysis of the yellow liquid was also consistent with it being tungsten chloride pentafluoride [Found: W, 58.4; Cl, 10.9.  $\text{WClF}_5$  requires W, 58.5; Cl, 11.3].

### 2.1.3. Preparation of Tungsten Dichloride Tetrafluoride

Tungsten dichloride tetrafluoride was prepared by fluorination of tungsten hexachloride in a flow system in the same manner as that described in the preparation of  $\text{WClF}_5$ . [see previous section]. The yield of  $\text{WCl}_2\text{F}_4$  obtained by this fluorination increased to an optimum when the reaction temperature was at  $50^{\circ}$  - further increase in the temperature merely causing the red and orange solids, formed initially, to distill into cooler parts of the reaction mixture before being further fluorinated. The volatile products, obtained by treating the



$^{19}\text{F}$  N.M.R. Spectra of Tungsten Dichloride Tetrafluoride

tungsten hexachloride with a slow stream of fluorine ( 500 ml./hr.) diluted with an equal volume of nitrogen, were held at  $-180^{\circ}$  and eventually fractionated under vacuum; fractions being collected at  $-30^{\circ}$ ,  $-78^{\circ}$  and  $-180^{\circ}$ . The  $-30^{\circ}$  fraction contained only  $WCl_2F_4$ ; this being identified by  $^{19}F$  spectroscopy as a 1:1 cis:trans mixture showing reasonable analytical results [Found: W, 54.9; Cl, 21.0  $WCl_2F_4$  requires W, 55.6; Cl, 21.4%]. The fraction at  $78^{\circ}$  contained mainly  $WClF_5$  contaminated with  $WCl_2F_4$  and  $WF_6$  - identified by  $^{19}F$  spectroscopy. The  $-180^{\circ}$  fraction contained chlorine and a little tungsten hexafluoride.

[Note - Samples of  $WCl_2F_4$  were purified by trap to trap distillation. The  $-30^{\circ}$  trap held pure  $WCl_2F_4$  while traps at lower temperatures held some  $WCl_2F_4$ , but this was usually contaminated with  $WClF_5$  and  $WF_6$ .]

#### 2.1.4. Attempted Preparation of $WCl_3F_3$ and $WCl_4F_2$ .

Unsuccessful attempts were made to prepare tungsten trichloride trifluoride and tungsten tetrachloride difluoride by fluorination of tungsten hexachloride in a flow system. Tungsten trichloride trifluoride would distil under vacuum with some decomposition to tungsten hexafluoride and tungsten hexachloride. It had been observed during fluorination of tungsten hexachloride that initially yellow, and subsequently orange, droplets were deposited a small distance along the tube from the reacting  $WCl_6$ . These did not vapourise at atmospheric pressure but remained until further fluorinated. In order to condense these products apparatus [see fig. 2.1.3.] was devised. However, by this method, fluorination was inefficient, as the path of the fluorine was not directly over the tungsten hexa-

Figure 2.1.3.

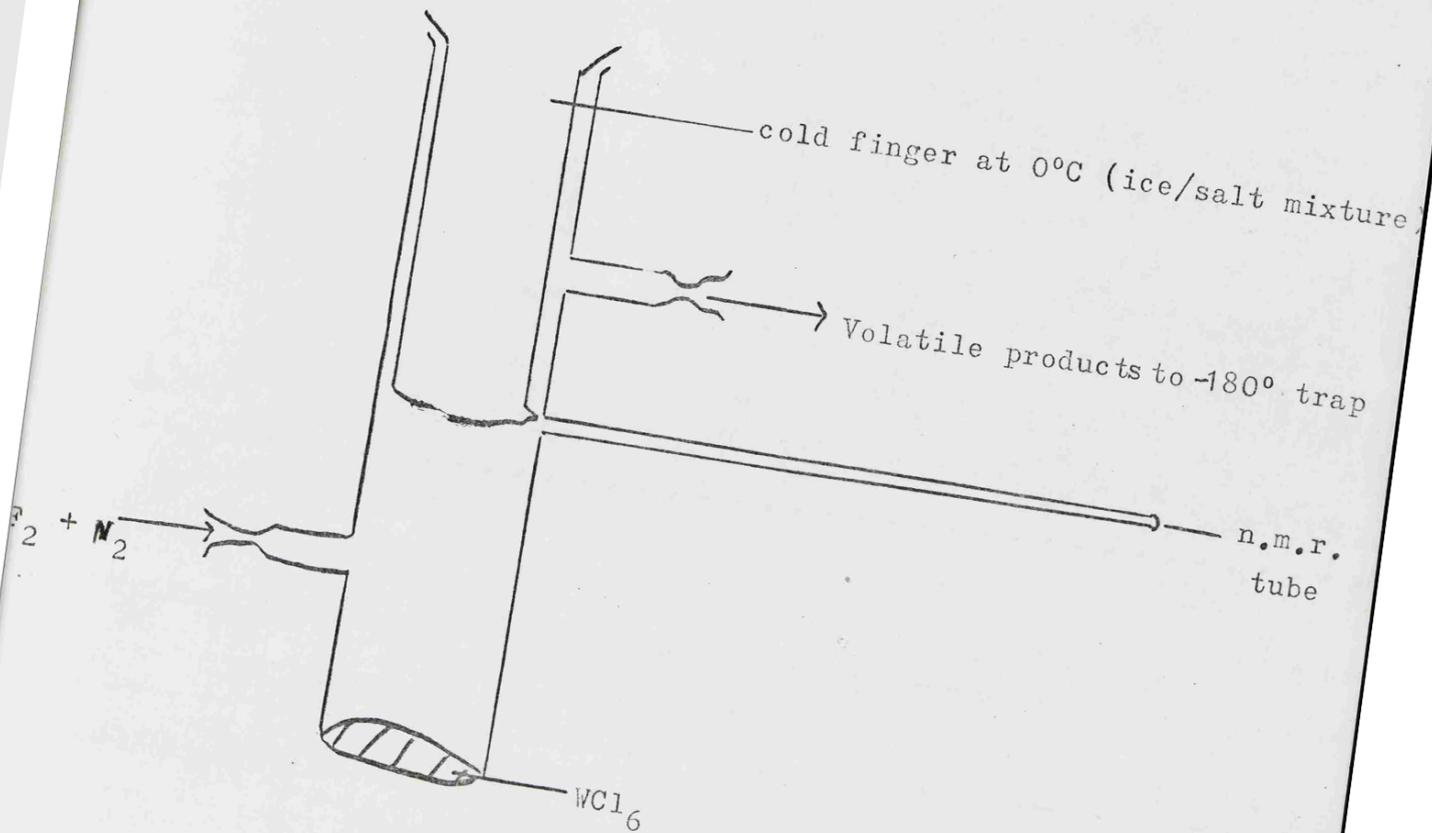
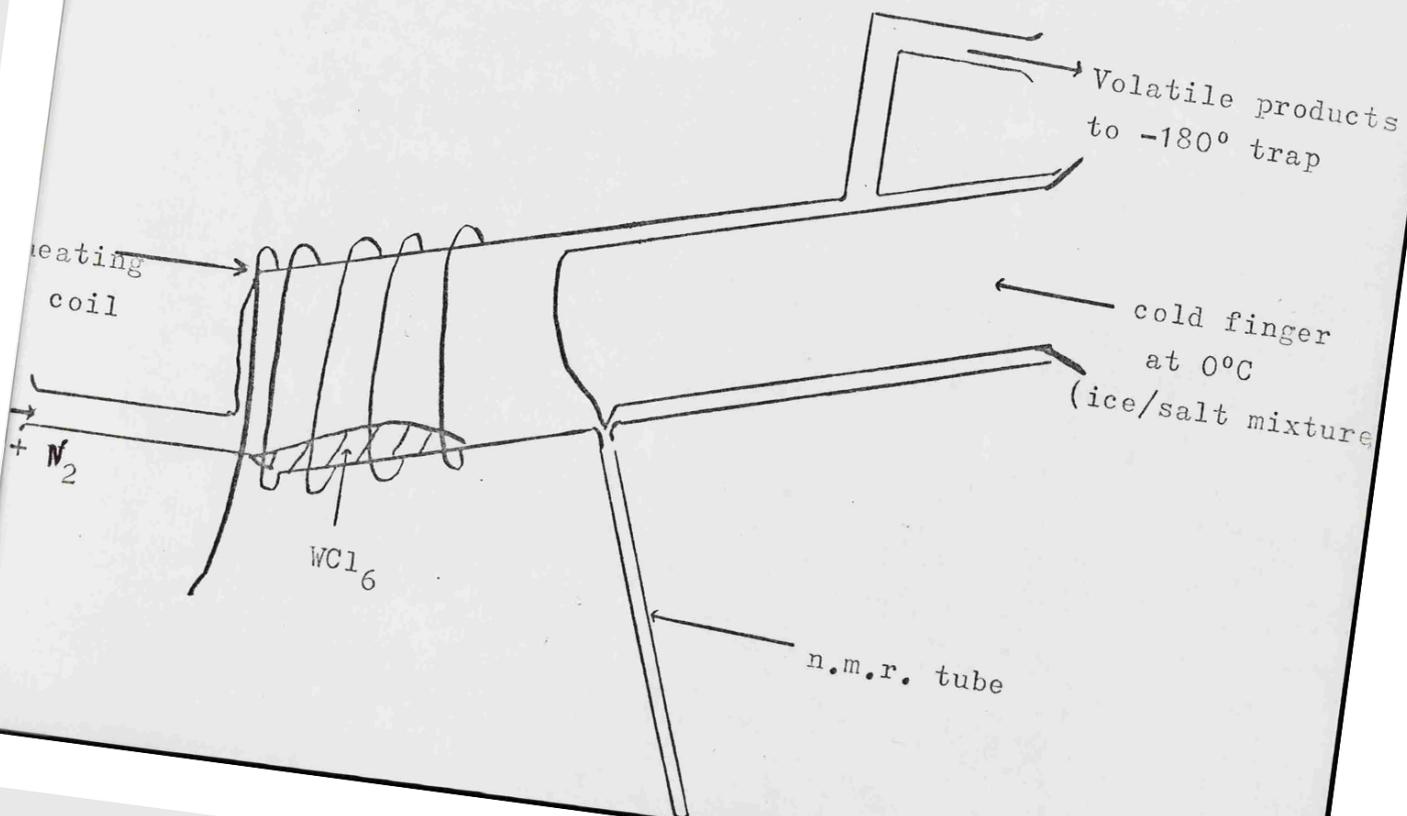


Figure 2.1.4.



chloride: some yellow solid did condense on the cold trap but as this could not be removed until after the termination of the fluorine flow, further reaction resulted.

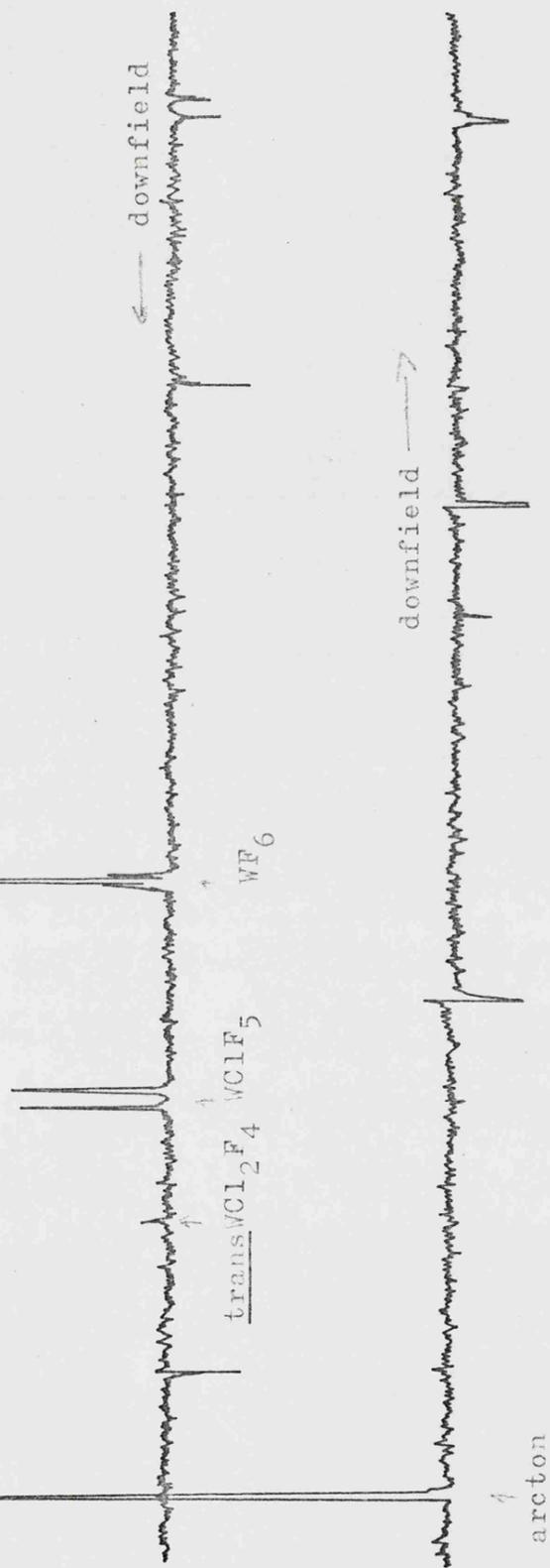
A modification [see fig. 2.1.4.] was made; the tungsten hexachloride being heated to  $120^{\circ}$  and the flow of nitrogen increased, to give the ratio  $F_2:N_2 = 1:3$ , so as to reduce the extent of fluorination and speed up the removal of the volatile products. A pale yellow solid condensed on the  $-20^{\circ}$  cold finger and when this was in sufficient quantity fluorination was stopped: the cold finger being slowly allowed to warm up until the yellow liquid melted and ran into an n.m.r. tube. The  $^{19}F$  spectrum of this liquid showed peaks attributed to tungsten dichloride tetrafluoride and tungsten chloride pentafluoride but none due to tungsten trichloride trifluoride or tungsten tetrachloride difluoride. The same result was obtained with the cold finger at  $0^{\circ}C$ .

#### 2.1.5. Preparation of Tungsten(VI) Chloride Fluorides by Chlorination of Tungsten Pentafluoride

Excess chlorine-dried by bubbling through concentrated sulphuric acid and passing through a column packed with phosphorus pentoxide - was distilled on to tungsten pentafluoride (made by reducing tungsten hexafluoride on a tungsten wire<sup>69</sup>). Arcton was added to act as a solvent. The solution was held at  $-30^{\circ}$  for twenty-four hours with a resulting slow colour change from yellow, to deep red and eventually to dark brown. Chlorine was distilled from the reaction mixture held at  $-78^{\circ}$  before products, volatile at  $-50^{\circ}$ , were distilled into an n.m.r. tube. The less volatile fraction was decanted into an n.m.r. tube attached to the apparatus.

The more volatile fraction was a pale yellow solution

$^{19}\text{F}$  Spectrum of Least Volatile Product of Reaction of  $\text{WF}_5$  and  $\text{Cl}_2$  in Arcton



which gave an  $^{19}\text{F}$  n.m.r. spectrum showing signals which were attributed to tungsten hexafluoride, tungsten chloride pentafluoride and arcton. The less volatile fraction was a yellow/orange solution heavy with yellow solid. It gave an  $^{19}\text{F}$  n.m.r. spectrum showing signals attributable to tungsten hexafluoride, tungsten chloride pentafluoride and arcton and a very weak singlet due to trans tungsten dichloride tetrafluoride [see fig. 2.1.5.].

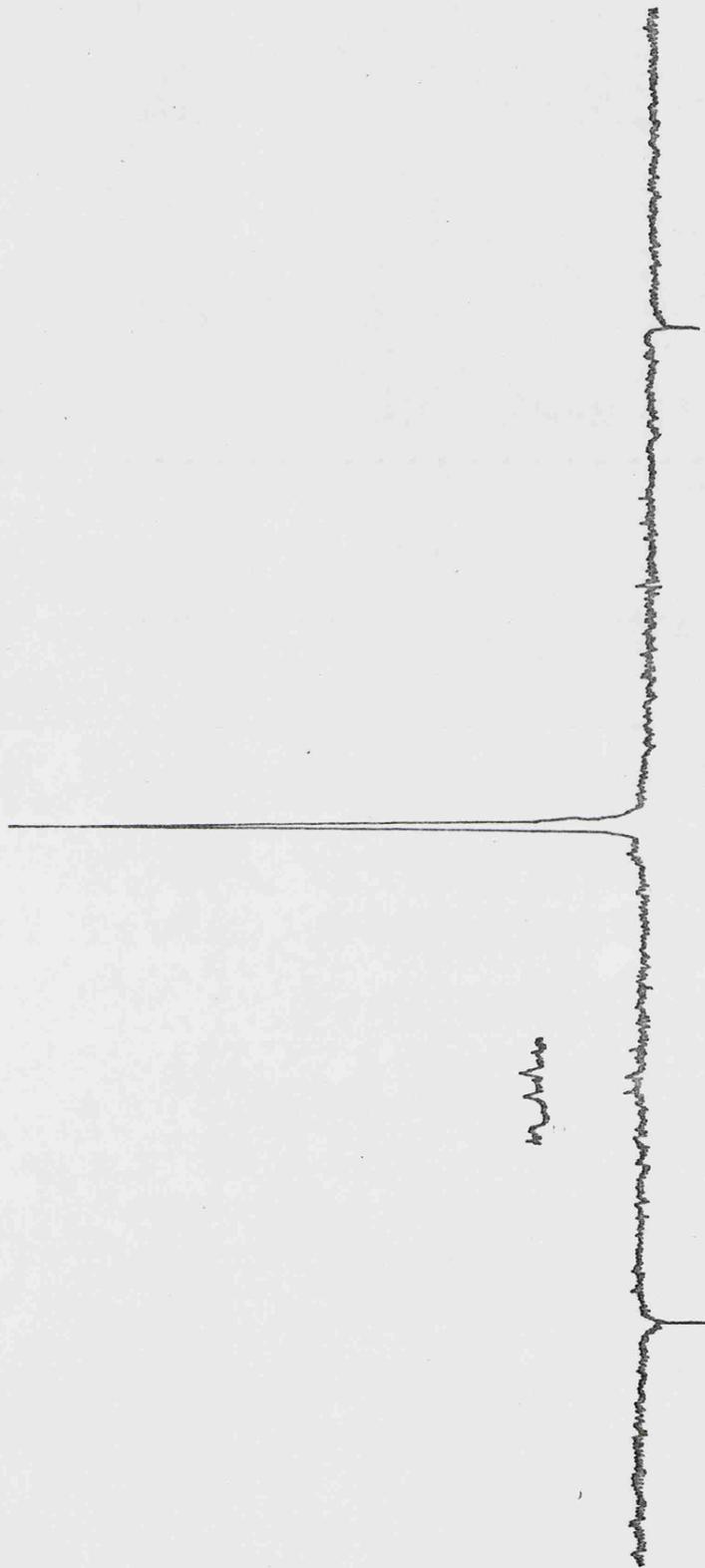
#### 2.1.6. Attempted Preparation of Tungsten(VI) Bromide Fluorides by Bromination of Tungsten Pentafluoride

The bromine was purified by several distillations and dried by standing over phosphorus pentoxide for a day before distilling into the reaction vessel. The tungsten pentafluoride was impure and was made by reducing tungsten pentafluoride on a hot tungsten wire and pumping off any excess tungsten hexafluoride remaining.<sup>69</sup> It was yellow/brown in colour presumably because the tungsten pentafluoride was contaminated with tungsten tetrafluoride.

A small quantity of bromine was distilled into the tungsten pentafluoride and arcton was added as a solvent. The reaction mixture was held at  $-50^{\circ}$  for twenty-four hours. The brown solution had not been decolourised but a volatile fraction was distilled at  $-50^{\circ}$  into an n.m.r. tube and the remaining liquid was decanted into an n.m.r. tube, attached to the reaction vessel - so as to avoid decomposition of the reaction products. The  $^{19}\text{F}$  spectrum of the more volatile fraction, a pale yellow solution, at  $-20^{\circ}$  showed signals attributed to arcton and tungsten hexafluoride, while that of the less volatile fraction, a deep red/brown solution containing brown/black solid, showed singlets due to tungsten

Figure 2.1.6.

$^{19}\text{F}$  Spectrum of Least Volatile Fraction of Reaction of  $\text{WF}_5$  and  $\text{Br}_2$



hexafluoride and arcton and a very weak doublet  $18 \pm 1$  p.p.m. downfield from tungsten hexafluoride with a coupling constant of  $67 \pm 1$  cycles/sec. This very weak doublet could be attributable to the equatorial fluorine atoms in tungsten bromide pentafluoride [see fig. 2.1.6.].

## 2.2. Attempted Physical Separation of the Tungsten Dichloride Tetrafluoride Isomers

Tungsten dichloride tetrafluoride was distilled through a  $-30^{\circ}\text{C}$  trap to which two n.m.r. tubes were attached. When sufficient of the compound had been distilled to fill both tubes to a level great enough to enable an  $^{19}\text{F}$  spectrum to be obtained, the system was sealed off under vacuum at  $-30^{\circ}$ . The solution was decanted into one tube and the temperature slowly lowered (to  $-33^{\circ}$ ) until half the solution had solidified. The liquid fraction was decanted into the other n.m.r. tube and both tubes were then sealed off at  $-30^{\circ}$ . Difficulty was encountered in decanting the liquid because it proved very difficult to pour it out of the narrow confines of an n.m.r. tube.

The  $^{19}\text{F}$  spectrum at  $-20^{\circ}$  of both these fractions still showed the cis:trans isomers in the usual 1:1 ratio.

