

THERMOCHEMICAL AND RELATED PROPERTIES OF HALIDES
OF REFRACTORY METALS.

Submitted in part fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Science of the University of Leicester.

I. HAIGH

1973.

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STATEMENT

The accompanying thesis submitted for the degree of Doctor of Philosophy and entitled "Thermochemical and Related Properties of Halides of Refractory Metals" is based on work conducted by the author mainly in the Department of Chemistry of the University of Leicester during the period between October 1968 and September 1971.

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.

I Haigh

Date.

28/2/73

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SUMMARY

The basis of this thermochemical study has been the determination of enthalpies of formation from measured enthalpies of hydrolysis.

The enthalpies of formation of the gaseous hexafluorides of tungsten, molybdenum and rhenium, the solid pentafluorides of tungsten and molybdenum and the solid oxytetrafluorides of tungsten and molybdenum have been determined as -411.85 ± 1.4 , -374.8 ± 2.5 , -322.6 ± 3.2 , -349.9 ± 3.5 , -331.4 ± 1.3 , -358.5 ± 2.2 , and -329.8 ± 1.2 kcal mol⁻¹ respectively. Bond strengths and stabilities have been discussed.

The enthalpies of formation of the salts $\overline{\text{V}}\text{KW}\overline{\text{F}}_6$, $\overline{\text{V}}\text{KMo}\overline{\text{F}}_6$ and $\overline{\text{IV}}\text{K}_2\overline{\text{W}}\overline{\text{Cl}}_6$ have been determined as -532.0 ± 2.6 , -493.25 ± 1.9 and -329.9 ± 1.8 kcal mol⁻¹ respectively.

From the enthalpies of formation, the first electron affinities of tungsten and molybdenum hexafluorides and the second electron affinity of tungsten hexachloride have been estimated as 117.9 ± 4 , 115.4 ± 4 and -52.0 kcal mol⁻¹ respectively (at 0 K). The fluoride ion affinities of solid tungsten and molybdenum pentafluorides have also been estimated as 119.1 ± 6 and 98.1 ± 6 kcal mol⁻¹ respectively (at 298 K).

The use of fluorides in tungsten halogen incandescent lamps has been investigated. Using infra-red spectroscopy, it has been found that all the covalent fluorides which were investigated formed silicon tetrafluoride in small quartz envelope incandescent lamps.

Radiochemical tracer experiments in twin filament lamps

have shown that tungsten is transferred from a cold (non-running) filament to a hot (running) filament in the presence of a suitable fluoride. The distribution of the transferred tungsten has been measured and compared with transfer in the presence of a bromide. The hypothesis that the presence of fluorine in a lamp leads to the setting up of a regenerative cycle which minimises the rate of formation of "hot spots" and hence extends filament life is supported.

Preliminary attempts to prepare mixed bromide fluorides of tungsten (VI) have shown N.M.R. evidence for tungsten(VI) bromide pentafluoride.

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CHAPTER 1 . INTRODUCTION.1.1. The Development of Inorganic Fluorine Chemistry.

Because of the very high oxidation potential of F^- (-2.87eV)¹, early attempts to prepare fluorine by electrolytic methods in aqueous solutions failed. Fluorine was first isolated by Moissan² in 1886 by electrolysis of fluorides with no other anions present. However, it was not until 1946 that a cheap, safe and efficient source of fluorine became readily available.

Since that time progress has been rapid, with much of the early work of Ruff and co-workers being repeated and in some cases corrected. For example, the highest fluoride of osmium, originally reported to be the octafluoride³ has since been shown to be the hexafluoride⁴. Also, in this thesis (section 2.5.2), the enthalpy of formation of rhenium hexafluoride, originally reported as -275kcal mol^{-1} ⁵, has been shown to be $-322.6\text{kcal mol}^{-1}$.

In the field of refractory metal fluorides, significant advances have been made in the preparative line (for example, the recent ingenious preparation of tungsten pentafluoride)⁶, and in the reactions of the fluorides (for example, the comparison of the reactions of tungsten and molybdenum hexafluorides⁷). Some physical measurements have also been made, for example, the vapour pressure measurements on tungsten hexafluoride.⁸ Only a small amount of the thermochemistry of the transition metal fluorides has been investigated.