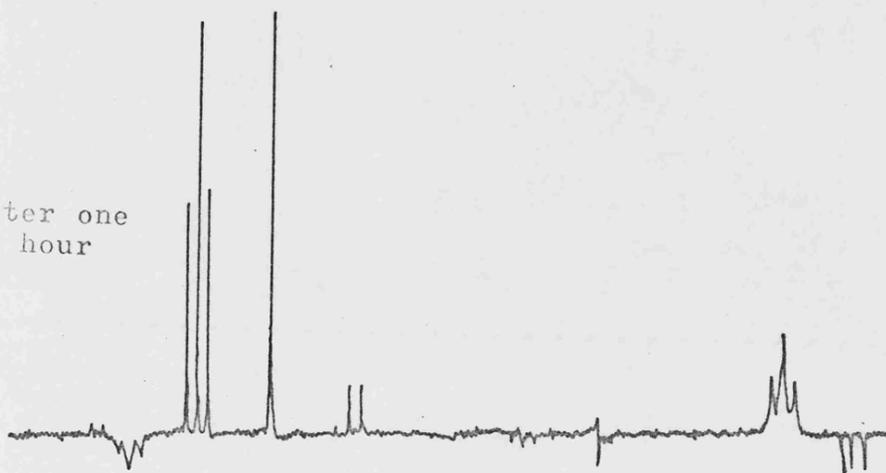
A similar experiment in which solid  $\text{WCl}_2\text{F}_4$  was allowed to slowly warm till half the sample was a liquid and then decanting the liquid, still gave an  $^{19}\text{F}$  spectrum at  $-20^{\circ}$  of both the samples which showed the cis:trans isomers in a 1:1 ratio.

## 2.3. Thermal Decomposition of Tungsten Dichloride Tetrafluoride

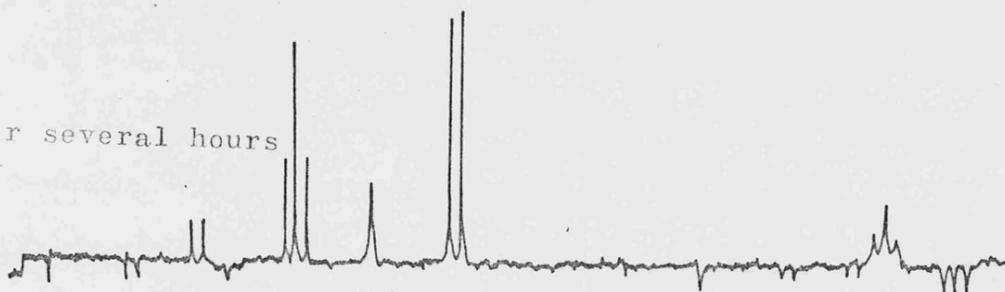
Tungsten dichloride tetrafluoride can be stored for long periods at  $-30^{\circ}$  but is unstable at room temperature, slowly decomposing to give the other chloride fluorides. The decom-

$^{19}\text{F}$  Spectrum of Tungsten Dichloride Tetrafluoride  
Decomposing at Room Temperature.

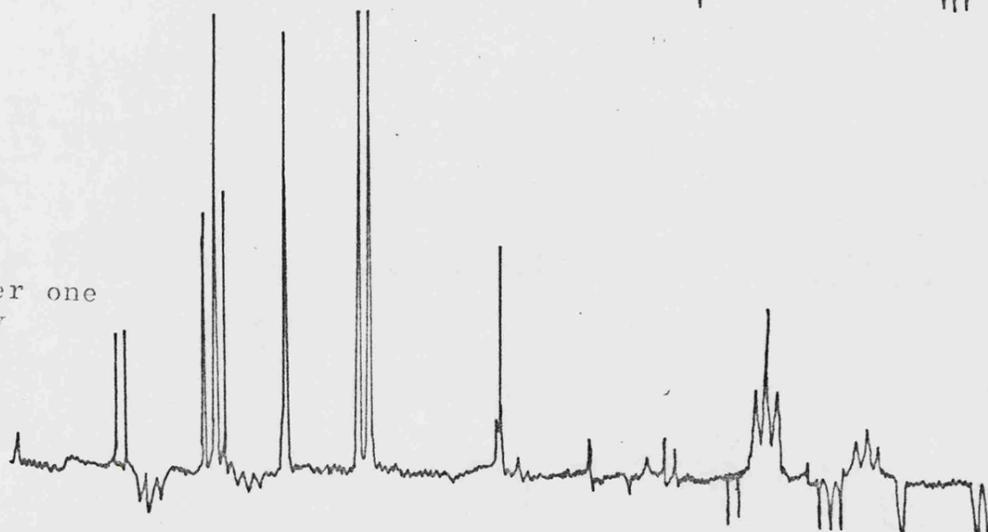
After one  
hour



After several hours



After one  
day



position may be followed by  $^{19}\text{F}$  n.m.r. spectroscopy [see fig. 2.3.1.]. After several hours at room temperature the signals in the  $^{19}\text{F}$  spectrum due to cis and trans tungsten dichloride tetrafluoride had decreased in intensity and a series of new peaks was observed. A doublet and quintet to high field of the dichloride tetrafluoride were identified as tungsten chloride pentafluoride,  $\text{WClF}_5$ . A doublet and triplet were observed downfield from the dichloride tetrafluoride signals and were attributed to mer tungsten trichloride trifluoride,  $\text{WCl}_3\text{F}_3$ . Two single lines were also observed and were attributed to tungsten hexafluoride and fac tungsten trichloride trifluoride. Further decomposition, over a period of a day, produced two new signals which were postulated to be cis and trans tungsten tetrachloride difluoride. Finally, a very weak signal was observed which was assigned to tungsten pentachloride fluoride,  $\text{WCl}_5\text{F}$ . After two days only a trace of the dichloride tetrafluoride remained ( $\sim 8\%$ ), the principal components being tungsten hexafluoride and solid tungsten hexachloride and tungsten pentachloride fluoride.

Tungsten dichloride tetrafluoride decomposed rapidly when heated to  $100^\circ\text{C}$ . After thirty minutes at this temperature the decomposition of the sample, followed by  $^{19}\text{F}$  spectroscopy, showed large signals, upfield of those of the dichloride tetrafluoride and attributed to tungsten chloride pentafluoride. A corresponding decline in the proportion of the dichloride tetrafluoride indicated that the proportions of  $\text{WCl}_2\text{F}_4$  and  $\text{WClF}_5$ , now in the sample, were approximately equal - the solution had deepened from orange to deep red and contained red and purple solids. After allowing the solution to decompose for several hours at  $100^\circ$  less than 1% of the dichloride tetrafluoride remained; the ratio of tungsten chloride pentafluoride

to hexafluoride was approximately 1:1, no further volatile products were observed. The solid precipitate was red and deep purple (having the appearance of  $WCl_5F$  and  $WCl_6$ ), the purple being predominant. After allowing this solution to stand at room temperature for five weeks, the  $^{19}F$  spectrum of the volatile products showed them to be predominantly tungsten hexafluoride but a little tungsten chloride pentafluoride was still present.

## 2.4. Exchange Reactions

### 2.4.1. Reaction with $PCl_3$

The reaction between phosphorus trichloride, purified by trap to trap distillation, with excess  $WCl_2F_4$  has proved slow (in comparison with reaction of tungsten(VI) chloride fluorides and phosphorus oxychlorides [see following sections]). The mixture deepened in colour after four hours at room temperature and gave an  $^{19}F$  spectrum which indicated the presence of  $WF_6$ ,  $WClF_5$  and cis and trans  $WCl_2F_4$ . On standing for several days at room temperature a deep purple/black crystalline solid, having the appearance of  $WCl_6$ , precipitated. The  $^{19}F$  spectrum of the volatile solution above this solid showed signals which were attributed to  $WF_6$ ,  $WClF_5$  and  $PF_3$ .

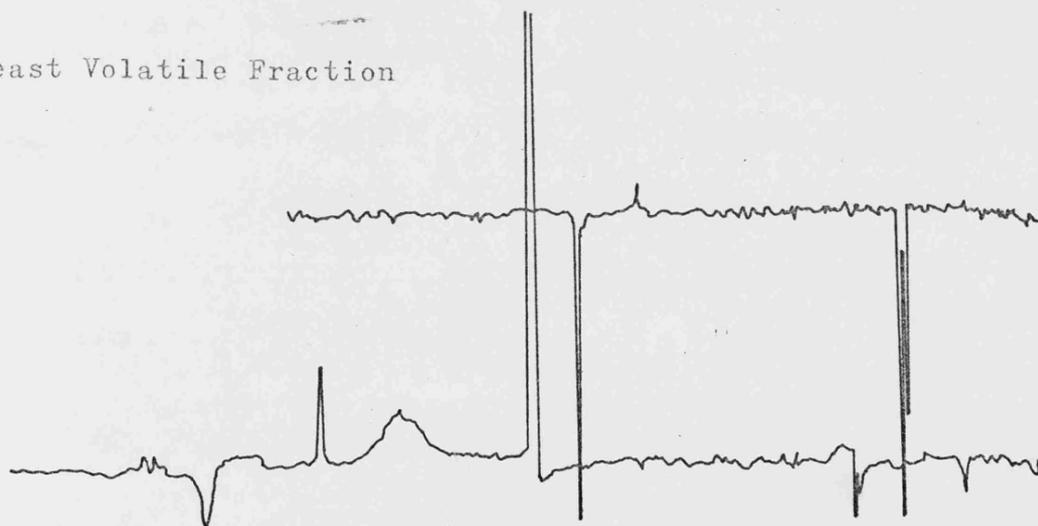
No reaction occurred when a mixture of tungsten hexafluoride and phosphorus trichloride, purified by trap to trap distillation, were allowed to stand at room temperature for a week. The colour of the solution deepened from colourless to a very pale yellow, but the  $^{19}F$  spectrum of the sample still showed only the singlet attributed to  $WF_6$ .

Figure 2.4.1.

$^{19}\text{F}$  Spectrum of Reaction of  $\text{WCl}_2\text{F}_4$  and  $\text{POCl}_3$  After  
Half an Hour at Room Temperature.



1 Least Volatile Fraction



2 Most Volatile Fraction

Table 2.4.1.

$^{19}\text{F}$  Spectrum Peaks obtained, by Heating or Prolonged Standing at Room Temperature a Reaction Mixture of  $\text{POCl}_3$  and  $\text{WCl}_2\text{F}_4$  or  $\text{WClF}_5$ .

Type of Peak	$\delta_{(\text{F})}^*$ (in p.p.m.)	$J_{(\text{F}-\text{F})}^\dagger$	$J_{\text{W}-\text{F}}^\dagger$
singlet	+65		
doublet	+81	82	
singlet	+91		
large singlet	+112		63
broad singlet	+130		

\* Chemical shifts were measured with respect to  $\text{WF}_6$  as internal standard, the error in these values being dependent on the concentration of  $\text{POCl}_3$  and of the order of  $\pm 5$  p.p.m.

† Coupling constants were estimated to  $\pm 3$  MHz.

2.4.2. Reactions of  $WCl_2F_4$ ,  $WClF_5$  and  $WF_6$  with Phosphorus  
Oxychloride

Phosphorus oxychloride, purified by trap to trap distillation was distilled into excess tungsten dichloride tetrafluoride and the mixture was allowed to warm to room temperature; a resulting colour change from orange/red to deep red occurring. After half an hour the volatile products were distilled into n.m.r. tubes; the resulting  $^{19}F$  spectrum of the more volatile spectrum showing peaks due to mer and fac  $WCl_3F_3$ , cis and trans  $WCl_2F_4$ ,  $WF_6$ ,  $POF_3$  and  $POClF_2$  and of the less volatile fraction showing signals due to cis and trans  $WCl_4F_2$ , mer and fac  $WCl_3F_3$  and cis and trans  $WCl_2F_4$  [see fig. 2.4.1.]. When all volatile components had been removed a deep purple/black crystalline solid, with the appearance of tungsten hexachloride, and traces of red and orange solids, probably  $WCl_5F$  and  $WCl_4F_4$ , remained. The lower chloride fluorides,  $WCl_4F_2$  and  $WCl_3F_3$  were obtained in better yield by decanting the least volatile fraction - as distillation resulted in decomposition of the  $WCl_4F_2$  and  $WCl_3F_3$  into other chloride fluorides, but mainly into  $WCl_6$  and  $WF_6$ . With all  $^{19}F$  spectrum observed, in the region normally associated with the doublet of  $WClF_5$  there was a very broad peak; all other peaks being sharp and distinct.

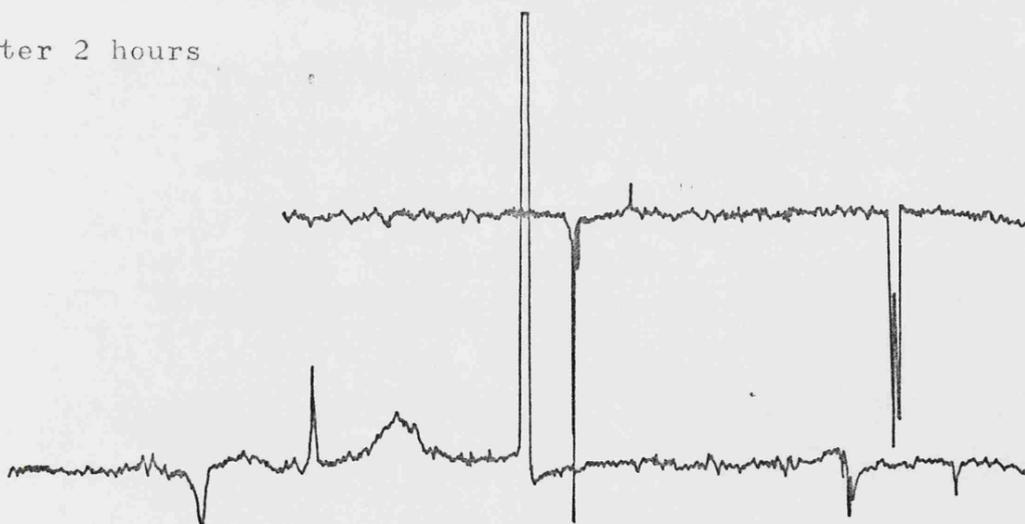
On adding excess  $WClF_5$  to  $POCl_3$  and warming the reaction mixture to room temperature, the  $^{19}F$  spectrum [see fig. 2.4.2.] showed a very broad peak in the region usually associated with the doublet of  $WClF_5$ . On allowing the mixture to stand at room temperature, it deepened in colour; the  $^{19}F$  spectrum after a further hour showing that this large broad peak had been appreciably reduced in size and that signals due to  $WF_6$ ,

Figure 2.4.2.

$^{19}\text{F}$  Spectrum Showing Reaction of  $\text{WCl}_5$  and  $\text{POCl}_3$   
at Room Temperature.



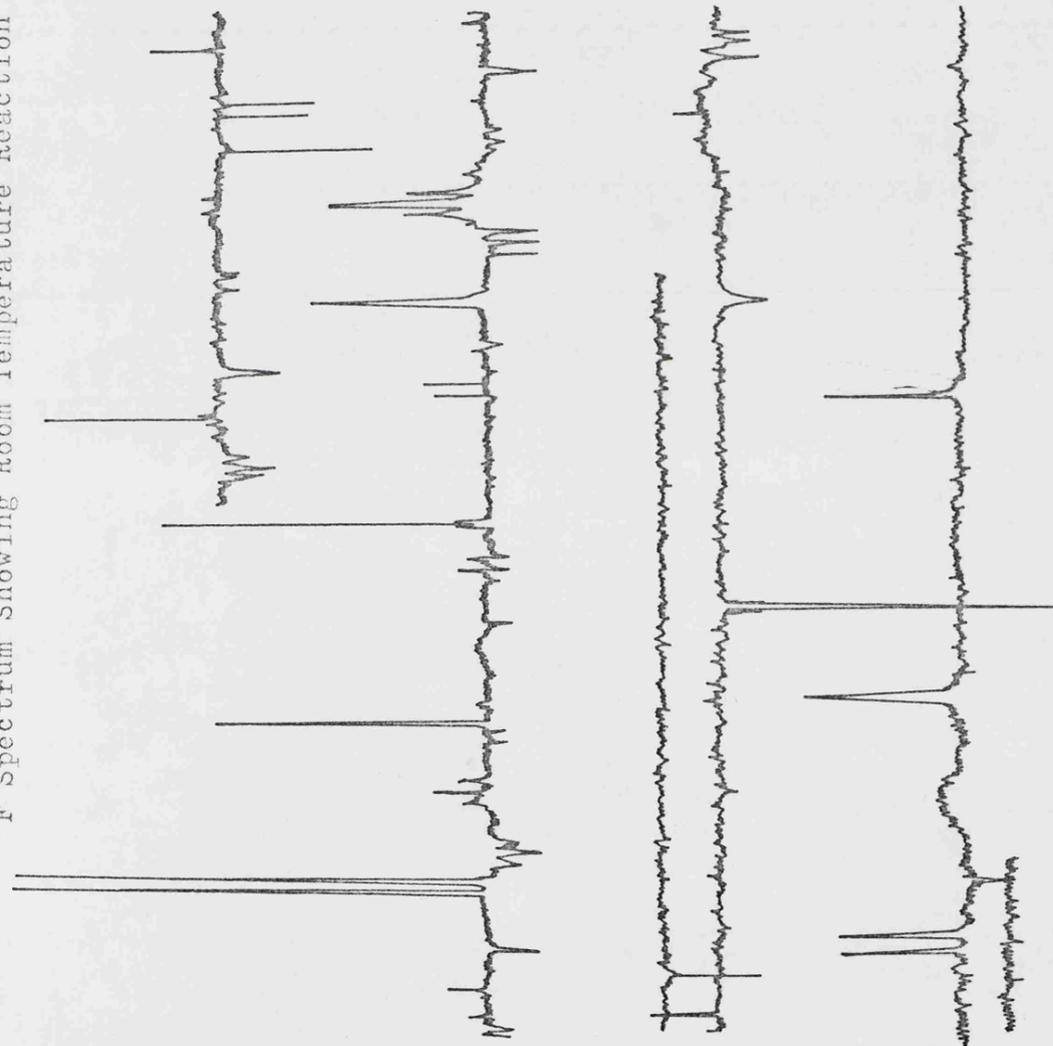
2 After 2 hours



1 After 1 hour

Figure 2.4.3.

$^{19}\text{F}$  Spectrum Showing Room Temperature Reaction of  $\text{POCl}_3$  and  $\text{WClF}_5$

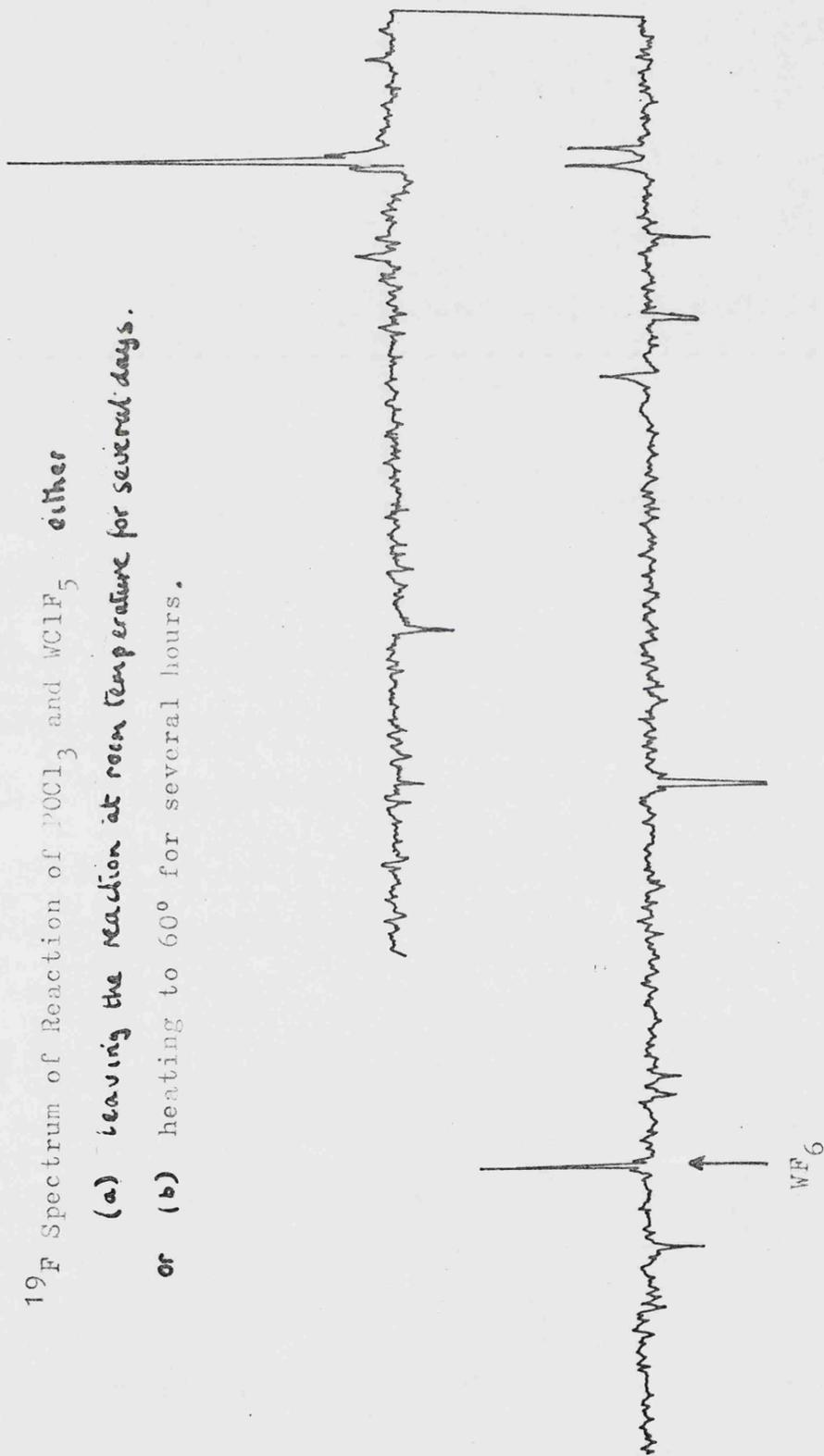


After 4 hours

3 After 3 hours

Figure 2.4.4.

$^{19}\text{F}$  Spectrum of Reaction of  $\text{POCl}_3$  and  $\text{WClF}_5$  either  
(a) leaving the reaction at room temperature for several days.  
or (b) heating to  $60^\circ$  for several hours.



cis and trans  $WCl_2F_4$ , mer and fac  $WCl_3F_3$  and cis and trans  $WCl_4F_2$  had begun to appear. After standing for another hour at room temperature the broad peak, in the region expected for the doublet of  $WClF_5$ , was no longer distinguishable in the  $^{19}F$  spectrum, further halogen exchange having occurred: the mer and fac  $WCl_3F_3$  and the cis and trans  $WCl_4F_2$  signals increasing at the expense of the cis and trans  $WCl_2F_4$  [see fig. 2.4.3.].

On allowing excess of either  $WCl_2F_4$  or  $WClF_5$  to react with  $POCl_3$  for several days at room temperature the only  $^{19}F$  spectrum peak attributed to the halides of tungsten(VI) that remained was that of the sharp singlet of  $WF_6$ , quantities of purple/black solid,  $WCl_6$  being precipitated. With the decline in the tungsten chloride fluoride peaks a sharp singlet,  $\sim +112$  p.p.m. upfield from  $WF_6$ , and a weak singlet appeared in the  $^{19}F$  spectrum. On allowing the reaction mixture to stand for a further few days at room temperature or on warming it to  $60^\circ$  for an hour, a doublet and singlet also appear in the spectrum [see Table 2.4.1. and fig. 2.4.4.].

On treating  $POCl_3$  with  $WF_6$  the solution turned pale yellow after about six hours at room temperature - its  $^{19}F$  spectrum showed a large singlet due to  $WF_6$  and a very small singlet, possibly  $WOF_4$ , 95 p.p.m. upfield from  $WF_6$ . On standing at room temperature for a further week the solution deepened to an orange colour, but no other signals in the  $^{19}F$  spectrum of the reaction solution were observed.

### 2.4.3. Reaction with $MePOCl_2$

The  $MePOCl_2$  was purified by distilling several times until the boiling and melting points were those given in the

Figure 2.4.5.

$^{19}\text{F}$  Spectrum of Room Temperature Reaction of  $\text{WCl}_2\text{F}_4$  and  $\text{MePOCl}_2$



literature [M.P. =  $40^{\circ}$  and b.p. =  $168^{\circ}$ ]. On treating excess  $WCl_2F_4$  with  $MePOCl_2$  and warming to room temperature the solution deepened from orange to deep red. On leaving to stand at room temperature for an hour the  $^{19}F$  spectrum showed signals due to mer and fac  $WCl_3F_3$ , cis and trans  $WCl_2F_4$ ,  $WClF_5$  and  $WF_6$ . Two further signals, a small singlet at 66 p.p.m. upfield from  $WF_6$  and a larger singlet at 105 p.p.m. upfield from  $WF_6$ , were observed [see fig. 2.4.5.]. After standing for a further hour red and deep purple/black crystalline solids precipitated. An  $^{19}F$  spectrum of this solution still showed peaks due to cis and trans  $WCl_2F_4$ ,  $WClF_5$  and  $WF_6$  but they were all very broad presumably due to the quantity of solid material also present.

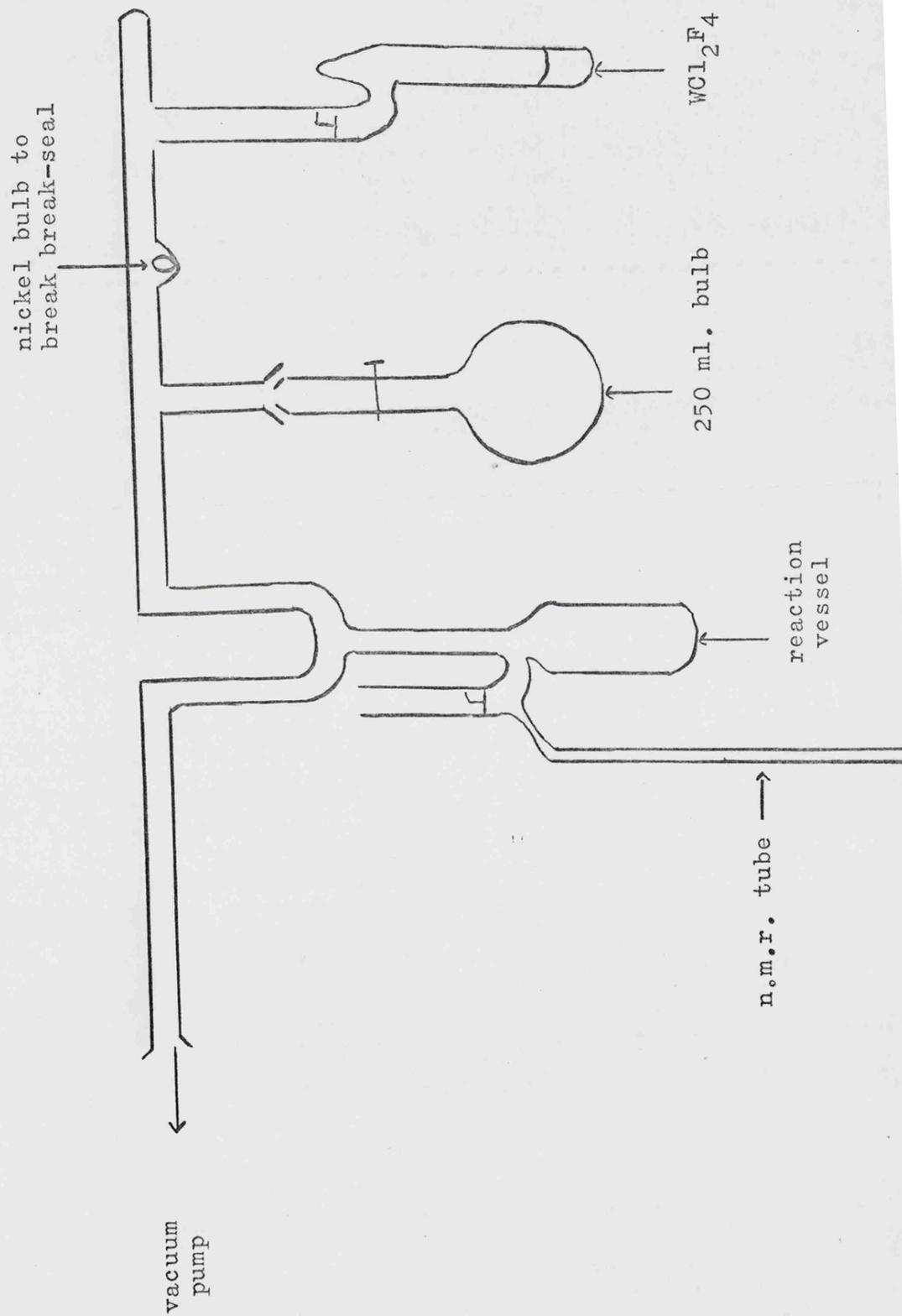
#### 2.4.4. Reaction with $PSCl_3$

On adding  $PSCl_3$  - dried over  $P_2O_5$  and distilled twice to remove all traces of moisture - to excess of  $WCl_2F_4$  and leaving to stand at room temperature for an hour, very little reaction occurred. The  $^{19}F$  spectrum showed only peaks due to cis and trans  $WCl_2F_4$  and weaker peaks due to mer and fac  $WCl_3F_3$  and  $WClF_5$ . On leaving overnight at room temperature, the  $^{19}F$  spectrum showed an increase in  $WClF_5$  [sharp doublet and quintet not broadened as in the reaction of  $POCl_3$ ] and mer and fac  $WCl_3F_3$  peaks but the solution was predominantly still cis and trans  $WCl_2F_4$ . On warming to  $60^{\circ}$  for one hour further, decomposition occurred, a deep purple/black crystalline solid being precipitated.

#### 2.4.5. Reaction with $P_4O_{10}$

Preliminary experiments showed that a gas with a high vapour pressure was one of the products resulting from the

Figure 2.4.4.5.

Reaction of  $P_2O_5$  and  $WCl_2F_4$ 

room temperature reaction between excess  $\text{WCl}_2\text{F}_4$  and  $\text{P}_2\text{O}_5$ . To collect this gas a 250 ml. bulb was incorporated into the apparatus [see fig. 2.4.5.]. The  $\text{WCl}_2\text{F}_4$  was distilled into the reaction vessel containing  $\text{P}_2\text{O}_5$  which had been left under a dynamic vacuum for a day to ensure the absence of any traces of moisture and the solution was left at room temperature for an hour. The mixture was then cooled to  $-78^\circ$  and any volatile products at this temperature distilled into the 250 ml. bulb held at  $-196^\circ\text{C}$ .

The  $-196^\circ$  trap contained a white solid, subliming to a colourless gas, part of which was distilled into an n.m.r. tube containing arcton. The  $^{19}\text{F}$  spectrum of this solution showed signals due to  $\text{WF}_6$  and arcton and a singlet +95 p.p.m. upfield from  $\text{WF}_6$  which was believed to be  $\text{WOF}_4$ . Two series of peaks upfield of arcton were also observed; a series of seven lines 159 p.p.m. upfield of arcton and a sharp singlet + 166 p.p.m. from arcton. These signals are in the region normally associated with silicon-fluorine compounds [ $\text{SiF}_4$  is reported to be a singlet 160<sup>128</sup> or 164 p.p.m.<sup>129</sup> upfield from arcton], and may well have resulted from attack of the glass by any traces of moisture present, evolving HF. No signals in the region associated with  $\text{POF}_3$  or  $\text{PF}_5$  were observed by  $^{19}\text{F}$  spectroscopy.

The  $^{19}\text{F}$  spectrum of the reactants undistilled at  $-78^\circ$  showed signals due to cis and trans  $\text{WCl}_2\text{F}_4$ ,  $\text{WClF}_5$  and  $\text{WF}_6$ . On standing overnight at room temperature, orange, red and deep purple/black crystalline products, having the appearance of respectively,  $\text{WCl}_4\text{F}_2$ ,  $\text{WCl}_5\text{F}$  and  $\text{WCl}_6$ , were precipitated from this fraction.

2.4.6. Reaction with  $\text{SO}_2$ 

Sulphur dioxide is reported to be a good solvent for  $\text{WF}_6$ .<sup>75</sup>  $\text{SO}_2$ , dried by passing it through a column packed with  $\text{P}_2\text{O}_5$ , was distilled onto tungsten dichloride tetrafluoride. On leaving the mixture at room temperature for two hours, or heating to  $40^\circ$  for half an hour, the  $^{19}\text{F}$  spectrum of the solution [see fig. 2.4.6.] showed strong signals due to cis and trans  $\text{WCl}_2\text{F}_4$  and signals due to  $\text{WClF}_5$  and  $\text{WF}_6$  (resulting presumably from decomposition of  $\text{WCl}_2\text{F}_4$  rather than from reaction with  $\text{SO}_2$ ) and a broad singlet  $\sim +100$  p.p.m. upfield of  $\text{WF}_6$ . The  $^{19}\text{F}$  spectrum of  $\text{WOF}_4$  gives a signal  $+91$  p.p.m. upfield of  $\text{WF}_6$ , hence this singlet at  $+100$  p.p.m. is unlikely to be  $\text{WOF}_4$ . The region of the  $^{19}\text{F}$  spectrum in which this singlet was found suggests that it may be an oxide chloride fluoride or an oxide fluoride of tungsten(VI) but no separation or characterisation of the compound was attempted.

2.4.7. Reaction with  $\text{BCl}_3$ 

Boron trichloride was dried by passing over  $\text{P}_2\text{O}_5$ . On adding  $\text{BCl}_3$  to excess  $\text{WCl}_2\text{F}_4$  and allowing the reactants to warm to room temperature, an immediate and vigorous reaction occurred, at approximately  $-30^\circ\text{C}$ ; orange, red and purple solids being precipitated. The  $^{19}\text{F}$  spectrum of the volatile products showed signals due to cis and trans  $\text{WCl}_2\text{F}_4$  and  $\text{BF}_3$  and weak signals due to mer and fac  $\text{WCl}_3\text{F}_3$ . The solid products were sublimed under vacuum: the orange product at  $\sim 46^\circ$ , the red at  $\sim 55^\circ$  and the purple at  $\sim 70^\circ$ . These solids were believed to be lower chloride fluorides of tungsten(VI).

Excess boron trichloride reacted with  $\text{WCl}_2\text{F}_4$  to give a deep purple crystalline product which analysed to  $\text{WCl}_6$  [Found:

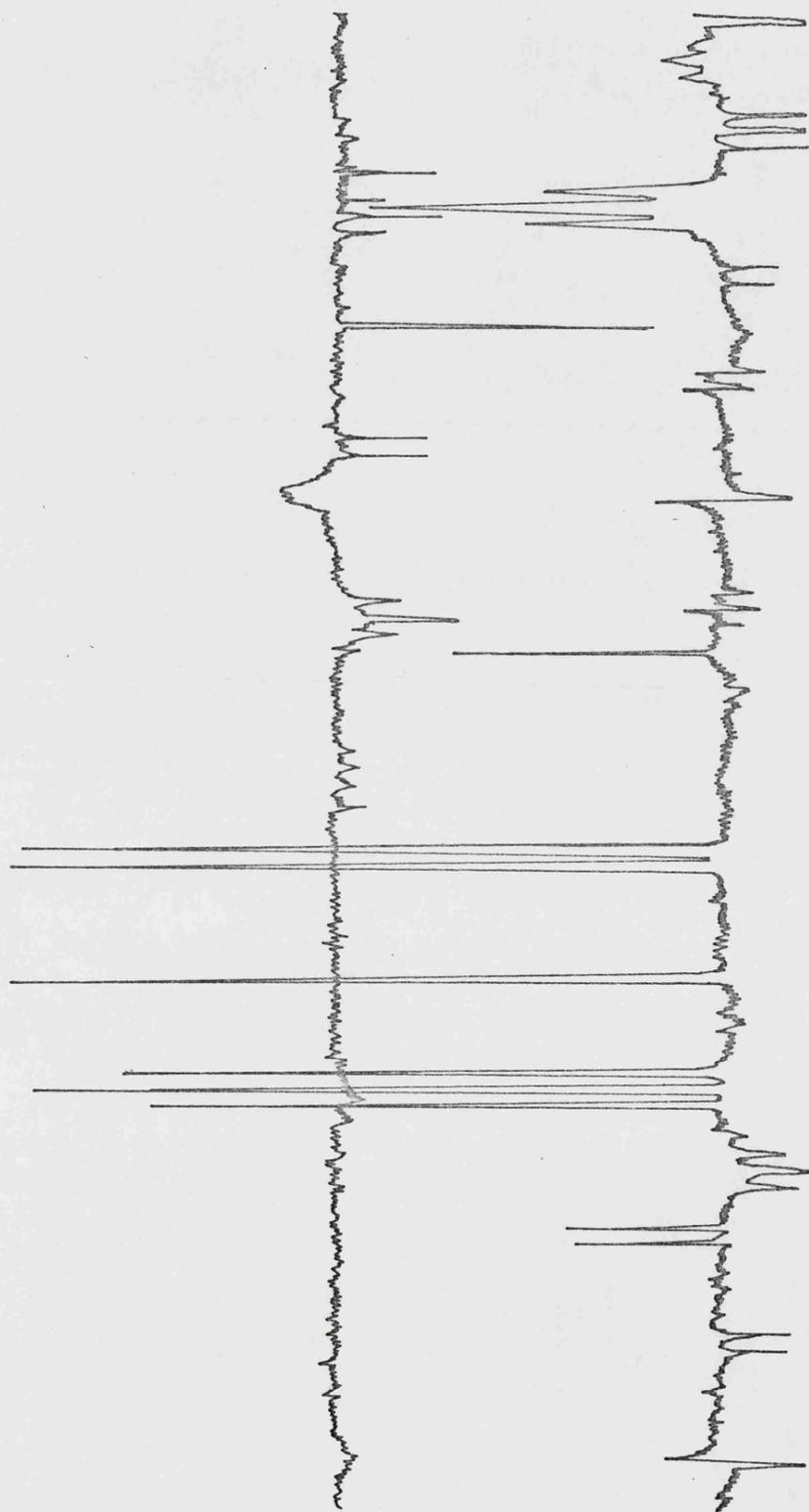


Figure 2.4.6.

$^{19}\text{F}$  Spectrum of the Reaction at  $40^\circ$  of  $\text{WCl}_2\text{F}_4$  and  $\text{SO}_2$

W, 46.5; Cl, 53.0. Calculated for  $WCl_6$  W, 46.4; Cl, 53.6%]. The volatile products gave an  $^{19}F$  spectrum which showed peaks due to  $BF_3$ ,  $BF_2Cl$  and  $BFCl_2$ .

#### 2.4.8. Reaction of Dimethyl Dichlorosilane

The dimethyl dichlorosilane was purified by trap to trap distillation. On adding excess  $WCl_2F_4$  to the  $Me_2SiCl_2$  a reaction occurred below  $0^\circ C$ , red and purple solids being precipitated. The volatile products gave an  $^{19}F$  n.m.r. spectrum indicating cis and trans  $WCl_2F_4$  (the isomers being in a 1:1 ratio) and weak signals indicating  $Me_2SiF_2$ , cis and trans  $WCl_3F_3$ . The red and purple solids had the appearance of respectively,  $WCl_5F$  and  $WCl_6$ .

### 2.5. Reaction with Mild Reducing Agents

#### 2.5.1. With Benzene

On adding excess of benzene to  $WCl_2F_4$  and warming the resulting solution to room temperature, the mixture deepened in colour from an orange/red to a very deep red. No change in the  $^{19}F$  n.m.r. spectrum was observed - signals due to cis and trans  $WCl_2F_4$  only being observed. Heating the solution to  $40^\circ$  merely caused decomposition to give the solid tungsten(VI) chloride fluorides.

#### 2.5.2. With Carbon Disulphide

On mixing  $WCl_2F_4$  with excess of redistilled carbon disulphide and warming the resulting mixture to room temperature the solution deepened to a dark red colour but the  $^{19}F$  spectrum of this solution showed only peaks due to cis and trans  $WCl_2F_4$ .

## 2.5.3. With Carbon Tetrachloride

On adding excess of carbon tetrachloride (previously dried over  $P_2O_5$ ) to  $WCl_2F_4$  and warming the resulting mixture to room temperature, no reaction appeared to occur. The  $^{19}F$  spectrum of this solution showed only peaks due to cis and trans  $WCl_2F_4$ .

2.5.4. With  $SiCl_4$ 

No reaction occurred when  $WCl_2F_4$  has dissolved in excess of redistilled  $SiCl_4$  and the resulting mixture warmed to room temperature. The  $^{19}F$  spectrum of this solution showed only signals due to cis and trans  $WCl_2F_4$ .

## 2.5.5. With Hydrogen

$WCl_2F_4$  was distilled into a bulb containing one atmosphere of hydrogen (previously dried by bubbling through concentrated  $H_2SO_4$  and passing through a column packed with  $P_2O_5$ ). On allowing to stand at room temperature for an hour the  $^{19}F$  spectrum of this mixture still showed only signals due to cis and trans  $WCl_2F_4$ . Heating the mixture to  $80^\circ C$  for half an hour, merely caused decomposition of the chloride fluoride to give red and purple crystalline products (having the appearance of  $WCl_5F$  and  $WCl_6$  respectively). An  $^{19}F$  spectrum of the volatile products showed signals due to mer and fac  $WCl_3F_3$ , cis and trans  $WCl_2F_4$ ,  $WClF_5$  and  $WF_6$ .

2.6. Reaction of  $WCl_2F_4$  with  $NO_2$ 

Nitrogen dioxide was prepared by heating lead nitrate and passing the gases evolved through a  $P_2O_5$  packed drying tube. The resulting gases were pumped under vacuum through a  $-180^\circ$  trap - to remove any  $O_2$  formed - the contents of which

Table 2.6.1.

Powder Photograph Data of Yellow Solid obtained by the  
Reaction of  $WCl_2F_4$  and  $NO_2$ .

$\sin^2 \theta$	I(obs.)
.0210	S
.0232	VS
.0290	M
.0408	VS
.0462	S
.0483	M
.0513	W
.0697	W
.0762	MW
.0793	M
.0830	W
.0910	M
.0969	W
.1021	W
.1137	M
.1237	M
.1311	S
.1482	W-M
.1594	S

were further purified by trap to trap distillation.

On reacting excess  $WCl_2F_4$  with  $NO_2$  a vigorous reaction occurred, at  $0^\circ C$ , a pale yellow solid being precipitated. The mixture was left at  $0^\circ C$  for an hour, to ensure complete reaction, before the volatile products were distilled at room temperature. The  $^{19}F$  spectrum of the volatile products showed only signals due to cis and trans  $WCl_2F_4$ . The yellow solid was pumped on for a day and a powder photograph of it was taken [see Table 2.6.1.].