Some excellent reviews of some aspects of refractory metal fluorine chemistry are available.^{9 10 11}

1.2 Thermochemical Data on Refractory Metal Halides

The only pre 1960 experimental data on the fluorides are those of Ruff⁵ which are unreliable (see previous Section). However, estimates of some enthalpies of formation¹² were made. These have since proved to be very unreliable. The first reliable enthalpies of formation were determined in 1960 by Myers and Brady¹³ (WF_6 , MoF_6 , and NbF_5). The development of the fluorine bomb calorimeter led to some precise and reliable enthalpy data, which have, however, been limited to the binary fluorides, (for example, tungsten hexafluoride)¹⁴. Some data, have been obtained by mass spectrometric methods, for example, the enthalpy of formation of gaseous tungsten oxytetrafluoride,¹⁵ but this method lacks accuracy. In this thesis (Chapter 2) the hydrolysis method of Myers and Brady has been extended.

Thermochemical data on refractory metal chlorides are in far greater abundance, thanks to the work of Shchukarev and co-workers (on, for example, molybdenum and tungsten chlorides and oxychlorides¹⁶).

1.3. Application of Thermochemical Data

One of the many applications of existing thermochemical data on tungsten fluorides has been the prediction (based on the temperature dependence of the equilibrium $W(s) + nF(g) \rightleftharpoons WF_n(g)$) that tungsten will be deposited from gaseous tungsten fluorides at temperatures above $\sim 3100^\circ C$ whereas below that temperature fluorine will attack solid tungsten. These are highly desirable characteristics for the so-called "tungsten fluorine" incandescent lamp since

the rate of formation of "hot spots" on tungsten filaments could then be minimised and the filament life extended (see also Chapter 3).

The proposed "tungsten fluorine" lamp would be of the same family as the well known quartz iodine lamp. The choice of iodine for the first tungsten halogen lamps was based on thermochemical data¹² which is now known to be incorrect.

1.4. The Aim of this Thesis.

The aim of the work described in this thesis has been to extend the thermochemical knowledge of fluorides (and to a lesser extent chlorides) of the refractory metals (particularly tungsten and molybdenum) in order that chemical reactions can be more easily understood.

In addition to this thermochemical study, a study of the "tungsten fluorine" lamp has been made.

CHAPTER 2. THERMOCHEMICAL PROPERTIES OF SOME FLUORIDES
(AND SOME CHLORIDES) OF REFRACTORY METALS.

2.1. Introduction

To understand chemical processes it is necessary to understand the energetics of the systems involved. Thermochemistry is a study of the determination and application of these energetics.

An important part of thermochemistry involves the determination of enthalpies of formation. The determination of enthalpies of formation of transition metal fluorides was neglected until recently and much work is still necessary. More data are available for transition metal chlorides (see Section 1.2.)

Although numerous methods have been used in the determination of enthalpies of formation, such methods may be classified in two groups: direct methods, involving the direct combination or dissociation of the elements concerned; and indirect methods, which invoke Hess's Law of constant heat summation*. One common method which has been used extensively in this thesis, for the determination of enthalpies of formation of transition metal fluorides (and K_2WCl_6), is the indirect method via the enthalpies of hydrolysis.

Footnote*

Hess's Law of constant heat summation (1840) states that if a reaction starting with the reagents in defined conditions and finishing with the products in defined conditions, is carried out in stages, the algebraic sum of the quantities of heat evolved in the separate stages is equal to the total evolution of heat when the reaction occurs directly.

From the enthalpies of formation in this thesis it has been possible to determine bond strengths, electron affinities and halide ion affinities for various compounds. These quantities are useful in comparisons of reactivities.

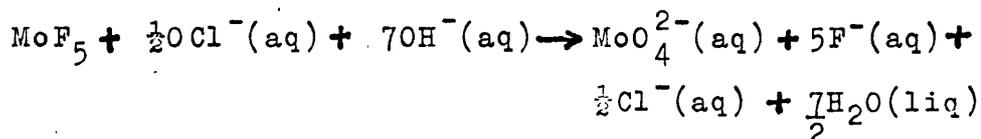
2.2. Useful Hydrolysis Reactions of Halides of Refractory Metals.

2.2.1. Hydrolysis of Tungsten and Molybdenum Halides.

The hydrolysis of tungsten (VI) and molybdenum (VI) halides in water or acidic solution is complex with the formation of tungsten or molybdenum blues. However, in alkaline solution the hydrolysis proceeds completely to form aqueous WO_4^{2-} or aqueous MoO_4^{2-} . This latter (alkaline) hydrolysis has previously been used in thermochemical determinations by Myers and Brady¹³ (for the enthalpies of formation of tungsten and molybdenum hexafluorides) and by Shchukarev and co-workers^{16,17} (for the enthalpies of formation of tungsten hexachloride and hexabromide).