On reacting excess  $NO_2$  with  $WCl_2F_4$  the same yellow solid (identified by its powder photograph) was obtained. This yellow crystalline solid did not sublime at temperatures up to  $100^\circ C$  under vacuum.

Infra-red spectra were run between  $4,000$  and  $700\text{ cm}^{-1}$  using both nujol and hexachloro 1.3 butadiene mulls but no strong bands were observed. Weak signals were seen at  $1728$ ,  $1655$  and  $1035\text{ cm}^{-1}$ .

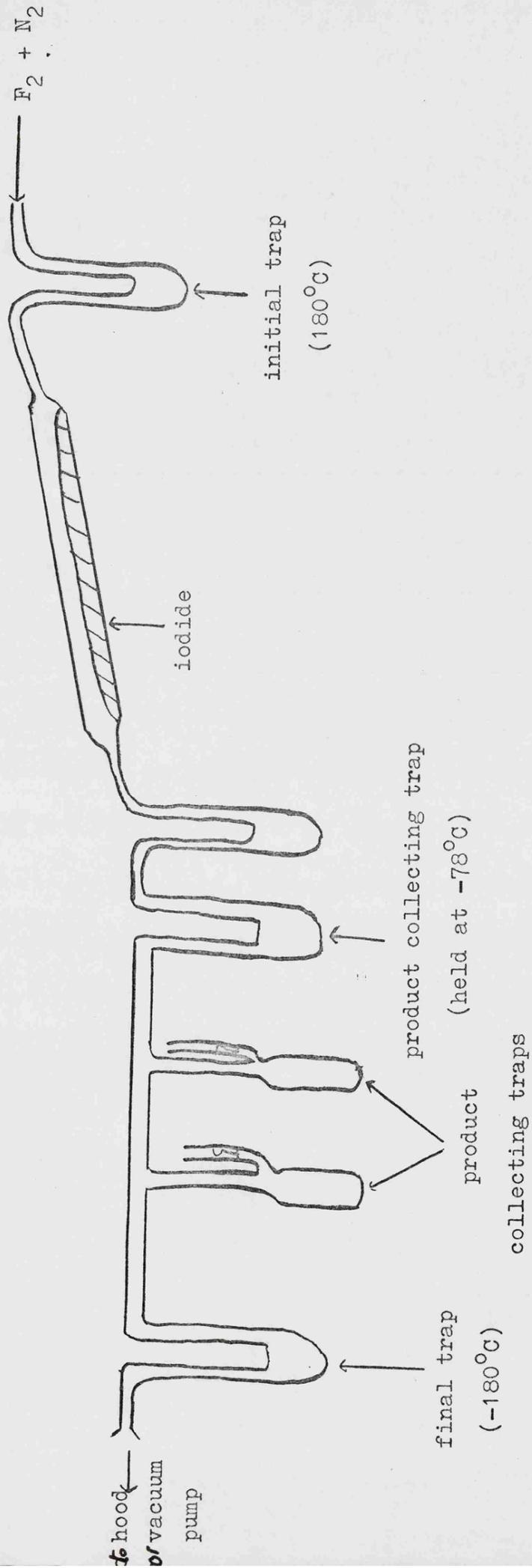
Analysis values on the yellow solid for tungsten, fluorine, chlorine and nitrogen were found to be inconsistent, the percentages of each element differing markedly for each separate sample. It had been anticipated that the compound might have been  $NO_2^+[WCl_2F_4]^-$  but it appears that the solid was a mixture. No attempts were made to find a suitable solvent for the compound.

## 2.7. Reaction with Iodine Pentafluoride

Iodine pentafluoride was prepared by fluorinating solid iodine in a flow system<sup>130</sup> [ $F_2:N_2 = 1:1$ ] along a long pyrex tube [see fig. 2.7.1.]. The volatile products were trapped out at  $-70^\circ$ ; the brown solution being warmed from time to time to remove any excess iodine which was dissolved

Figure 2.7.1.

Apparatus for Preparation of Iodine Pentafluoride



in the  $\text{IF}_5$ . The resulting colourless solution was further purified by trap to trap distillation.

$\text{WClF}_5$  was added to excess  $\text{IF}_5$  to see whether  $\text{IF}_5$  could be used as a solvent for  $\text{WClF}_5$  reactions. A vigorous reaction occurred below  $0^\circ\text{C}$ , a yellow solid being precipitated. On distilling this solution and observing its  $^{19}\text{F}$  spectrum [see fig. 2.7.2.] peaks due to  $\text{WF}_6$  and  $\text{IF}_5$  were observed. The yellow solid easily sublimed but condensed as a yellow solid in the n.m.r. tubes. It was believed that this solid was  $\text{ICl}_3$  and that the reaction proceeded:



On reacting  $\text{WCl}_6$  with excess  $\text{IF}_5$  a similar reaction occurred to that of  $\text{WClF}_5$  and  $\text{IF}_5$ ; the volatile products showing the same signals [see fig. 2.7.2.]. A yellow solid having the appearance of  $\text{ICl}_3$  was again present.

## 2.8. Attempted preparation of Salts of $\text{WClF}_5$

### 2.8.1. Reaction of KI with $\text{WClF}_5$

Analar potassium iodide was pumped under vacuum for two days to ensure complete absence of traces of moisture. Excess  $\text{WClF}_5$  was distilled onto the potassium iodide and the reactants were allowed to warm to room temperature. The solution deepened in colour from pale yellow to deep red/brown. On pumping off the volatile products, the resulting deep red solution gave an  $^{19}\text{F}$  spectrum showing only  $\text{WF}_6$ . The solid remaining was a mixture of red/brown products which sublimed at  $80^\circ$  leaving a green grey residue (possibly  $\text{WOF}_2$ ) and evolving iodine.

On reacting excess  $\text{WClF}_5$  with KI in sulphur dioxide (previously dried by passing through a tube packed with  $\text{P}_2\text{O}_5$ )

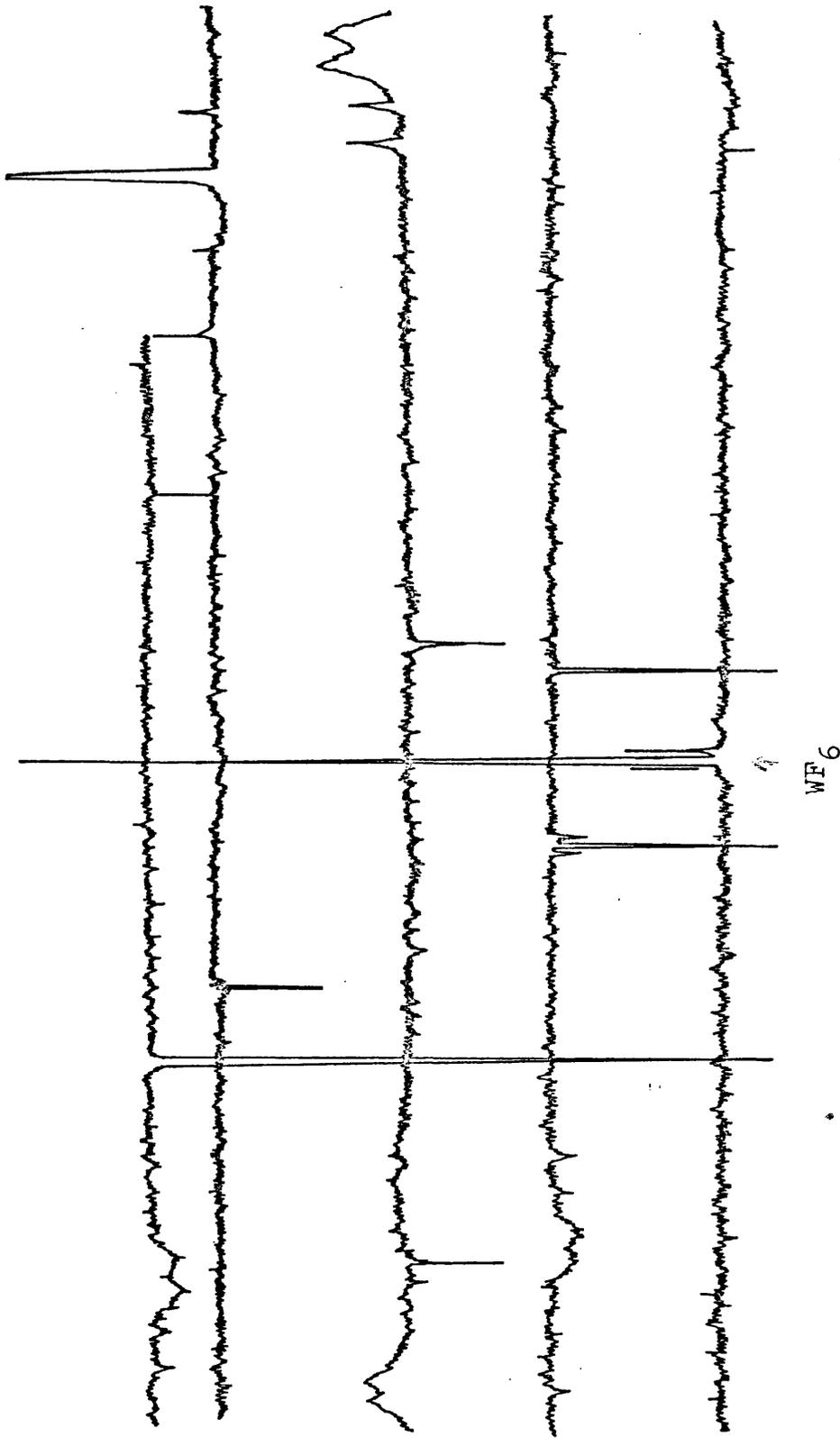


Figure 2.7.2.

$^{19}\text{F}$  Spectrum of Volatile Products of the Room Temperature Reaction of  
excess  $\text{IF}_5$  and  $\text{WClF}_5$ .

orange/brown solids were obtained which, on pumping at  $100^{\circ}\text{C}$  liberated iodine and sublimed, to give traces of an orange solid on cooler parts of the tube. A green grey residue remained which may have been a mixture of tungsten(VI) products (viz.  $\text{WOF}_2 \cdot \text{WF}_3\text{OH}$  obtained by reaction with the glass).

A powder photograph of the solid did not show any distinct bands. The smallness of the sample of orange solid obtained, prevented further characterisation.

### 2.8.2. Reaction of $\text{WClF}_5$ with $\text{CsF}$

Caesium fluoride was prepared by adding 40% HF to caesium carbonate, in a platinum dish, till the solution was neutral. This mixture was then heated until the white solid,  $\text{CsF}$ , was obtained. The solid was left in an evacuated desiccator until required.

$\text{WClF}_5$  containing  $\text{WF}_6$  was passed over moist  $\text{CsF}$ . A flocculent white solid resulted below room temperature: the remaining volatile products were then pumped off. An  $^{19}\text{F}$  spectrum of these products showed them to be  $\text{WClF}_5$  - the quantity of  $\text{WF}_6$  remaining was less than 2%. On distilling this  $\text{WClF}_5$  onto dry  $\text{CsF}$ , very little of the  $\text{CsF}$  dissolved initially, but an increase in the white solid was observed after leaving the reactants at room temperature for an hour.

On reacting  $\text{WClF}_5$  with  $\text{CsF}$ , dissolved in dry sulphur dioxide, and warming to  $0^{\circ}\text{C}$  a flocculent yellow solid precipitated after  $\sim$  five minutes. Pumping away the volatile products of this reaction resulted in yellow and white solids which could not be separated. Further attempts at preparing this yellow solid proved unsuccessful: the products obtained were always contaminated with either buff, or pale blue solids which could not be separated.

## 2.9. Reaction of Trimethylchlorosilane and $WF_6$

### 2.9.1. Preparation of an Orange Solid Product by Low Temperature Reaction

About 12 mls. of  $WF_6$  were introduced into a bulb containing about 100 mls. of redistilled trimethylchlorosilane. On standing at  $0^\circ C$  for half an hour, the colour of the solution changed from colourless to orange. This mixture was then left overnight at  $-20^\circ$ . An orange solution, containing large proportions of an orange solid, was obtained which was left for a further six hours at  $-20^\circ$  to ensure complete precipitation of the orange solid. The volatile products were then pumped on for a day at room temperature before the solid remaining was transferred to a dry box.

The orange solid dissolved only slightly in  $CFCl_3$  and  $SiCl_4$ , a little more readily in  $SO_2$  and very quickly in  $CCl_4$ ,  $CS_2$ ,  $CH_3CN$  and ether; in all cases, the resulting solutions were pale yellow. No  $^{19}F$  spectrum signals were obtained when the compound was dissolved in any of these solvents.

The orange solid could be sublimed under vacuum at  $\sim 40^\circ C$ . It was deposited on a  $-78^\circ C$  cold finger as fine orange needle crystals. The residue remaining was a grey solid; no volatile product was detected. This pure orange product dissolved completely in acetonitrile but no  $^{19}F$  spectrum signal could be obtained. On adding the pure orange solid to  $CCl_4$  it initially dissolved, but no  $^{19}F$  signals were found to be present; after several hours at room temperature a grey solid was precipitated.

On heating the impure orange solid to  $120^\circ$  in a long tube which was incased in a tightly fitting copper tube (to afford a good temperature gradient) a series of crystalline products were obtained; being in increasing order of volatility, deep

orange needle crystals, pale orange more finally divided crystals and yellow finely divided crystals. The separation of these distinct compounds was small, as too was the actual quantity of each obtained; hence no further work could be done in identification. A large quantity of grey solid residue remained, which was believed to be  $WOF_2$  caused by reaction with the glass (the pyrex was seen to be badly etched at the point of heating).

No analysis was done on the orange needle crystals obtained by sublimation.

Attempts at repeating the preparation of this orange solid all failed; only small quantities of orange solid being obtained - the predominant product being dark purple crystalline tungsten hexachloride.

#### 2.9.2. Attempts at Rate of Reaction Studies

Reaction of a large excess of trimethylchlorosilane with tungsten hexafluoride at room temperature resulted in the precipitation of a deep purple crystalline product [Found: W, 46.2; Cl, 53.1. Calc. for  $WCl_6$ : W, 46.4; Cl, 53.6%].

The  $^{19}F$  spectrum of the volatile products showed tungsten hexafluoride and trimethyl fluorosilane to be present. If the reactants were left for a week at room temperature the  $^{19}F$  spectrum of the volatile products indicated only the presence of  $WF_6$  and  $Me_3SiF$ . Allowing this volatile mixture to stand at room temperature for a day, resulted in further precipitation of tungsten hexachloride; hence, implying that the reaction was an equilibrium reaction.

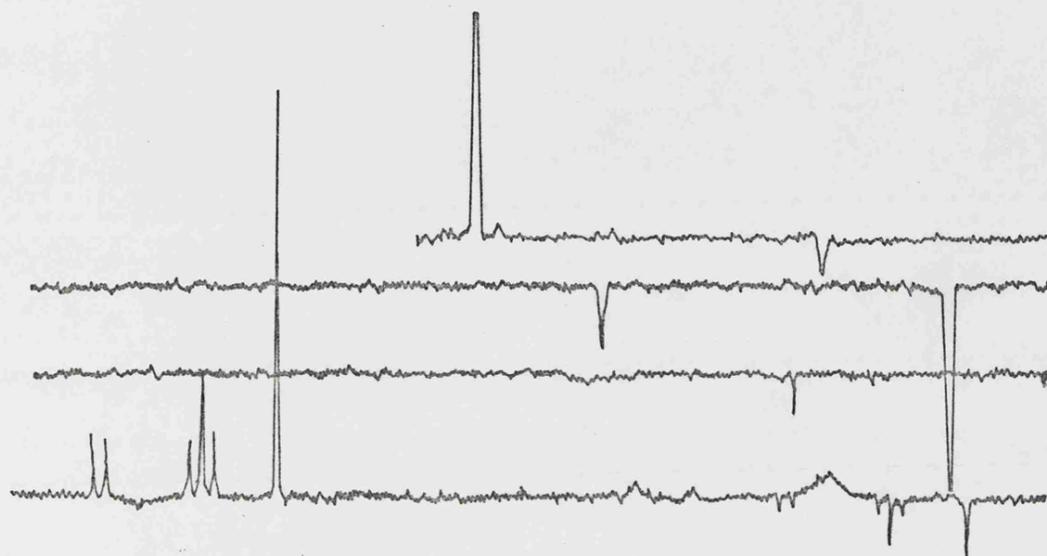
Kinetic studies were attempted on this reaction, the rate of which the reaction proceeded being measured by the decline in the proportion of  $WF_6$  in the mixture with time, as measured

by  $^{19}\text{F}$  spectroscopy. The tungsten hexafluoride was kept over sodium fluoride to remove any HF, and redistilled before use. The trimethyl chlorosilane was purified by trap to trap distillation. Tungsten hexafluoride and trimethylchlorosilane were distilled into graduated vessels fitted with traps so that the volume of each reactant could easily be obtained. The concentration of the reactants was ensured by distilling 10 mls. of the desired mixture into the reaction vessel and allowing it to warm up to room temperature. After thorough mixing of the solution, a small amount of it was decanted into an n.m.r. tube attached. The  $^{19}\text{F}$  spectra of the reactants at room temperature, in various concentrations,  $\text{WF}_6$ :  $\text{Me}_3\text{SiCl}$  = 1:3, 1:6, 1:9, 1:12 and 1:15, were observed every twenty minutes over a period of a day - the  $\text{WF}_6$  peak being integrated and this height being correlated with time. It was noted that on warming all solutions to room temperature, the mixtures turned yellow. After three hours, this colour had deepened to deep orange/red and tungsten hexachloride had begun to precipitate, but no  $^{19}\text{F}$  spectrum signals of the mixed tungsten chloride fluorides,  $\text{WCl}_n\text{F}_{6-n}$ , were obtained at  $-30^\circ$ . It was further observed that traces of orange solid were obtained when the reaction mixtures of  $\text{Me}_3\text{SiCl}$  and  $\text{WF}_6$  were initially allowed to warm to room temperature; this solid seemed to be formed irrespective of the concentration of the two reactants.

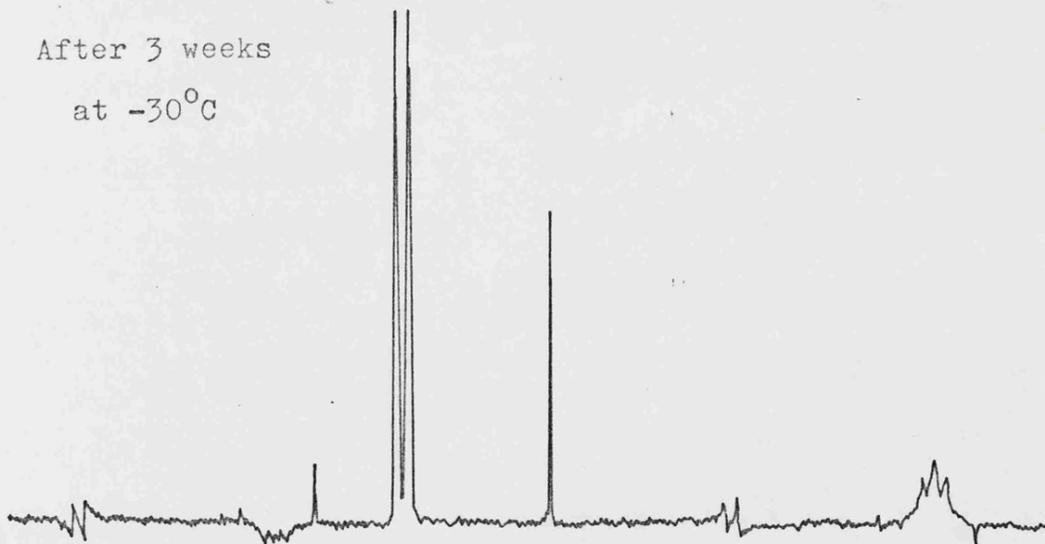
From these studies, no correlation could be obtained between the concentration of  $\text{WF}_6$  in a particular reaction solution and time. It was therefore concluded that this reaction does not follow simple first or second order reaction kinetics.

Figure 2.9.1.

$^{19}\text{F}$  Spectrum of the Reaction of  $\text{WF}_6$ ,  $\text{Me}_3\text{SiCl}$  and a Trace of Dry  $\text{HCl}$ .



(b) After 3 weeks  
at  $-30^\circ\text{C}$



(b) After 2 weeks at  $-30^\circ\text{C}$

### 2.9.3. With Traces of Dry Hydrogen Chloride Present

The hydrogen chloride was used directly from the cylinder containing the gas and was dried by bubbling it through concentrated sulphuric acid and passing it along a tube packed with  $P_2O_5$ . The trimethyl chlorosilane was purified by trap to trap distillation.

On adding half an atmosphere of dry hydrogen chloride to tungsten hexafluoride the liquid turned from colourless to pale yellow. The  $^{19}F$  spectrum of the mixture showed only a singlet of  $WF_6$ , however; even after the solution had been standing for a week at room temperature, no solid was precipitated and no further colour change was observed.

Excess trimethyl chlorosilane was condensed into an n.m.r. tube with  $WF_6$  (trimethyl chlorosilane:tungsten hexafluoride = 12:1) and a trace of dry hydrogen chloride was then added. The n.m.r. tube was sealed and held at  $-30^\circ$  for several weeks. The colourless solution turned yellow then orange and after three weeks orange and red solid chloride fluorides were deposited. The  $^{19}F$  spectrum of the solution was observed at  $-20^\circ$ , at regular intervals [see fig. 2.9.1.]. The tungsten hexafluoride signal gradually diminished and signals due to trimethyl fluorosilane, tungsten chloride pentafluoride, cis and trans tungsten dichloride tetrafluoride, mer and fac tungsten trichloride trifluoride and cis and trans tungsten tetrachloride difluoride appeared successively. After three weeks, the tungsten chloride pentafluoride signal had also disappeared and only signals due to trimethyl fluorosilane, cis and trans tungsten dichloride tetrafluoride, mer and fac tungsten trichloride trifluoride and cis and trans tetrachloride difluoride were observed. At this point, solid chloride fluorides were deposited and the above

signals decreased in intensity. After a further two weeks the solution contained predominantly red and a little purple solid.