Alkaline hydrolysis of halides of the lower oxidation states of tungsten or molybdenum is complex unless the products are oxidised to $\text{WO}_4^{2-}(\text{aq})$ or $\text{MoO}_4^{2-}(\text{aq})$. Shchukarev and co-workers^{16,17} have used hydrogen peroxide and bromine oxidations in the determination of the enthalpies of formation of molybdenum pentachloride and tungsten pentabromide respectively. In this thesis basic hypochlorite solutions have been used extensively, for example, molybdenum pentafluoride has been hydrolysed (Section 2.6.2) according to

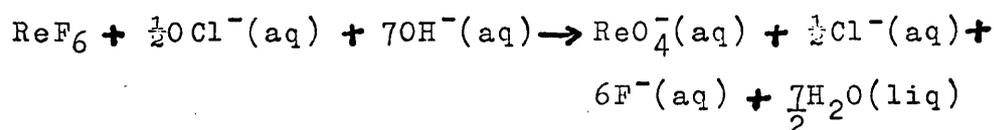
the equation



2.2.2. Hydrolysis of Rhenium Halides.

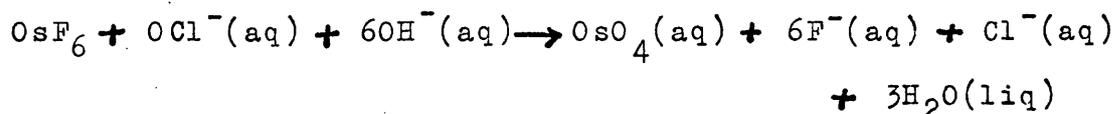
Rhenium heptafluoride, the only halide of rhenium (VII), is hydrolysed to ReO_4^- (aq) in alkaline solution¹⁸. Rhenium hexafluoride is hydrolysed to ReO_4^- (aq) and hydrated ReO_2 ¹⁹.

King and Cobble²⁰ have shown that basic hypochlorite solutions quantitatively oxidise ReCl_3 (c) to ReO_4^- (aq) giving a reaction useful for calorimetric determinations. Busey et al²¹ have since used a similar reaction to determine the enthalpy of formation of the hexachlororhenate (IV) ion. In this thesis (Section 2.5.2.) the basic hypochlorite solutions have been used to hydrolyse rhenium hexafluoride to ReO_4^- (aq) thus



2.2.3. Hydrolysis of Osmium Hexafluoride.

Osmium hexafluoride hydrolyses in alkaline solution to give OsO_4 (aq), F^- (aq) and OsF_6^{2-} (aq). Although the basic hypochlorite hydrolysis of osmium hexafluoride gives mainly OsO_4 (aq) according to the reaction



a certain amount of the stable species OsF_6^{2-} (aq) is also formed⁴.

2.3. Method for the Determination of Enthalpies of Hydrolysis and Formation.

2.3.1. Apparatus

In this thesis heats (enthalpies) of hydrolysis were determined using a simple calorimeter (Figure 2.3.1). The calorimeter consisted of a cylindrical Dewar vessel of approximately 150ml capacity (A). Into this fitted a teflon stopper (B) attached to an isothermal copper shield. A stirring rod (C), a heater(D) and a thermistor(E) were inserted into the calorimeter through holes in the stopper. A thin walled glass bulb (F) of known capacity (5-15ml known to 0.1ml), containing an accurately known mass of the compound to be hydrolysed, was fused on to the end of the stirring rod. A P.T.F.E. coated steel spike(G) rested on the bottom of the Dewar vessel. The whole calorimeter was contained in a copper case(H) which was immersed in a thermostatically controlled (25°C) water bath. The temperature of water bath was controlled 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 air temperature was slightly greater than 25°C*.

The temperature changes of the contents of the calorimeter were compared using a single thermistor (S.T.C. Ltd. type F - of resistance \sim 200 ohms) incorporated in a Wheatstone bridge circuit (Figure 2.3.2). The Wheatstone

Footnote *

The experiments were discontinued if the air temperature rose more than a few degrees above 25°C.

bridge was supplied by a 1.5 - 4 volt stabilised supply. The thermistor made up one arm of the bridge. Large resistances were used for the two ratio arms of the bridge to minimise the current and so prevent any internal heating effect in the thermistor. A recorder (type Kipp BD2 or Kipp-Zonen BD5), used as the galvanometer arm of the bridge, measured the out of balance of the bridge caused by the changing resistance of the thermistor with temperature. The recorder was calibrated by supplying a known amount of heat into the calorimeter through the heater.