When the above reaction mixture did not contain hydrogen chloride, no evidence for the presence of the volatile chloride fluoride intermediates could be obtained, although chloride fluorides of tungsten(VI) were eventually deposited.

### 3. Halogen Exchange with Rhenium Hexafluoride

#### 3.1. Preparation of Rhenium Hexafluoride

Rhenium hexafluoride was prepared by passing fluorine, diluted with nitrogen, over heated rhenium in a flow system. The apparatus used was the same as that used in the preparation of tungsten hexafluoride [~~see 2.1.1.~~]. Fluorination was carried out in a nickel reaction tube at  $300^{\circ}$  and the volatile products held at  $-180^{\circ}$ . The rhenium was first made active by heating to  $500^{\circ}$  in a stream of hydrogen for two hours, followed by cooling in hydrogen for a further two hours. The apparatus was purged with dry nitrogen before the nickel boat, containing the rhenium, was introduced. The apparatus was then purged for a further six hours before fluorine, diluted with an equal volume of nitrogen was allowed to flow through it. The yellow/orange product, held at  $-180^{\circ}$ , was further purified, from any  $\text{SiF}_4$  formed, by distilling at  $0^{\circ}\text{C}$  under vacuum into a trap held at  $-90^{\circ}$ . The  $\text{ReF}_6$  contaminated with  $\text{ReF}_7$  and  $\text{ReOF}_5$ , was stored at  $-30^{\circ}$  in glass break seal vessels containing sodium fluoride.

If pure rhenium hexafluoride was required, then this was obtained by passing the impure rhenium hexafluoride over heated rhenium: by this method, any rhenium heptafluoride was converted quantitatively to the hexafluoride.

The binary rhenium fluorides were purified from any oxyfluorides formed by trap to trap distillation under a dynamic vacuum.

#### 3.1.2. Boron trichloride and Boron Tribromide

Both these highly volatile liquids were obtained in 25 g. ampoules as laboratory grade reagents from B.D.H. The ampoules

were hot spotted and the contents purified by trap to trap distillation under vacuum. They were stored over  $P_2O_5$  in vessels sealed by "rotaflo" taps.

### 3.1.3. Chlorine and Bromine

Both were obtained directly from cylinders of the halogen. The gas was dried by bubbling through concentrated sulphuric acid and by passing along a 30 cm column packed with  $P_2O_5$ .

### 3.1.4. "Rhenium Tetrabromide"

Rhenium powder was treated with portions of 20 vol. hydrogen peroxide and evaporated to small volume after each addition. Portions of hydrobromic acid were then added, evaporation to small volume again being carried out after each addition. The brown solid which resulted was finally dried in a desiccator containing potassium hydroxide and phosphorus pentoxide. Vacuum pumping this solid for a day at room temperature still did not appear to completely dry the product: its infra-red spectrum still showed a large band in the rhenium oxygen stretching frequency region.

## 3.2. Reaction of Excess Boron Trichloride with Rhenium Hexafluoride in Liquid Chlorine

The rhenium hexafluoride used was contaminated with small quantities of rhenium heptafluoride. It was initially distilled into a trap (held at  $-90^\circ$ ) containing dry sodium fluoride and allowed to warm to room temperature before being distilled into the reaction vessel. Excess dry boron trichloride and chlorine were then distilled into the reaction vessel at  $-196^\circ$ . This reaction mixture was allowed to stand at  $-50^\circ$  for 6 hours.

Initially the solution turned pale green, the colour then deepened through dark green to dark brown. After about an hour a dark brown crystalline solid began to precipitate slowly. After six hours, the volatile products at  $0^{\circ}\text{C}$  were distilled into a trap held at  $-196^{\circ}$ : the brown/black crystalline solid remaining being pumped on for a further twelve hours at  $0^{\circ}\text{C}$  to ensure complete removal of the volatile products obtained in this way. If the volatile products were left at  $-30^{\circ}$  for twelve hours, further precipitation of the brown/black crystalline solid resulted. Debye X-ray powder photographs of both these solids were taken on a 19 cm. camera with filtered radiation from a copper target. The photographs obtained gave identical powder patterns. An infra-red of the brown solid showed no bands in the rhenium oxygen stretching region ( $\sim 1000\text{ cm}^{-1}$ ).

The volatile products were distilled through traps held at  $-30^{\circ}$ ,  $-78^{\circ}$  and  $-180^{\circ}$ . By  $^{19}\text{F}$  spectroscopy the  $-180^{\circ}$  fraction was found to contain  $\text{BF}_3$ ,  $\text{BClF}_2$  and  $\text{BClF}$ ; it was also believed to contain unreacted  $\text{BCl}_3$  and  $\text{ReF}_6$  (identified by their physical appearance when further distillation through a  $-90^{\circ}$  trap enabled them to be substantially separated from the boron fluorides). The  $-78^{\circ}$  fraction held a bright yellow crystalline solid, with all the physical characteristics of  $\text{ReF}_6$ , and a small quantity of a bright green crystalline solid: further fractionation of this product did not result in separation of the two solids, but merely in a diminution of the quantity of green solid present; hence further characterisation of the latter was not possible. The  $-30^{\circ}$  trap held dark red and brown solids, but the quantities of these obtained were always too small to facilitate further separation and characterisation.

### 3.3. Reaction of Excess Boron Trichloride and Rhenium Hexafluoride and Traces of Hydrogen Chloride

The rhenium hexafluoride used was contaminated with small quantities of rhenium heptafluoride. It was initially distilled into a trap, held at  $-90^{\circ}$ , containing dry sodium fluoride and allowed to warm up to room temperature before being distilled into the reaction vessel. Excess dry boron trichloride and traces of hydrogen chloride (obtained directly from a cylinder of the gas and dried by being bubbled through concentrated sulphuric acid and by passing along a long tube packed with  $P_2O_5$ ) were then distilled into the reaction vessel held at  $-196^{\circ}$ . The reaction mixture was allowed to stand at  $-30^{\circ}$  for three hours. Initially the solution turned pale green, the colour then deepening through dark green to dark brown. In less than an hour, a dark green/brown crystalline solid had precipitated. After three hours, the volatile products were distilled through traps held at  $-30^{\circ}$ ,  $-78^{\circ}$  and  $-196^{\circ}$ . The green/brown solid was left under dynamic vacuum for a further twelve hours and a Debye X-ray powder photograph of it was then taken [see section 1.5.].

$^{19}F$  spectroscopy identified the volatile products, held at  $-196^{\circ}$ , as  $BF_3$ ,  $BClF_2$  and  $BCl_2F$ . It was also believed, by further fractional separation of this product, that boron trichloride and  $ReF_6$  were also present. On allowing this  $-196^{\circ}$  fraction to stand at  $-30^{\circ}$  for a day quantities of a brown/green crystalline solid precipitated. The  $-78^{\circ}$  volatile fraction held mainly a bright yellow crystalline solid, with the physical characteristics of  $ReF_6$  and traces of a bright green crystalline solid. The  $-30^{\circ}$  volatile fraction held red and brown solids which were in too small a quantity to enable characterisation of them to be attempted.

### 3.4. Reaction of Excess Boron Trichloride with Rhenium Hexafluoride

The rhenium hexafluoride used was contaminated with a small proportion of rhenium heptafluoride. It was initially distilled into a trap, held at  $-90^{\circ}$ , containing dry sodium fluoride and allowed to warm to room temperature (so as to remove any HF present) before being distilled into the reaction vessel. Excess dry boron trichloride was distilled into the reaction vessel held at  $-196^{\circ}$ . Reaction mixtures were allowed to stand for a day at both  $-30^{\circ}$  and  $0^{\circ}$  and both gave the same products; initially the solution turned green and then deepened to a dark green before precipitating a dark green/brown crystalline solid. The volatile products at  $0^{\circ}\text{C}$  were distilled under a dynamic vacuum, through traps held at  $-30^{\circ}$ ,  $-78^{\circ}$  and  $-196^{\circ}$ . The dark green solid remained at  $0^{\circ}$  as an involatile product and a Debye X-ray powder photograph of it was found to be identical to that taken of the brown solid, obtained from the reaction of excess boron trichloride with rhenium hexafluoride in liquid chloride [see section 3.3.]. Analysis of this solid was also attempted but mutual interference of rhenium and chloride analysis render the results both inconsistent and uninterpretable, however the ratio of rhenium to chlorine always seemed to be between 1:5 and 1:6.

The  $-30^{\circ}$  trap held traces of a dark brown/black solid but the quantities of this compound were always insufficient to enable further characterisation. The  $-78^{\circ}$  trap held a bright yellow crystalline product, which had the physical characteristics of rhenium hexafluoride, and some boron trichloride. The  $-196^{\circ}$  trap held white and yellow solids, an  $^{19}\text{F}$  spectrum of which showed boron trifluoride, boron chloride difluoride

and boron dichloride fluoride to be present. Further fractionation of the contents of this  $-196^{\circ}$  trap through traps held at  $-90^{\circ}$  and  $-196^{\circ}$  indicated, by visual observation only, boron trichloride and rhenium hexafluoride to be present.

If the volatile products of the reaction mixture of excess boron trichloride and rhenium hexafluoride were allowed to stand for a day at  $-30^{\circ}$  or  $0^{\circ}$  further precipitation of the dark brown/black solid resulted.

### 3.5. Reaction of Excess Boron Tribromide with Rhenium Hexafluoride in Liquid Bromine

The rhenium hexafluoride used was contaminated with small quantities of rhenium heptafluoride. It was initially distilled into a trap (held at  $-90^{\circ}$ ) containing dry sodium fluoride and allowed to warm to room temperature (to remove any HF present) before being distilled into the reaction vessel. Excess dry boron tribromide and bromine were then distilled into the reaction vessel held at  $-196^{\circ}\text{C}$ . This reaction mixture was then allowed to stand at  $0^{\circ}\text{C}$  for several hours. As the reactants slowly warmed up from  $-196^{\circ}$  to  $0^{\circ}\text{C}$  a vigorous reaction took place (well below  $0^{\circ}\text{C}$ ) with the resultant precipitation of a dark brown/black crystalline solid in the red/brown liquid. The volatile products at  $0^{\circ}\text{C}$  were distilled into an n.m.r. tube and the  $^{19}\text{F}$  spectrum of them showed signals due to  $\text{BF}_3$ ,  $\text{BF}_2\text{Br}$  and a very weak broad signal possibly  $\text{BFBr}_2$ . Further precipitation of the brown/black solid resulted from leaving this volatile fraction at  $0^{\circ}\text{C}$  for a day.

A Debye X-ray powder photograph of this brown/black solid was taken on a 19 cm camera with filtered radiation from a

copper target. A magnetic moment on this black/brown solid (measured by the Gouy Method) gave a  $\mu_{\text{eff}}$  of 3.9 B.M. for the rhenium in the compound [see section 1.4.].

### 3.6. Reaction of Excess Boron Tribromide with Rhenium Hexafluoride

The rhenium hexafluoride was contaminated with small quantities of rhenium heptafluoride. It was initially distilled into a trap, held at  $-90^{\circ}\text{C}$ , which contained dry sodium fluoride (to remove any HF present) and then allowed to warm to room temperature before being distilled into the reaction vessel. Excess dry boron tribromide was then distilled into the reaction vessel, held at  $-196^{\circ}$ . This reaction mixture was then allowed to stand at  $0^{\circ}\text{C}$  overnight. As the reactants slowly warmed up from  $-196^{\circ}$  a vigorous reaction occurred (well below  $0^{\circ}\text{C}$ ) the solution deepening to a dark brown colour and quantities of dark brown solid were precipitated. Fractional distillation of this mixture through  $-30^{\circ}$ ,  $-78^{\circ}$  and  $-196^{\circ}$  traps gave, respectively, traces of bromine, bromine, rhenium hexafluoride and a little boron tribromide and rhenium hexafluoride, boron dibromide fluoride, boron bromide difluoride and boron trifluoride. [The boron fluoride compounds in the  $-196^{\circ}$  trap being identified by  $^{19}\text{F}$  spectroscopy.] A Debye X-ray powder photograph of the dark brown solid was obtained. An infra-red spectrum of the solid showed no signals in the rhenium-oxygen stretching region. If the volatile products of the exchange reaction between rhenium hexafluoride and boron tribromide were allowed to stand at  $0^{\circ}\text{C}$ , further precipitation of the brown/black solid resulted.

#### 4. Heats of Hydrolysis

##### 4.1. Apparatus

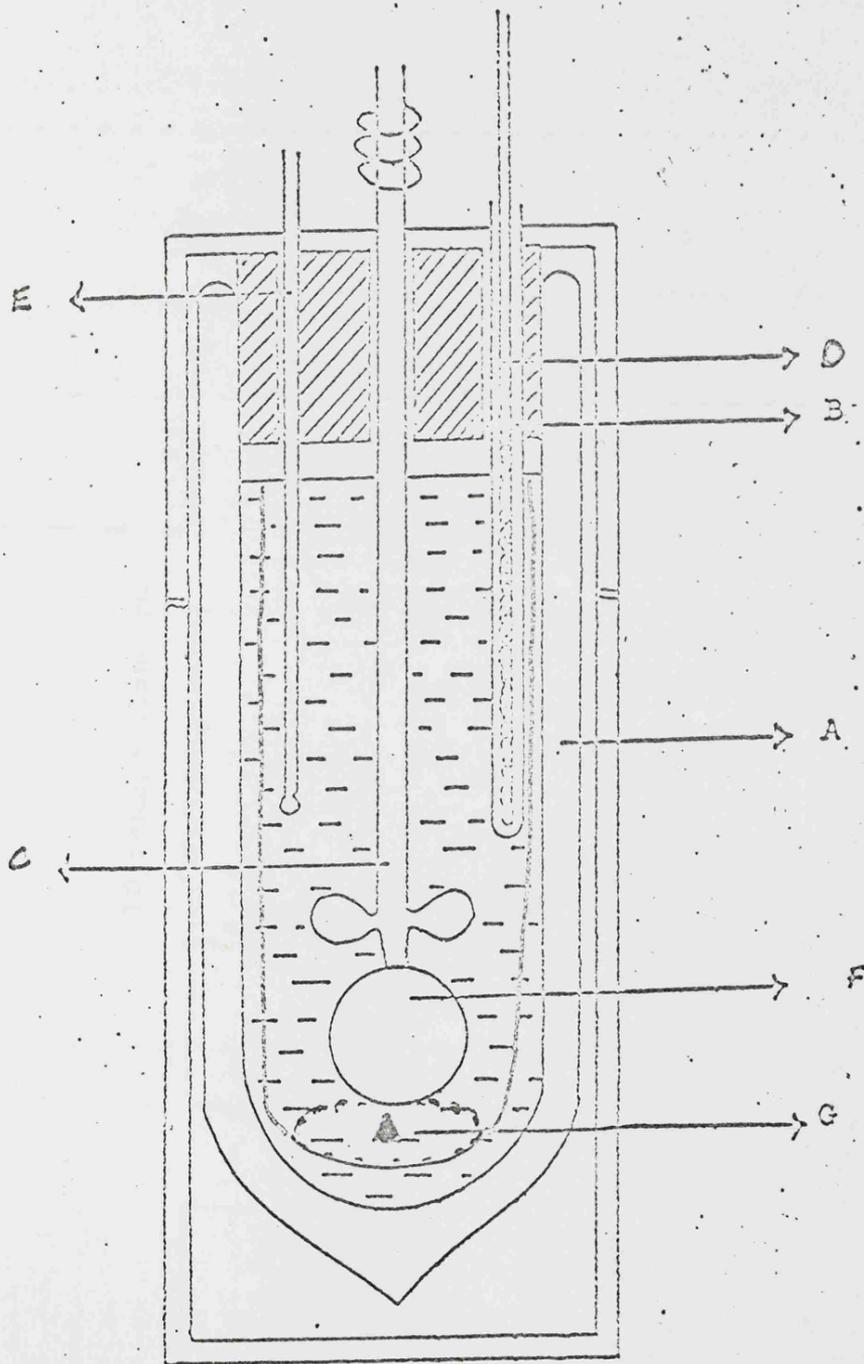
The calorimeter used [see fig. 4.1.1.] consisted of a cylindrical dewar vessel of about 150 ml. capacity [A]. Into this fitted a teflon stopper [B] attached to an isothermal copper shield. Holes in this stopper allowed for a stirring rod [C], a heater [D] and a thermister [E] to be inserted. A thin walled glass bulb of 5 to 10 ml. capacity [F] (its volume being accurately measured  $\pm 0.1$  ml.) contained the compound to be hydrolysed and was fused onto the end of the glass stirring rod. A P.T.F.E. coated metal spike [G] was supported from the teflon stopper by four P.T.F.E. coated stainless steel rods.

The heater consisted of 38 s.w.g. "Eureka" resistance wire wound round a glass tube and encased in an outer glass tube. The current supplied to this heater was controlled by a variable  $1\frac{1}{2}$  - 4 volt stabilised supply and was determined via the potential across a standard ten ohm. resistance, wired in series with the circuit [see fig. 4.1.2.]. The current to the potentiometer was obtained from a 2 volt stabilised supply.

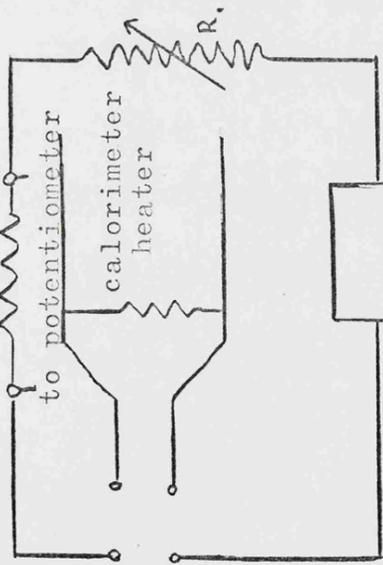
Temperature changes in the calorimeter were measured using a single thermistor [type F] of resistance  $\sim 200$  ohms. at  $20^{\circ}$  [supplied by Messrs. Standard Telephones and Cables Ltd.]. The circuit which incorporated this thermistor was basically a Wheatstone bridge circuit, with the thermistor being one of its arms; the current for it being from a six volt stabilised supply. Large resistance values were chosen for the ratio arms opposite both the thermistor and the fourth variable resistance, so that the current that passed through the thermistor was slight which prevented it from heating and, thus, giving unreliable results.

Figure 4.1.1.

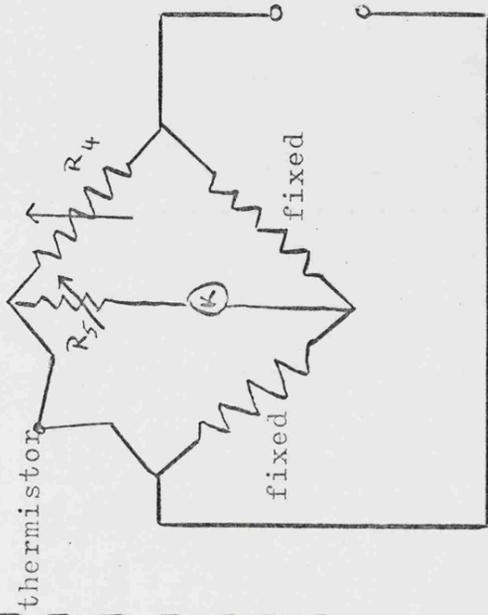
Diagram of Calorimeter used for Heat of Hydrolysis Experiments.



10 (ohm.) standard



1 1/2 - 4 volt  
stabilised supply



thermistor

R<sub>4</sub>

R<sub>5</sub>

fixed

fixed

R<sub>2</sub>

HEATER CIRCUIT

THERMISTOR CIRCUIT

6 volt stabilised  
supply

Figure 4.1.1.2.

Heater and Thermistor Circuit.

A Kipp micrograph recorded (B.D.2.) (marked (K) on fig. 4.1.2.) was used as a galvanometer to measure the out of balance of the Wheatstone Bridge circuit, caused by the change in resistance of the thermister resulting from heat changes in the calorimeter. The recorder was so arranged that initially the Wheatstone bridge was slightly out of balance in one direction and approximately the same degree out of balance in the opposite direction after mixing.

#### 4.2. Experimental Procedure

All compounds investigated were moisture and air sensitive. Introduction of the sample into the frangible bulbs was thus carried out in one of two ~~possible~~ <sup>alternative</sup> ways: if the sample was volatile the bulb was attached to a U-tube through which the sample could be distilled but if the sample was involatile under vacuum, it could be introduced into the bulb in a dry box [see fig. 4.2.1.]. In either case, the volume of the bulb was measured before it was washed, dried and weighed to constant weight. All bulbs were flamed out and pumped on for several days before the given sample was introduced. The frangible bulb was then cooled in liquid nitrogen and sealed off under vacuum. The U tube or cone was washed and dried before reweighing with the sample containing bulb to constant weight.

All bulbs were kept at  $-30^{\circ}$  until required. They were then sealed into the glass stirrer while the contents of them were cooled to  $-196^{\circ}$  [since heating of all samples resulted in decomposition].

Approximately 150 ml. of sodium hydroxide (the strength depending on the particular experiment) were poured into the Dewar flask, the apparatus was then assembled, immersed in a constant temperature water bath at  $25^{\circ}\text{C}$  and allowed to

Figure 4.2.1.