The heater consisted of 38 swg 'Eureka' resistance wire wound round a glass tube, encased in an outer glass tube, and the whole sealed with 'Araldite'*. (Figure 2.3.3) The resistance of the heater was accurately known. The heater circuit (Figure 2.3.4) was supplied by a 6 volt stabilised supply. The current supplied to the heater was controlled by a variable resistance in series with the heater, and determined by measuring (with a potentiometer) the potential difference across a standard 10 ohm resistance in series with the heater. The potentiometer was supplied from a 2 volt stabilised supply.

2.3.2. Experimental Procedure.

(a) Summarised Procedure.

For each determination a frangible glass bulb, containing a known mass of the compound, was broken into

Footnote *

Tradename

FIGURE 2.3.1. The Calorimeter.

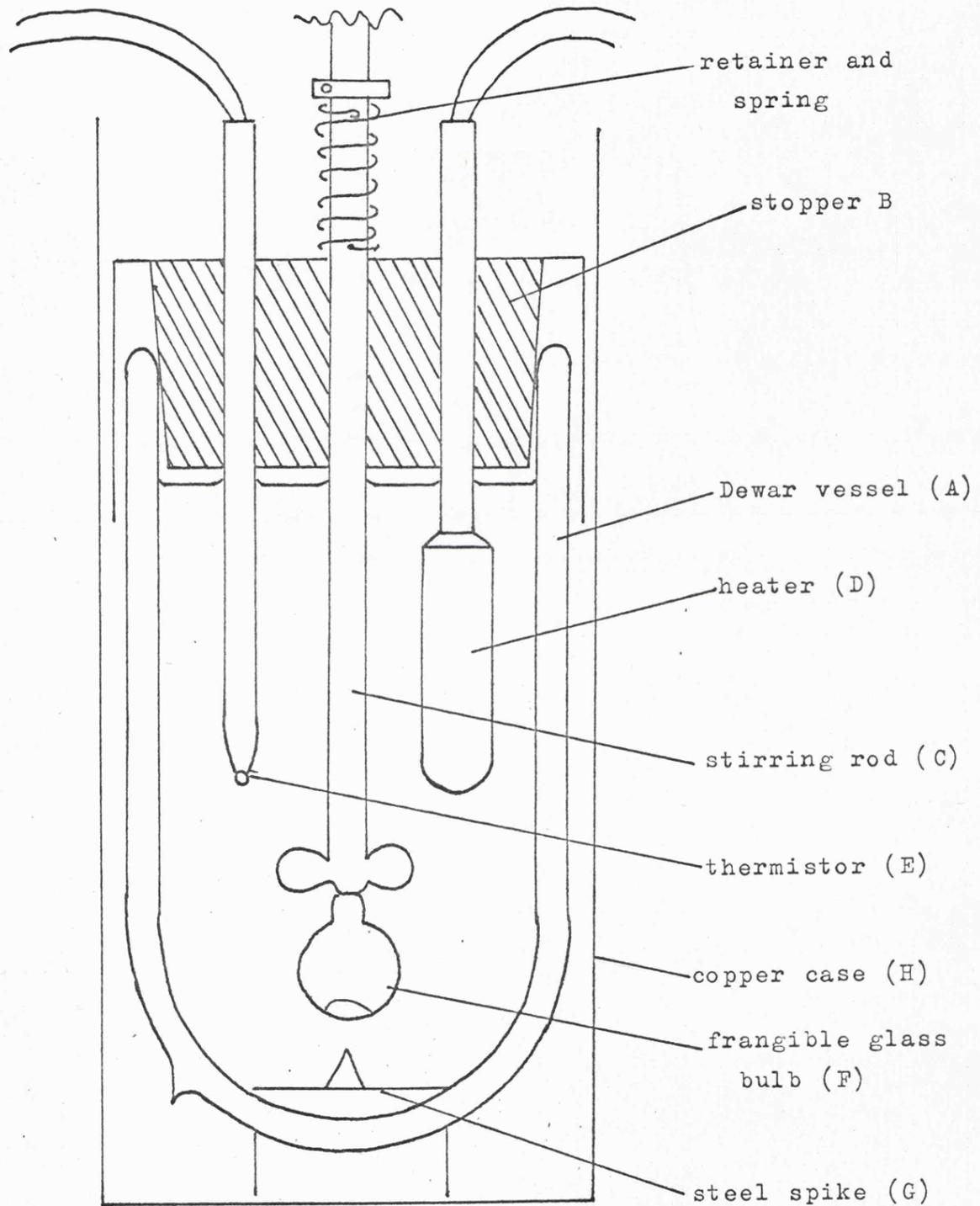


FIGURE 2.3.2. The Wheatstone Bridge Circuit.