Apparatus for Volatile Samples.

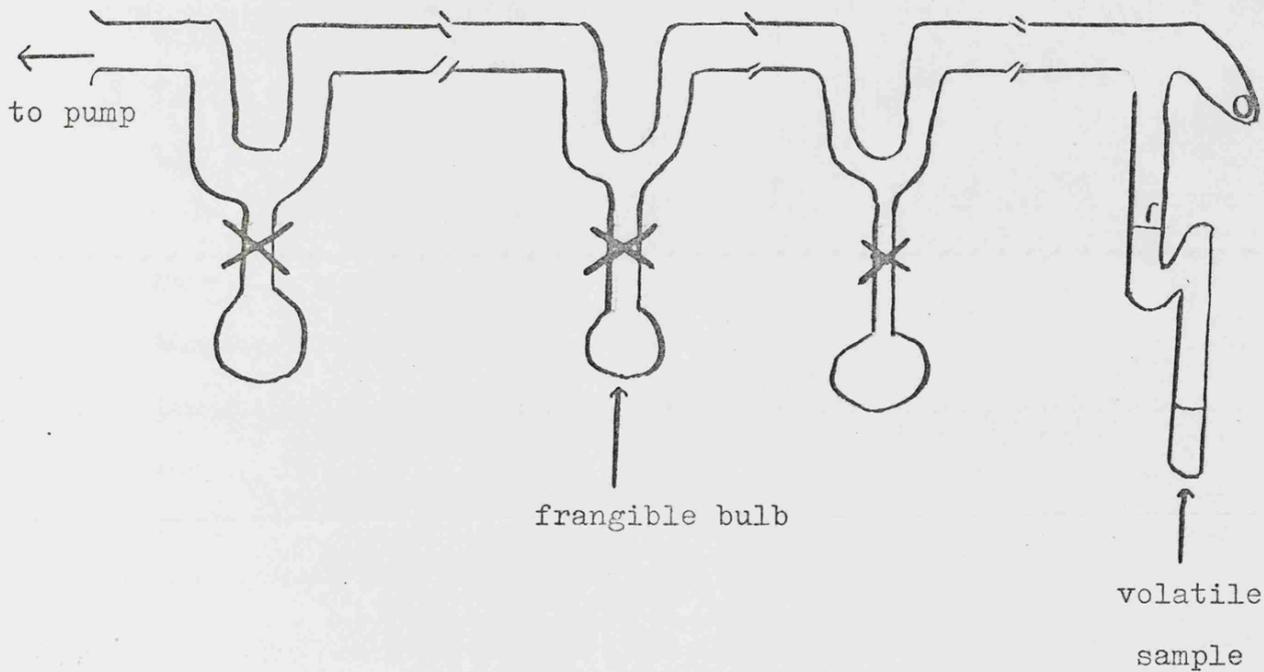
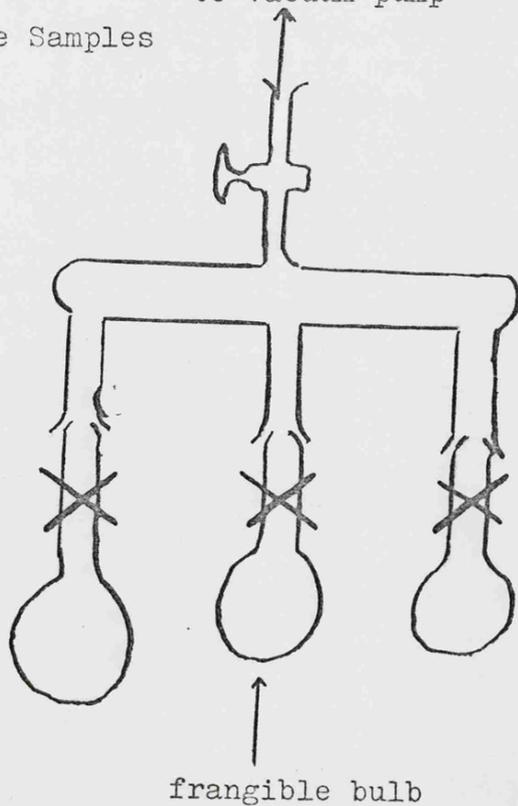


Figure 4.2.2.

Apparatus for  
Involatile Samples

to vacuum pump



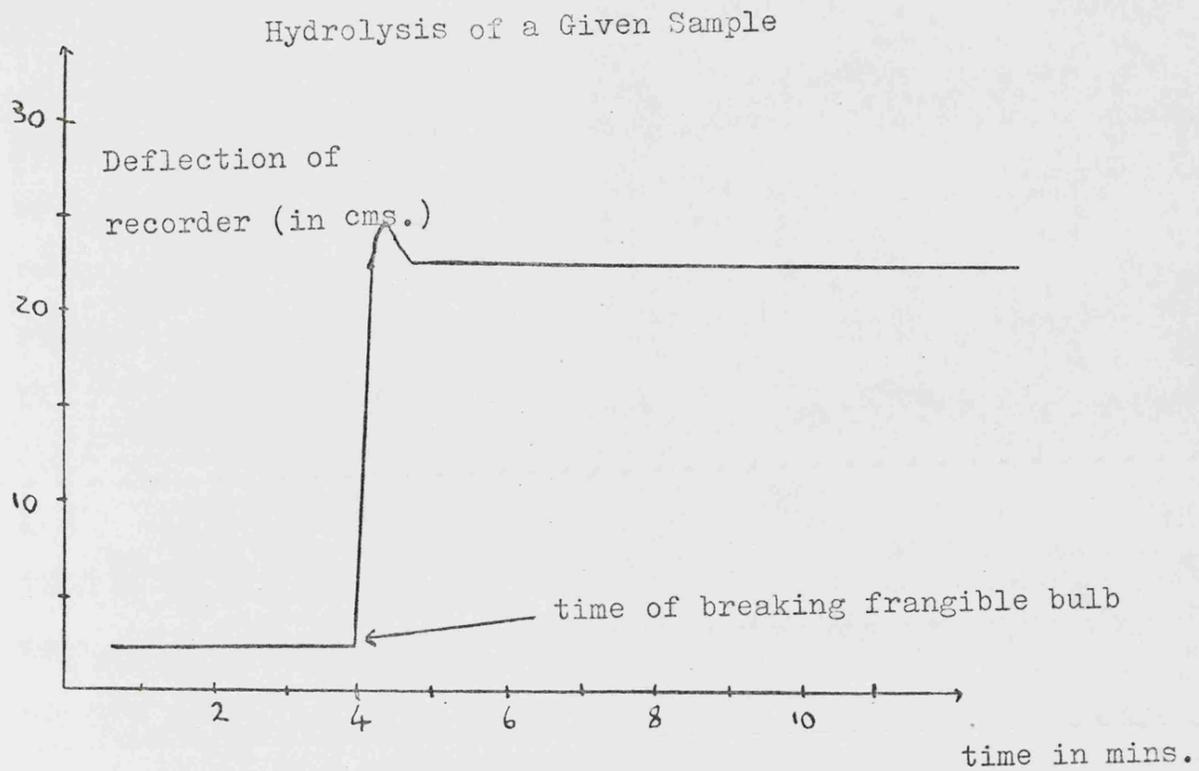
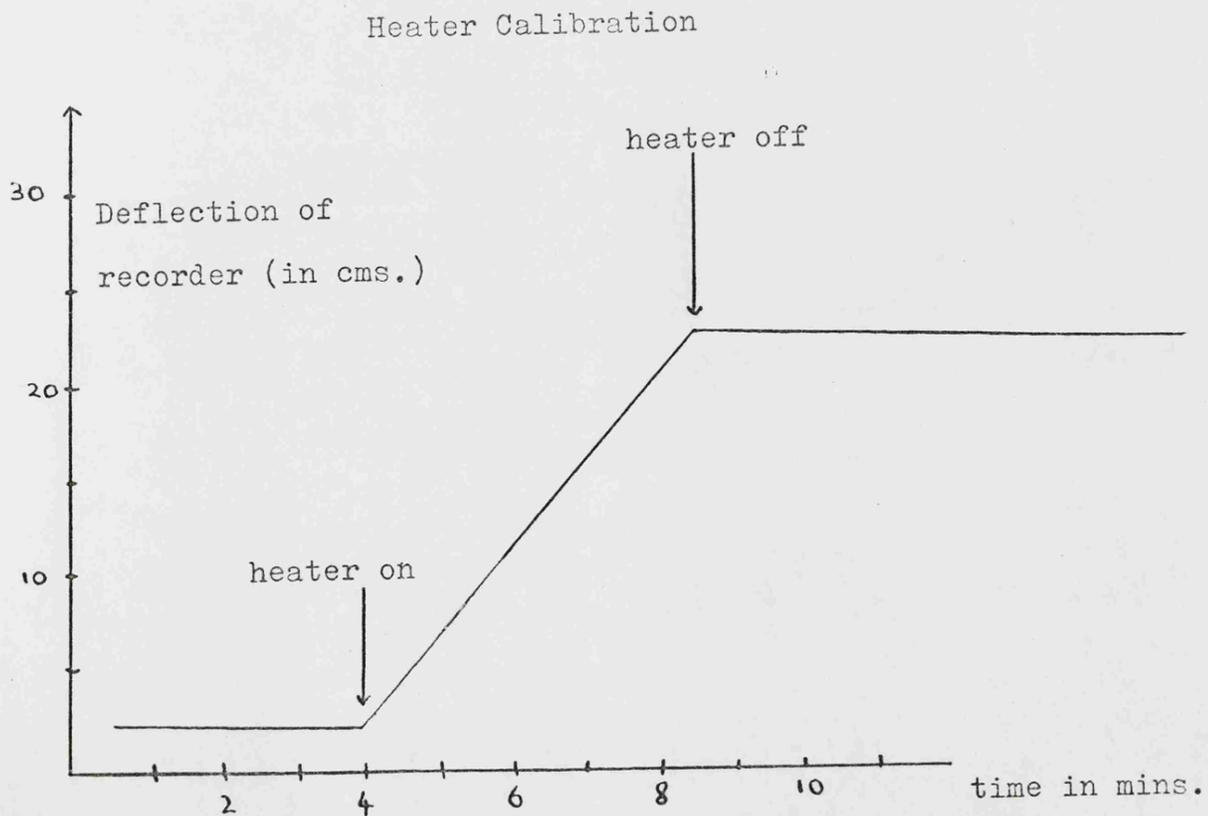
Where X is the sealing  
off point.

for involatile samples

equilibrate for twelve hours. The stirrer was then allowed to rotate at a constant speed and the galvanometer attached to the potentiometer and the recorder was switched on. The deflection of the recorder was set at zero and its sensitivity adjusted so that the hydrolysis reaction would result in a full scale deflection. A further four hours were allowed for the total system to come once more to equilibrium.

The pen of the recorder was activated for at least five minutes before the sample was brought into contact with the alkali by depressing the glass stirrer, to which the frangible bulb was attached, onto the spike. A cooling curve was then plotted by allowing the recorder pen to continue for a full twenty minutes after the deflection of the recorder deflection had reached its maximum.

Several heating calibrations were then carried out by introducing a known quantity of heat into the system - via the heater circuit. These gave a comparable deflection to that obtained by the hydrolysis reaction. The reliability of the apparatus was tested by measuring the heat of precipitation of silver chloride<sup>131</sup> (i.e. the heat of reaction of potassium chloride in excess dilute silver nitrate) and heat of hydrolysis of liquid tungsten hexafluoride:<sup>76,89,91</sup> Both values of which are well documented. Six consistent values for each were obtained giving the heat of precipitation of silver chloride in 0.1 M silver nitrate as  $-15 \pm 0.2$  kcals/mole and a heat of formation of liquid tungsten hexafluoride (via its heat of hydrolysis in 0.1 M sodium hydroxide) of  $-419 \pm 5$  kcals/mole. The values obtained using this apparatus were within all the literature values stated for these two heats - given the inherent error factor.

Figure 4.3.1.Figure 4.3.2.

4.3. A Typical Experiment

The deflection of the recorder with time for a typical run for both  $\alpha$  hydrolysis reaction and a heater calibration may be seen in fig. 4.3.1. and fig. 4.3.2. respectively. All hydrolysis reactions were carried out at 25°C.

Weight of sample in bulb =  $W$  (gms.)

[If  $W_1$  represents the difference in weight before and after filling the bulb apparatus with sample and  $v$  is the volume (in mls.) of air weighed in the bulb when empty, but absent when the bulb is reweighed containing sample. Then where the density of air is 0.001296 gms/ml. the actual weight of the sample is  $W = W_1 + (0.001296 v)$  (in gms.).]

Molarity of sodium hydroxide =  $x(M)$

Heater resistance =  $R$  (ohms.)

Heater current =  $I$  (amps)

Time of passing current through heater =  $T$  (secs.)

Recorder deflection for hydrolysis reaction =  $A$  (cms.)

Recorder deflection for heater calibration =  $B$  (cms.)

Molecular weight of compound =  $M$ .

Since heat dissipated =  $\frac{I^2 RT}{4.1842}$  (calories)

heat induced electrically =  $\frac{I^2 RT}{4.1842}$  (calories)

heat liberated during hydrolysis =  $\frac{I^2 RT}{4.1842} \cdot \frac{A}{B}$  (calories)

Then the heat of hydrolysis of the compound  $\cdot XMNaOH$  =

$$\frac{I^2 RT}{4.1842} \cdot \frac{A}{B} \cdot \frac{W}{M} \text{ (cals/mole)}$$

#### 4.4. Alkaline Hydrolysis of Tungsten Dichloride Tetrafluoride

The U tubes with frangible bulbs attached [see fig. 4.2.1.] were weighed and the volume of the bulb measured approximately before they were connected, three at a time, to a vacuum line. After pumping for two days (the U tubes being flamed out) they were held at  $-30^{\circ}$  and tungsten dichloride tetrafluoride was allowed to distil into them. When the required volume had been introduced each bulb was sealed off under vacuum at  $-196^{\circ}$ , the U tubes washed and dried, and the total apparatus weighed to constant weight. The weight of sample in each bulb was then obtained by difference: a small correction being made for the volume of air in the bulb when weighed empty, which was absent when reweighed with the bulb containing the sample under vacuum. The bulbs were then kept at  $-30^{\circ}$  until required. Large sample weights were used so that the sample should be predominantly a liquid: the heat of hydrolysis would then be a heat of reaction of liquid  $WCl_2F_4$ , a small error factor being allowed for the gaseous part of the sample.

The bulb, while held at  $-196^{\circ}$ , was sealed on to the end of a glass stirring rod [see fig. 4.1.1.] and fixed into the teflon stopper. This was then fitted on to a Dewar vessel containing  $\sim 150$  mls. of 0.106 M sodium hydroxide and the whole apparatus placed in a copper sheath which was immersed in a  $25^{\circ}C$  constant temperature water bath. The system was allowed to equilibrate for twelve hours before the stirrer and recorder were switched on. After a further four hours equilibrium period a run was commenced [see section 4.2.].

Eight runs were undertaken from which six consistent

Table 4.4.1.Heat of Hydrolysis of  $\text{WCl}_2\text{F}_4$ 

Weight of $\text{WCl}_2\text{F}_4$ (in grams.)	Heat of Hydrolysis (in kcals/mole)
0.4261	-145
0.1350	-143
0.1701	-145
0.2253	-145
0.2965	-146
0.1540	-144

$\Delta\text{H}$  of hydrolysis of  $\text{WCl}_2\text{F}_4(1) = -145 \pm 4$  kcal/mole.

The strength of sodium hydroxide used for all runs was 0.106 M.

readings were obtained [see Table 4.4.1.]. The value calculated for the heat of hydrolysis of liquid  $WCl_2F_4$  was  $-145 \pm 4$  kcals/mole. After each run the sodium hydroxide was filtered, to remove fragments of broken bulb and analysed gravimetrically for tungsten, using the tannin-antipyrine method [see Appendix II] and for chlorine, by precipitation as silver chloride [see Appendix III]. With all samples the weight of tungsten dichloride tetrafluoride, obtained from analytical data, was consistent with that obtained by difference from the weight of the bulbs before and after filling with sample - to a degree of error of less than  $\pm 1\%$ .

#### 4.5. Heat of Alkaline Hydrolysis of Tungsten Chloride Pentafluoride

The same procedure for determining the heat of hydrolysis of tungsten chloride pentafluoride was utilised as for determining the heat of hydrolysis of tungsten dichloride tetrafluoride [see previous section]. The preparation of pure  $WClF_5$  has already been described [see section 2.12.]. After weighing the bulb apparatus and leaving the system under a dynamic vacuum for 2 days, to remove all traces of moisture,  $WClF_5$  was distilled into the bulbs held at  $-78^\circ$ . The bulbs were then sealed off at  $-196^\circ$ . A large quantity of  $WClF_5$  was used (between 0.2 and 0.7 gm. in each bulb) so that the heat of hydrolysis measured would be for liquid  $WClF_5$  - a small error factor accommodating the gaseous sample present.

Analysis for tungsten and chloride [see Appendixes II and III] in the hydrolysis solution gave values which correspond to the weight of  $WClF_5$  obtained by weighing the bulbs before and after filling with samples to an error

Table 4.5.1.Heat of Hydrolysis of  $\text{WClF}_5$ 

Weight of $\text{WClF}_5$ (in grams.)	Heat of Hydrolysis (in kcals/mole)
0.3752	147
0.6100	150
0.6694	146
0.7414	144
0.1751	147
0.2543	148

Heat of hydrolysis of liquid  $\text{WClF}_5$  =  $-147 \pm 2$  kcals/mole.

Strength of sodium hydroxide in all cases = 0.106 M.

factor of  $\pm 1\frac{1}{2}\%$ .

Six consistent runs were obtained [see Table 4.5.1.] and a value for the heat of hydrolysis of  $WClF_5$  of  $-147 \pm 2$  kcals/mole obtained.

#### 4.6. Heat of Alkaline Hydrolysis of Tungsten Hexachloride

##### 4.6.1. Preparation of Tungsten Hexachloride

Tungsten hexachloride was made by the room temperature reaction of excess boron trichloride with tungsten hexafluoride. The tungsten hexafluoride was initially distilled into a vessel held at  $-180^\circ$ , containing sodium fluoride, and allowed to warm to room temperature before being distilled into the reaction bulb, held at  $-180^\circ$ . The boron trichloride (technical grade B.D.H.) was dried by passing through a column packed with phosphorus pentoxide and distilled into the reaction vessel containing tungsten hexafluoride at  $-180^\circ$ . The reaction bulb was then sealed off under vacuum and allowed to stand at room temperature for a day. A deep purple/black crystalline solid precipitated. The volatile products were pumped off and the solid was then freed from any remaining reactants or products by being left overnight in a dynamic vacuum. A chlorine and tungsten analysis of this product was undertaken [see Appendixes II and III] [Found W, 46.3; Cl, 53.4. Calc. for  $WCl_6$ : W, 46.4; Cl, 53.6%].

##### 4.6.2. Alkaline Hydrolysis of Tungsten Hexachloride

The solid tungsten hexachloride was introduced into weighed frangible bulbs [see fig. 4.2.1. (1)] in a dry box. The bulbs were then cooled to  $-196^\circ$  and sealed off under

vacuum and the cone was washed, dried and reweighed, with the bulb, to constant weight. The bulb, held at  $-196^{\circ}$ , was sealed on to the stirrer and the calorimeter unit assembled [see section 4.2.]. Initially, 150 ml. of 0.1 M sodium hydroxide were used but the hydrolysis reaction was too slow for accurate results to be obtained: the heat given out during the reaction, as indicated by the deflection of the Kipp's recorder, showed that the reaction was incomplete even after half an hour.

It was thought that the large crystal size of the tungsten hexachloride used might inhibit reaction, but grinding the compound in a pestle and mortar in a dry box until it was a fine powder did not increase the speed of reaction. The use of smaller samples - of the order of 0.05 gm. of tungsten hexachloride - still resulted in a reaction which occurred over a longer period of time than half an hour.

The hydrolysis reaction was repeated in both molar and two molar solutions of sodium hydroxide but in both cases even when small samples of tungsten hexachloride were used, the reaction still continued after half an hour.

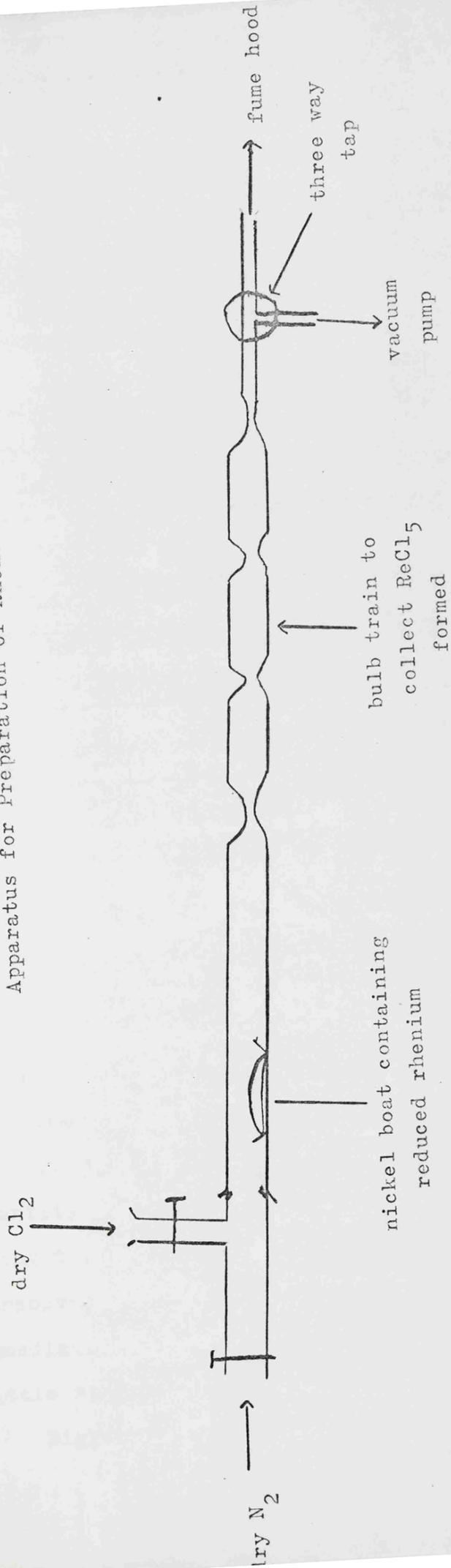
#### 4.7. Heat of Alkaline Hydrolysis of Rhenium Pentachloride

##### 4.7.1. Preparation of Rhenium Pentachloride

Rhenium pentachloride was prepared by the chlorination of reduced rhenium in a flow system [see fig. 4.7.1.]. Commercial chlorine was dried by bubbling through a concentrated sulphuric acid bubbler and along a tube packed with phosphorus pentoxide. Dry nitrogen was initially passed through the system to displace the air in it and the whole

Figure 4.7.1.

Apparatus for Preparation of Rhenium Pentachloride



apparatus was flamed out under a stream of dry nitrogen. The nitrogen flow was then stopped and the reduced rhenium metal (reduced in a stream of hydrogen at  $500^{\circ}$ ) burned, in an atmosphere of dry chlorine at  $400^{\circ}$ . When reaction was complete the rhenium pentachloride was gently sublimed further along the tube in a stream of chlorine. The system was then purged with dry nitrogen and the sections containing the  $\text{ReCl}_5$  were sealed off.

The rhenium pentachloride thus obtained, was introduced into vacuum line apparatus in a dry box and then pumped, under a hard vacuum at  $50^{\circ}$ , to remove all traces of oxychloride which might have been present.

A powder photograph of the solid showed it to be  $\text{ReCl}_5$  and an infra-red spectrum of it showed no rhenium-oxygen stretching frequency in the  $1,000 \text{ cm}^{-1}$  region.

#### 4.7.2. Hydrolysis Reaction with Rhenium Pentachloride

The solid rhenium pentachloride was introduced into the frangible bulbs, previously dried and evacuated, in a dry box and then pumped on, under a dynamic vacuum, for a day at room temperature (to ensure the absence of any rhenium oxide chloride) before being sealed off at  $-196^{\circ}$ .

The 0.1 M NaOH was initially boiled, to expel any dissolved oxygen, and then cooled before a sufficient quantity of boiled and cooled distilled water was added to bring the concentration back to its original value. The dissolved oxygen was removed from the sodium hydroxide immediately before each run so that the alkali would have as little time as possible to absorb more oxygen from the air.

Eight runs were recorded using 0.1 M sodium hydroxide

Table 4.7.1.Heat of Hydrolysis of  $\text{ReCl}_5(\text{c})$  in 0.106 M NaOH.

Weight of $\text{ReCl}_5$ (in gms.)	Heat of Hydrolysis (in kcals/mole)
0.1154	-138
0.0675	-138
0.0529	-137
0.1095	-137
0.1798	-137
0.1036	-136

Heat of Hydrolysis of  $\text{ReCl}_5(\text{c}) = -137 \pm 2$  kcals/mole.Table 4.7.2.Heat of Hydrolysis of  $\text{ReCl}_5(\text{c})$  in 1.004 M NaOH.

Weight of $\text{ReCl}_5$ (in gms.)	Heat of Hydrolysis (in kcals/mole)
0.2041	-137
0.0729	-137
0.1524	-137
0.1951	-136

Heat of Hydrolysis of  $\text{ReCl}_5(\text{c}) = -137$  kcals/mole.

(the highest and lowest value being rejected) and a value for the heat of hydrolysis of solid  $\text{ReCl}_5$  of  $-137 \pm 2$  kcals/mole obtained [see Table 4.7.1.].

Using molar sodium hydroxide the same value for the heat of hydrolysis of solid  $\text{ReCl}_5$  was obtained [see Table 4.7.2.]. This confirmed that hydrolysis was complete using 0.1 M alkali.

#### 4.7.3. Heat of Reaction of Rhenium Pentachloride with Alkaline Hyperchlorite

The solid rhenium pentachloride was introduced into previously dried and evacuated frangible bulbs in a dry box and then pumped on, under a dynamic vacuum, for a day at room temperature (to ensure the absence of any rhenium oxide chloride) before being sealed off at  $-196^\circ\text{C}$ .

The M/10 sodium hydroxide used was boiled and cooled and made up to the required strength with boiled and cooled distilled water to ensure the absence of dissolved oxygen in it. For this reaction 130 mls. of M/10 NaOH were mixed with 20 ml. of hypochlorite solution ( $\sim 1.25$  gm./ml.).

Four runs were recorded and a value for the heat of reaction, of solid rhenium chloride with alkaline hypochlorite, of  $-192 \pm 5$  kcals/mole of  $\text{ReCl}_5$  was obtained [see Table 4.7.3.].

#### 4.8. Heat of Hydrolysis of Antimony Pentafluoride

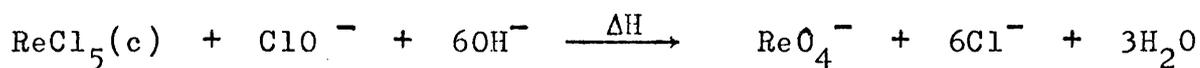
Antimony pentafluoride was prepared by direct fluorination of antimony metal; initially heated to  $400^\circ$ , in a flow system. The volatile antimony pentafluoride was held at  $-180^\circ$  and further purified by trap to trap distillation.

Table 4.7.3.

Heat of Reaction of Rhenium Pentachloride with Alkaline Hypochlorite.

Weight of Solid $\text{ReCl}_5$ (in gms.)	Heat of Reaction (in kcals/mole)
0.0558	-192
0.0702	-192
0.0954	-192
0.1235	-193

For the reaction:



$\Delta\text{H}$  = Heat of reaction =  $-192 \pm 5$  kcals/mole of  $\text{ReCl}_5$ .

Table 4.8.1.Heat of Hydrolysis of Liquid  $\text{SbF}_5$  in 0.1006 M NaOH.

Weight of Sample used (in gms.)	Heat of Hydrolysis (in kcals/mole)
0.4581	-72
0.2364	-73
0.1569	-72.4

Heat of hydrolysis of liquid  $\text{SbF}_5$  =  $-72.5 \pm 2$  kcals/mole.Table 4.8.2.Heat of Hydrolysis of Liquid  $\text{SbF}_5$  in 1.004 M NaOH.

Weight of Sample (in gms.)	Heat of Hydrolysis (in kcals/mole)	
0.07909	-108	
0.08326	-104.5	
0.1131	-110	
0.03458	-108	
0.1257	-108	
0.0954	-109	
0.1746	-99	} these values were rejected
0.1262	-95	
0.3574	-81.3	
0.4371	-75	

Heat of hydrolysis of liquid  $\text{SbF}_5$  =  $-108 \pm 2$  kcals/mole.

Antimony pentafluoride was distilled under vacuum into the previously dried frangible bulb apparatus [see 4.2.1. (a)] held at  $-78^{\circ}$  and the bulbs were then sealed off at  $-196^{\circ}$ . Three consistent values for the heat of hydrolysis of liquid  $\text{SbF}_5$  of  $-72.5 \pm 2$  kcal/mole were obtained using 0.1 M NaOH [see Table 4.8.1.]. Values were inconsistent using molar alkali only if the sample of  $\text{SbF}_5$  hydrolysed was small [see Table 4.8.2.]. The heat of hydrolysis of liquid  $\text{SbF}_5$  in molar alkali was  $-108 \pm 2$  kcal/mole.

Hydrolysis of  $\text{SbF}_5$  caused a white crystalline solid to be precipitated immediately in M NaOH and over a period of twelve hours with M/10 NaOH. A debye X-ray powder photograph of both these solids was taken on a 19 cm camera with filtered radiation from a copper target.

#### 4.9. Heat of Hydrolysis of Antimony Pentachloride

The antimony pentachloride used was reagent grade from B.D.H. It was further purified by trap to trap distillation on a vacuum line. With successive distillations the deep yellow colour was slowly reduced in intensity but samples were never obtained which were absolutely colourless. No analysis was done to check the purity of the sample, but a 1 - 2% error factor was allowed to compensate for this expected inaccuracy.

Antimony pentachloride was distilled into the bulbs (attached to U tubes) held at  $-78^{\circ}$  under vacuum and sealed off at  $-196^{\circ}$  [see section 4.2. and fig. 4.2.1.].

Many runs were required before six consistent results could be obtained. The highest heats of hydrolysis were taken to be correct, as impurities would be expected to reduce

Table 4.9.1.Heat of Hydrolysis of  $\text{SbCl}_5$  in 1.004 M NaOH.

Weight of $\text{SbCl}_5$ (in gms.)	Heat of Hydrolysis (in kcals/mole)	
0.3292	-129	
0.3012	-134	
0.3168	-134	
0.3458	-128	
0.2350	-130	
0.2452	-131	
0.3902	-100	} from one sample
0.4055	-111	
0.1270	-111	
0.09212	-97	} from one sample
0.1308	-95	
0.0920	-95	

these  
values  
were  
rejected

Heat of hydrolysis of liquid  $\text{SbCl}_5$  =  $-131 \pm 7$  kcals/mole.

this value. Runs with some bulbs filled with  $\text{SbCl}_5$  from the same sample gave similar results, some being very low in value. Six consistent readings were eventually obtained from three different samples of antimony pentachloride [see Table 4.9.1.]. From these the heat of hydrolysis of liquid  $\text{SbCl}_5$  in molar sodium hydroxide was found to be  $-131 \pm 7$  kcals/mole. Hydrolysis of antimony pentachloride caused immediate precipitation of a white crystalline solid in molar sodium hydroxide and precipitation after about 12 hr. with M/10 sodium hydroxide. A debye powder photograph of both these solids was taken on a 19 cm. camera with filtered radiation from a copper target.

#### 4.10. Heat of Alkaline Hydrolysis of Xenon Difluoride

Xenon difluoride was made by irradiation of a mixture of xenon and fluorine with ultra violet light. It was distilled into the frangible bulbs, attached to U tubes, held at  $-78^\circ$  [see section 4.2.]. The bulbs were then pumped on at  $-78^\circ$  for half an hour to remove any xenon and fluorine which might have resulted from decomposition during distillation. The bulbs were then sealed off at  $-196^\circ$ .

The values obtained for the heat of alkaline hydrolysis of  $\text{XeF}_2$  in 0.1 M sodium hydroxide were not consistent [see Table 4.10.1.]. The deflection of the recorder rose fairly slowly over a period of eight minutes before levelling off to a constant deflection. With molar alkali, the hydrolysis of the xenon difluoride was more rapid - usually taking less than two minutes - but consistent results were still not obtained. Addition of platinum black to the molar alkali did not render results consistent.

Table 4.10.1.

## Heat of Hydrolysis of Xenon Difluoride.

Weight of XeF <sub>2</sub> (in gms.)	Heat of Hydrolysis (in kcals/mole)
0.0633	-28
0.0466	-41.5
0.05761	-48.2 using 0.106 M NaOH
0.1972	-74.9
0.0724	-108
0.0739	-60.1
0.09466	-74.6
0.1542	-57.9 using 1.004 M NaOH
0.0571	-82.1
0.1037	-60.4
0.1175	-65.2
0.1397	-52
0.07044	-66.1
0.1014	-69.4 using 1.004 M NaOH
0.0783	-75.7 and platinum dioxide
0.1065	-86.0
0.07031	-90.0

Using results obtained from hydrolysis of XeF<sub>2</sub> in 1.004 M NaOH + PtO<sub>2</sub> a value of  $-73 \pm 15$  kcals/mole could be suggested.

#### 4.11. Heat of Alkaline Hydrolysis of $\text{XeF}_2 \cdot 2\text{SbF}_5$

The  $\text{XeF}_2 \cdot 2\text{SbF}_5$  was prepared by distilling excess  $\text{SbF}_5$  on to  $\text{XeF}_2$  and warming the mixture to a little above room temperature.<sup>132</sup> Initially, the  $\text{XeF}_2$  dissolved in the  $\text{SbF}_5$  giving a clear yellow solution but, on allowing to stand for several hours at room temperature under vacuum, a yellow crystalline product separated from the colourless liquid of excess  $\text{SbF}_5$ . The yellow solid was pumped on for a day to remove any excess  $\text{SbF}_5$ .

The  $\text{XeF}_2 \cdot 2\text{SbF}_5$  was introduced into the frangible bulbs in a dry box and pumped on for a day under a "hard" vacuum before being sealed off at  $-196^\circ$  [see section 4.2. and fig. 4.2.1. (1)].

Initial runs were carried out using 0.1 M NaOH and gave a consistent heat of hydrolysis of  $-219 \pm 2$  kcal/mole [see Table 4.11.1.]. Hydrolysis using molar sodium hydroxide gave results which were not so consistent; a value being obtained for the heat of hydrolysis of  $\text{XeF}_2 \cdot 2\text{SbF}_5$  in molar sodium hydroxide of  $-281 \pm 7$  kcal/mole [see Table 4.11.2.].

Hydrolysis of  $\text{XeF}_2 \cdot 2\text{SbF}_5$  resulted in the immediate precipitation of a white crystalline solid in molar sodium hydroxide and precipitation only after standing for about twelve hours with M/10 sodium hydroxide. A Debye X-ray powder photograph of both these white solids was taken.

Table 4.11.1.

Heat of Hydrolysis of  $\text{XeF}_2 \cdot 2\text{SbF}_5$  in 0.1006 M NaOH.

Weight of $\text{XeF}_2 \cdot 2\text{SbF}_5$ (in gms.)	Heat of Hydrolysis of $\text{XeF}_2 \cdot 2\text{SbF}_5$ (in kcals/mole)
0.0598	-220
0.0535	-219
0.0692	-218
0.1354	-219
0.0954	-218

Heat of hydrolysis of solid  $\text{XeF}_2 \cdot 2\text{SbF}_5 = -219$  kcals/mole.

Table 4.11.2.

Heat of Hydrolysis of  $\text{XeF}_2 \cdot 2\text{SbF}_5$  in 1.004 M NaOH.

Weight of $\text{XeF}_2 \cdot 2\text{SbF}_5$ (in gms.)	Heat of Hydrolysis of $\text{XeF}_2 \cdot 2\text{SbF}_5$ (in kcals/mole)
0.05747	-280
0.08783	-278
0.1151	-274
0.1213	-275
0.1744	-290
0.1065	-287

Heat of hydrolysis of solid  $\text{XeF}_2 \cdot 2\text{SbF}_5 = -281 \pm 7$  kcals/mole.

## 5. Some Physical Properties of $\text{XeF}_2 \cdot 2\text{SbF}_5$

### 5.1. Determination of the Melting and Boiling Point of $\text{XeF}_2 \cdot 2\text{SbF}_5$ and the Study of Possible Modes of Thermal Decomposition of the Sample below its Boiling Point

$\text{XeF}_2 \cdot 2\text{SbF}_5$  [see section 4.11. for preparation] was introduced into the silica vessel [see fig. 5.1.1.] in a dry box. A fine capillary was placed (open end downwards) in this silica apparatus to facilitate measurement of the boiling point of the compound. This system was then attached to a vacuum line through a concentrated sulphuric acid manometer and a tube filled with dry potassium iodide paper.

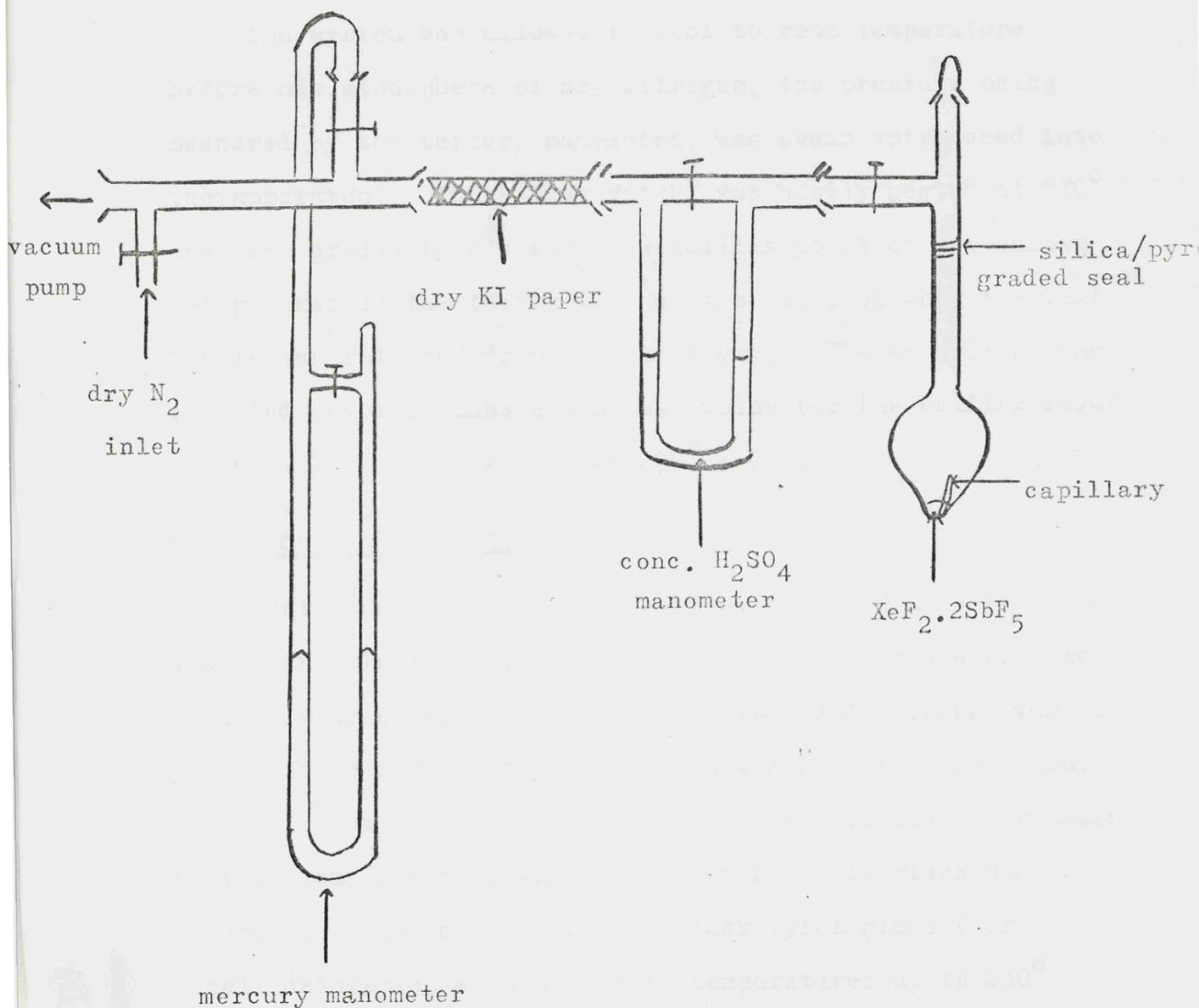
The system was pumped on for a day, to ensure the complete absence of moisture, before one atmosphere of dry nitrogen was introduced. The vessel containing the yellow solid was then slowly heated, using an oil bath, until the solid just began to melt; the temperature of the bath at this point being noted. The temperature of the oil bath was then raised a further  $5^\circ$  and allowed to slowly cool; the temperature being noted when the liquid just began to solidify. This experiment was repeated several times and a mean value for the melting point of the adduct  $\text{XeF}_2 \cdot 2\text{SbF}_5$  of  $63^\circ \pm \frac{1}{2}^\circ\text{C}$  was obtained.

The apparatus was evacuated and the temperature of the oil bath slowly increased. As the temperature rose a slight depression of the sulphuric acid manometer was noted but this was attributed to "degassing" of the  $\text{XeF}_2 \cdot 2\text{SbF}_5$  because, when the manometer tap was opened and the gas released, no decoloration of the potassium iodide paper resulted. On

Figure 5.1.1.

Apparatus for Study of Decomposition and Boiling Point

of  $\text{XeF}_2 \cdot 2\text{SbF}_5$



continuing to increase the temperature of the oil bath, no further change in the pressure shown by <sup>the</sup> manometer was noted. At  $160^{\circ}$   $\text{XeF}_2 \cdot 2\text{SbF}_5$  was seen to condense on cooler parts of the reaction vessel. The oil bath was heated to  $220^{\circ}$  under vacuum but no decomposition was observed.

The system was allowed to cool to room temperature before one atmosphere of dry nitrogen, the pressure being measured by the mercury manometer, was again introduced into the apparatus. The silica vessel was slowly heated to  $230^{\circ}$  and then gradually cooled; the boiling point of the sample being taken as the temperature of the oil bath when the last bubble was released from the capillary. The experiment was repeated several times and a mean value for the boiling point of  $\text{XeF}_2 \cdot 2\text{SbF}_5$  was taken to be  $220^{\circ} \pm 5^{\circ}\text{C}$ .

## 5.2. Conductivity Studies

Preliminary studies were carried out to find a suitable vessel and electrode material for determining the electrical conductivity of  $\text{XeF}_2 \cdot 2\text{SbF}_5$ . The compound  $\text{XeF}_2 \cdot 2\text{SbF}_5$  was found not to decompose, or etch soda glass, at temperatures up to  $100^{\circ}$  under vacuum but on standing for more than four hours at this temperature slight attack of the soda glass was observed. The adduct did not attack pyrex glass (or itself decompose) when heated to temperatures up to  $230^{\circ}$  under vacuum - however, all traces of moisture had to be rigorously excluded from the apparatus.

Liquid  $\text{XeF}_2 \cdot 2\text{SbF}_5$  did not react with platinum wire, but decomposition resulted at the surface of tungsten wire: xenon being identified by the strong blue colour resulting from passing an electric discharge through the vessel and tun-

gsten hexafluoride being identified by  $^{19}\text{F}$  spectroscopy of the volatile reaction products. Decomposition of liquid  $\text{XeF}_2 \cdot 2\text{SbF}_5$  also resulted with copper wire.

The construction of a conductivity cell proved more difficult than expected. Vacuum tight seals between pyrex glass and platinum wire proved impossible and, as yet, no apparatus has been built using soda glass and platinum wires which has not either cracked before completion, or which has held a vacuum for longer than half an hour.

### 5.3. Raman Studies on Solid and Liquid $\text{XeF}_2 \cdot 2\text{SbF}_5$

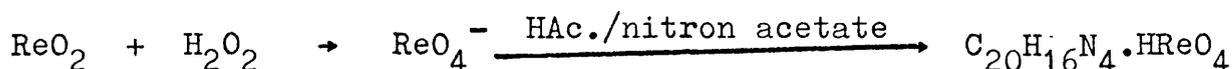
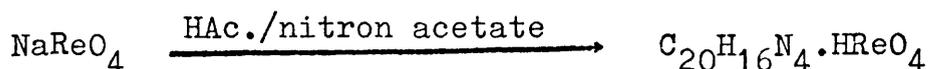
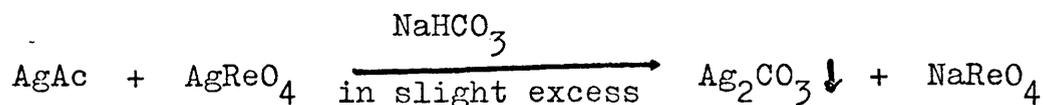
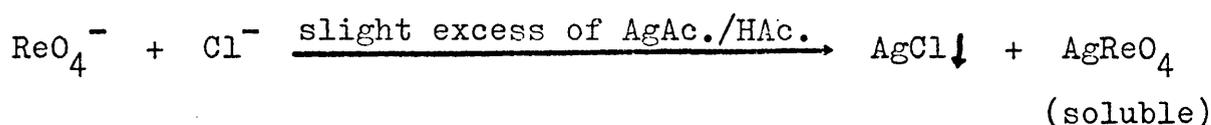
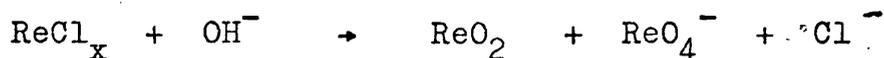
For all Raman studies a cell made out of square sided pyrex glass tubing was used. Each cell was about 1 ml. in volume and attached to a tap so that after a solid spectrum had been obtained the sample could be degassed by heating above  $60^\circ\text{C}$ , under a dynamic vacuum, before liquid Raman studies were obtained. Spectra were recorded of solid  $\text{XeF}_2 \cdot 2\text{SbF}_5$ , (using a circulating coil of water at  $80^\circ$ )<sup>133</sup> and on the solid after it had been cooled from the liquid.

Raman spectra were recorded on a Coderg PH 1 spectrometer, equipped with helium - neon laser excitation (632.8 AM., 60 MW) and a PO transfer plate with multipass optics.

Appendix IAnalysis for Rhenium<sup>134</sup> (gravimetrically)

Samples analysed were rhenium chlorides: hence the chloride had first to be removed as chloride ion interferes with the gravimetric analysis of rhenium using nitron acetate.

The basic analysis scheme was:



The rhenium chloride was dissolved in sodium hydroxide, boiled for several minutes and the precipitated rhenium dioxide filtered. Dilute acetic acid was added to the filtrate before the solution was boiled and a slight excess of silver acetate added with stirring. The solution was then boiled for a further few minutes to allow the silver chloride precipitate to coagulate. After cooling to room temperature in a dark cupboard, the white precipitate was filtered through a weighed sinter [see Appendix III] and the filtrate was boiled with a slight excess of sodium bicarbonate. All the silver ion precipitated from solution as silver carbonate leaving the filtrate as a solution of sodium perrhenate.

The rhenium dioxide was oxidised to perrhenate by

boiling with excess twenty volume hydrogen peroxide. Both solutions of perrhenate were then combined, reduced in volume to a minimum and ten percent nitron acetate solution added. Before filtering through a weighed sintered glass filter, the solution was again reduced in volume and then cooled in ice (because nitron salts are appreciably soluble in water). The nitron perrhenate precipitate was washed successively with nitron acetate solution, saturated nitron rhenate solution and finally with a little cold water before being dried at  $110^{\circ}\text{C}$  and after cooling weighed to constant weight.

Appendix IIAnalysis for Tungsten<sup>135</sup> (Tannin-Antipyrine Method)

All tungsten(VI) compounds analysed were initially hydrolysed in 0.1 M sodium hydroxide. The solutions were made faintly ammoniacal and sufficient distilled water was added till the volume was ~ 200 mls. Each analysis sample contained no more than 0.15 gm. of tungstate ion. Six to seven mls. of concentrated  $H_2SO_4$  and seven to eight gms. of  $(NH_4)_2SO_4$  were added to the analysis solution and the mixture was heated to boiling. The solution was then heated with 10% tannin solution and allowed to boil for a further few minutes. As the solution cooled to room temperature, a flocculent dark brown precipitate separated. When cold, 10 mls. of 10% antipyrine ("phenazone") were stirred into the solution and the precipitate was filtered through a previously weighed porcelain filtering crucible. The precipitate was washed with a special wash solution\*, ignited to constant weight at  $800^\circ C$  and weighed as tungsten trioxide.

\* The special wash liquid contained 1 ml. of concentrated sulphuric acid, 10 gms. of ammonium sulphate and 0.4 gm. of antipyrine in 200 mls. of distilled water.

Appendix IIIAnalysis for Chloride<sup>136</sup> (Gravimetrically as Silver Chloride)

Heavy metals interfere with chloride analysis by this method; hence they are initially removed by precipitation [for rhenium, see Appendix I and for tungsten see Appendix II].

Ten drops of concentrated nitric acid were added to approximately 0.15 gms. of chloride solution (made up to 200 mls. volume with distilled water) and the solution was then heated to 80° before a slight excess of 0.2 M silver nitrate solution was slowly added with continual stirring. The resulting suspension was heated for a further few minutes to allow the precipitate to coagulate before the solution was placed in a dark cupboard to cool. The solution was then filtered through a weighed sintered glass filter and the precipitate was further washed using distilled water containing one drop of concentrated nitric acid per 100 mls. of distilled water (to prevent peptisation of the silver chloride). The filtrate was dried at 110° for an hour, cooled to room temperature and weighed to constant weight as silver chloride.

REFERENCES

1. J. H. Canterford and R. Colton in "Halides of the 2nd and 3rd Row Transition Metals", A Wiley Interscience Publication, 1968, p.28.
2. O. Ruff and P. Ipsen, Ber., 1903, 36, 1777.
3. B. Cohen A. J. Edwards, Mary Mercer and R. D. Peacock, Chem. Comm., 1965, 322.
4. K. Dehnicke, Angew Chem., 1962, 74, 495.
5. K. S. Vorres and F. B. Dutton, J. Am. Chem. Soc., 1955, 77, 2019.
6. A. W. Savage, J. Am. Chem. Soc., 1956, 78, 2700.
7. V.L. Kolditz, V. Newmann and G. Kilch, Z. anorg. Chem., 1963, 325, 275.
8. V.L. Kolditz and G. Frucht, Z. anorg. Chem., 1961, 312, 11.
9. V.L. Kolditz, C. Kurschner and V.S. Calov, Z. anorg. Chem., 1964, 329, 172.
10. G. B. Hargreaves and R. D. Peacock, J. Chem. Soc., 1960, 2618.
11. H. L. Roberts and N. H. Ray, J. Chem. Soc., 1960, 665.
12. G. W. Fraser, R. D. Peacock and P. M. Watkins, Chem. Comm., 1968, 1257.
13. G. W. Fraser, Mary Mercer and R. D. Peacock, J. Chem. Soc., 1967, 1091.
14. R. D. Peacock and D. F. Stewart, Inorg. Nucl. Chem. Lett., 1967, 3, 255.
15. I. Haigh, personal communication.
16. B. Cohen and A. G. MacDiarmid, Chem. Ind., 1962, 1866.
17. C. I. Merril OTS. U.S. Dept. Commerce AD 285205 [Chem. Abs., 1964, 60, 6463].

18. G. W. Fraser, C. Joy W. Gibbs and R. D. Peacock,  
J. Chem. Soc., 1970, 1708.
19. P. M. Watkins, Ph.D. Thesis, Leicester University, 1968.
20. T. A. O'Donnell and D. F. Stewart, Inorg. Chem.,  
1966, 5, 1434.
21. Mary Mercer, Chem. Comm., 1967, 119.
22. I. Haigh, personal communication.
23. T. A. O'Donnell and D. F. Stewart, Nature, 1966, 210,  
836.
24. F. O. Sladky, P. A. Bulliner and N. Bartlett, J. Chem.  
Soc. A, 1969, 2179.
25. Gibler, unpublished results.
26. N. K. Jha, Ph.D. Thesis, University of British Columbia,  
1965.
27. N. Bartlett and D. H. Lohmann, J. Chem. Soc., 1964, 619.
28. W. Noddack, Z. Electrochem., 1928, 34, 627.
29. F. Scharcher, Chem. Listy, 1929, 23, 632.
30. A. A. Woolf, Quart. Rev., 1961, 15, 372.
31. R. Colton, Nature, 1962, 193, 872.
32. W. Geilmann, F. W. Waggi and W. Biltz, Z. anorg. allgem.  
Chem., 1933, 214, 248.
33. R. Colton, Nature, 1962, 194, 374.
34. J. H. Canterford, T. A. O'Donnell and A. B. Waugh,  
unpublished observations.
35. C. M. Nelson, G. E. Boyd and W. T. Smith, J. Am. Chem.  
Soc., 1954, 76, 348.
36. D. Brown and R. Colton, J. Chem. Soc., 1964, 714.
37. J. H. Canterford and A. B. Waugh, unpublished observations.

38. J. H. Canterford and R. Colton in "Halides of the 2nd and 3rd Row Transition Metals", Wiley Interscience Publishers, 1968, p. 285.
39. S. A. Shchukarev and A. V. Suvorov, Russian J. Inorg. Chem., 1961, 6, 763.
40. D. A. Edwards and A. A. Woolf, J. Chem. Soc. A, 1966, 91.
41. H. Selig, F. A. Cafasso, D. N. Gruen and J. G. Malm, J. Chem. Phys., 1962, 36, 3440.
42. B. N. Figgis in "Introduction to Ligand Fields", Interscience Publishers, 1964, chapter 10.
43. W. E. Dasent in "Non Existent Compounds", Edward Arnold Ltd., 1965, p. 117 - 119.
44. M. Baaz, V. Gutmann and M. Y. A. Talaat, Mh. Chem., 1961, 92, 714.
45. V. Gutmann, U.S. Dept. Comm. Office Tech. Serv., P.B. Rept. 152, p. 848.
46. W. R. Smith and J. E. Hora, J. Am. Chem. Soc. 1904, 265, 632.
47. W. Biltz and E. Meinecke, Z. anorg. allgem. Chem., 1923, 131, 1.
48. W. Biltz and K. Jeep, Z. anorg. allgem. Chem., 1927, 162, 32.
49. N. A. Pushin and Makuc, Z. anorg. allgem. Chem., 1938, 237, 177.
50. J. P. King and J. W. Cobble, J. Am. Chem. Soc., 1960, 82, 2111.
51. S. A. Shchukarev, G. I. Novikov, I. V. Vasil'kova, A. V. Suvorov, N. V. Andreeva, B. N. Sharupin and A. B. Baev, Russian J. Inorg. Chem., 1960, 5, 802.

52. J.A.N.A.F. "Thermochemical Tables", The Dew Chemical Co., Midland, Mich.
53. O. Ruff and W. Kwasnik, Z. anorg. Chem., 1932, 209, 113.
54. W. M. Latimer in "The Oxidation State of the Elements and their Potentials in Aqueous Solution", 2nd Edition, New Jersey, Prentice Hall, 1952.
55. R. D. Peacock, personal communication.
56. R. Colton, J. Chem. Soc., 1962, 2078.
57. M. Hagan and A. Sieverts, Z. anorg. allgem. Chem., 1933, 215, 111.
58. J. E. Fergusson and J. H. Hickford, Aust. J. Chem., 1970, 23, 453.
59. L. B. Handy and F. E. Bruickman, Chem. Comm., 1970, 214.
60. A. M. Noble and J. M. Winfield, Chem. Comm., 1969, 151.
61. P. A. W. Dean and D. F. Evans, J. Chem. Soc., A, 1968, 1154.
62. A. M. Noble and J. M. Winfield, J. Chem. Soc. A, 1970, 501.
63. F. N. Tebbe and E. L. Meutterties, Inorg. Chem., 1968, 7, 172.
64. A. M. Noble and J. M. Winfield, Inorg. and Nucl. Chem. Lett., 1968, 4, 339.
65. T. A. O'Donnell and D. F. Stewart, J. Inorg. and Nucl. Chem. Lett., 1962, 24, 309.
66. G. W. Fraser, unpublished work.
67. H. J. Clase, A. M. Noble and J. M. Winfield, Spectrochem. Acta., 1969, 25A, 293.
68. H. F. Priest and W. S. Schumb, J. Am. Chem. Soc., 1948, 70, 3378.

69. J. Schröder and F. J. Grewe, *Chem. Ber.*, 1970, 1536.
70. V. A. Nieberlein and H. Kenworthy, U.S. Bureau of Mines Rept. Invest. No. 5539 [*Chem. Abs.*, 1960, 54: 4298(a)].
71. R. D. Peacock, *J. Chem. Soc.*, 1957, 467.
72. G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.*, 1958, 2170.
73. G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.*, 1958, 4390.
74. H. C. Clark and H. J. Eméleus, *J. Chem. Soc.*, 1957, 4778.
75. G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.*, 1957, 4212.
76. O. E. Myers and A. P. Brady, *J. Phys. Chem.*, 1960, 64, 591.
77. A. C. Legon, *Trans. Far. Soc.*, 1969, 65, 2595.
78. D. M. Adams, G. W. Fraser, D. M. Morris and R. D. Peacock, *J. Chem. Soc. A*, 1968, 1131.
79. R. V. G. Ewans and M. W. Lister, *Trans. Far. Soc.*, 1938, 34, 1358.
80. M. Kimura, V. Schomaker, W. Smith and B. Weinstock, *J. Chem. Phys.*, 1968, 48, 4001.
81. G. H. Cady and G. B. Hargreaves, *J. Chem. Soc.*, 1961, 1563.
82. R. Kewsley, K.S.R. Murty and T. M. Sugden, *Trans. Far. Soc.*, 1960, 56, 173.
83. D. P. Craig and E. A. Magnusson, *J. Chem. Soc.*, 1956, 4895.
84. H. F. Leach and H. L. Roberts, *J. Chem. Soc.*, 1960, 4693.

85. L. H. Cross, H. L. Roberts, P. Goggin and L. A. Woodward, *Trans. Far. Soc.*, 1960, 56, 945.
86. J. E. Griffith, *Spectrochem. Acta*, 1967, 23A, 2145.
87. C. W. Gullikson, J. Red Nielson and A. T. Stair, Jun., *J. Mol. Spectroscopy*, 1957, 1, 151.
88. T. G. Burke, D. F. Smith and A. H. Nielson, *J. Chem. Phys.*, 1952, 20, 447.  
K. N. Tanner and A. B. Duncan, *J. Am. Chem. Soc.*, 1951, 73, 1164.
89. P.A.G. O'Hare and W. N. Hubbard, *J. Phys. Chem.*, 1966, 70, 3353.
90. J. Schröder and F. J. Sieben, *Chem. Ber.*, 1970, 103, 76.
91. J. L. Settle, H. F. Feder and W. N. Hubbard, *J. Phys. Chem.*, 1961, 65, 1337.
92. K. Mucker, G. S. Smith and Q. Johnson, *Acta Cryst.*, 1968, B24, 874.
93. I. Noddack and W. Noddack, *Z. anorg. Chem.*, 1933, 215, 177.
94. V. G. Tronev and R. A. Dovylatshina, *Russian J. Inorg. Chem.*, 1965, 10, 161.
95. P. W. Fraiss, A. Guest and C. J. L. Lock, *Can. J. Chem. Soc.*, 1969, 47, 1069.
96. M. J. Bennett, F. A. Cotton, B. M. Foxman and D. F. Stokely, *J. Am. Chem. Soc.*, 1967, 89, 2759.
97. R. E. Mc. Carley and B. A. Torp, *Inorg. Chem.*, 1963, 2, 540.
98. M. Elder and B. R. Penfold, *Inorg. Chem.*, 1966, 5, 1197.
99. R. Colton and G. Wilkinson, *Chem. Ind.*, 1959, 1314.

100. R. D. Peacock, A. J. E. Welch and C. F. Wilson,  
J. Chem. Soc., 1958, 2901.
101. J. E. Fergusson, B. H. Robinson and W. R. Roper,  
J. Chem. Soc., 1962, 2113.
102. R. Colton and R. L. Martin, Nature, 1965, 205, 239.
103. I. R. Anderson and J. C. Sheldon, Inorg. Chem.,  
1968, 7, 2602.
104. R. H. Busey, K. H. Gayer, R. A. Gilbert and R. B.  
Bevan, Jr., J. Phys. Chem., 1966, 70, 2609.
105. G. E. Boyd, J. W. Cobble and W. T. Smith, J. Am.  
Chem. Soc., 1953, 75, 5783.
106. J. E. McDonald, J. P. King and J. W. Cobble, J.  
Phys. Chem., 1960, 64, 1345.
107. V. M. McRae, R. D. Peacock and D. Russel, Chem.  
Comm., 1969, 62.
108. H. A. Levy and P. A. Argon in "Noble Gas Compounds",  
Ed. H. H. Hyman, University of Chicago press,  
Chicago, 1963, p. 221.
109. N. Bartlett, C. Campbell and F. I. Sladky, paper  
presented at the 154th Meeting of the American  
Chemical Society, Chicago, Sept. 12th, 1967 [Abst.  
1967, K17].
110. J. J. Fuggle, personal communication to R. D.  
Peacock.
111. W. A. Mazeika and H. M. Newmann, Inorg. Chem., 1966,  
5, 309.
112. R. W. G. Wyckoff in "Crystal Structures", 2nd ed.  
Vol. 3, Interscience Publishers, 1965, p. 329.

113. "Handbook of Chemistry and Physics", Chemical Rubber Co., 1964, Editor in Chief, R. C. Weast.
114. A. A. Woolf, personal communication to R. D. Peacock.
115. M. J. Nichols, Ph.D. Thesis, Durham, 1958.
116. J. G. Malm, B. D. Holt and R. W. Bane in "Noble Gas Chemistry", University of Chicago Press, Ed. H. H. Hyman, 1963, p. 169.
117. F. A. Cotton and G. Wilkinson in "Advanced Inorganic Chemistry", 2nd ed., Interscience Publishers, 1967, p. 597.
118. J. H. Holloway, personal communication to R. D. Peacock.
119. D. F. Smith, J. Chem. Phys., 1963, 38, 270.
120. K. H. Boswijk, J. van der Meide, A. Vos and E. M. Wiebenga, Acta Cryst., 1956, 9, 274.
121. N. Bartlett, W. Wechsberg, F. O. Sladky, P. A. Bulliner, G. R. Jones and R. D. Burbank, Chem. Comm., 1969, 703.
122. P. A. W. Dean and R. J. Gillespie, J. Am. Chem. Soc., 1969, 91, 7260.
123. P. A. W. Dean and R. J. Gillespie, J. Am. Chem. Soc., 1969, 91, 7264.
124. A. F. Kapustinskii, Quart. Rev. Chem. Soc., 1956, 10, 283.
125. Elmsley, Feeney and Sutcliffe in "High Resolution Nuclear Magnetic Resonance", two Vols. Pergamon Press.
126. B. N. Figgis and R. S. Nyholm, J. Chem. Soc., 1958, 4190.

127. P. M. Selwood in "Magnetochemistry", 2nd Ed., Interscience Publishers, New York, 1956, p. 92.
128. E. L. Muetterties and W. D. Phillips, J. Am. Chem. Soc., 1959, 81, 1084.
129. E. Schnell and E. G. Rochow, J. Am. Chem. Soc., 1956, 78, 4178.
130. G. B. Hargreaves, Ph.D. Thesis, University of London, 1959.
131. G. J. Ewing and C. J. Mazac, Anal. Chem., 1938, 11, 1575.
132. A. J. Edwards, J. H. Halloway and R. D. Peacock, Proc. Chem. Soc., 1963, 275.
133. D. Waddington, unpublished design.
134. R. D. Peacock in "The Chemistry of Technetium and Rhenium", Elsevier Publishing Co., 1966, p. 123.  
R. Colton in "The Chemistry of Rhenium and Technetium", Interscience Publishers, 1965, p. 21.
135. A. L. Vogel in "A Text Book of Quantitative Inorganic Analysis", Longmans, 1962, p. 567.
136. A. L. Vogel in "A Text Book of Quantitative Analysis", Longmans, 1962, p. 461.