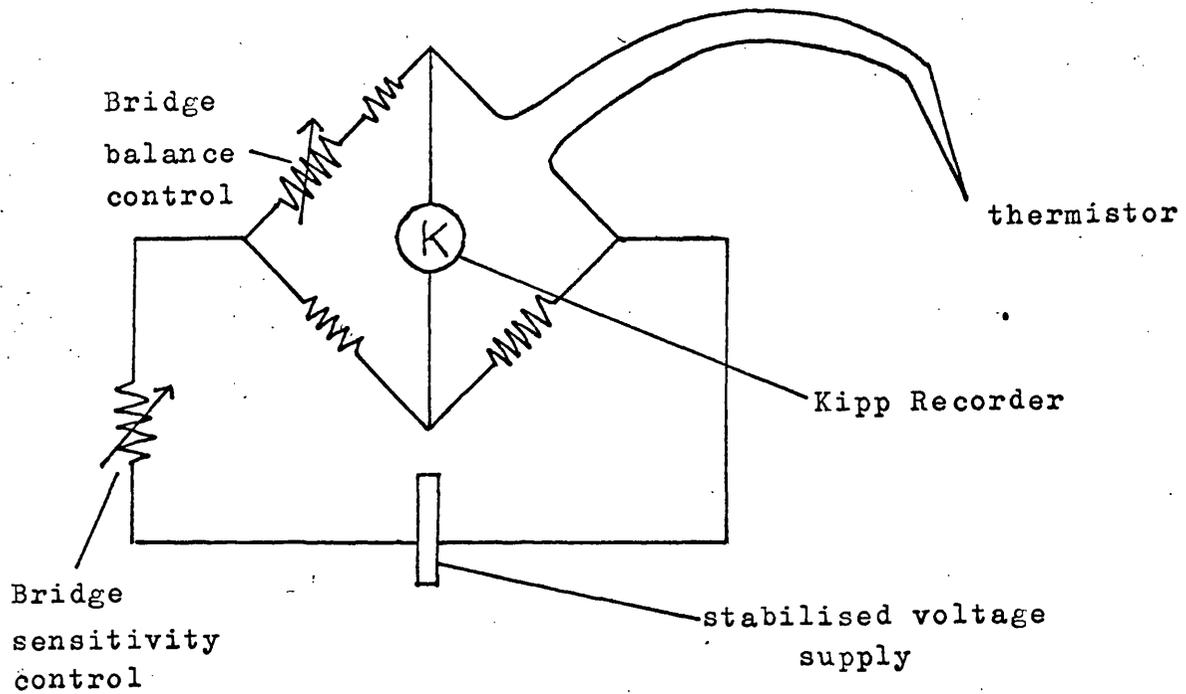


FIGURE 2.3.3. The Glass Heater.

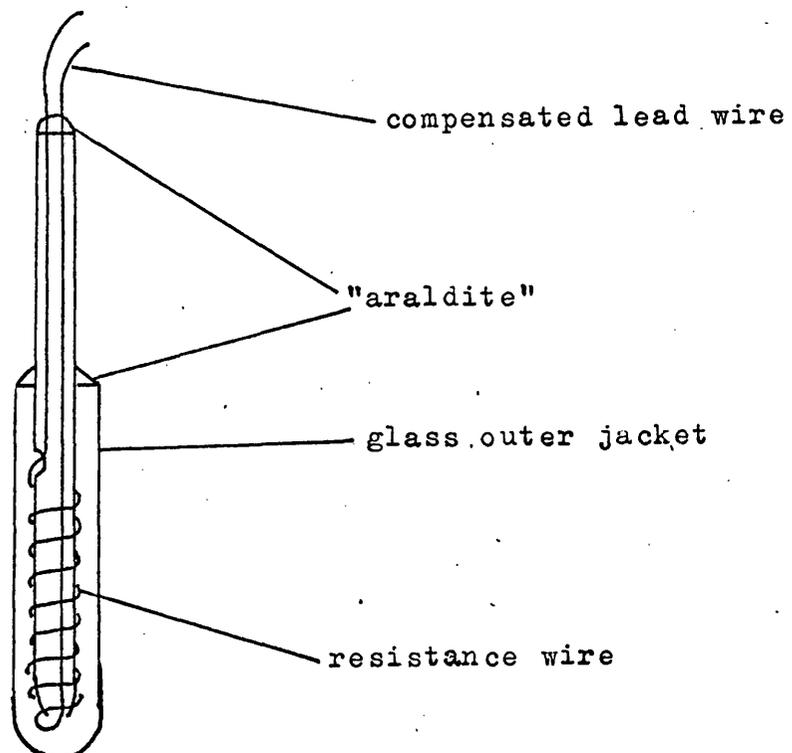


FIGURE 2.3.4. The Heater Circuit.

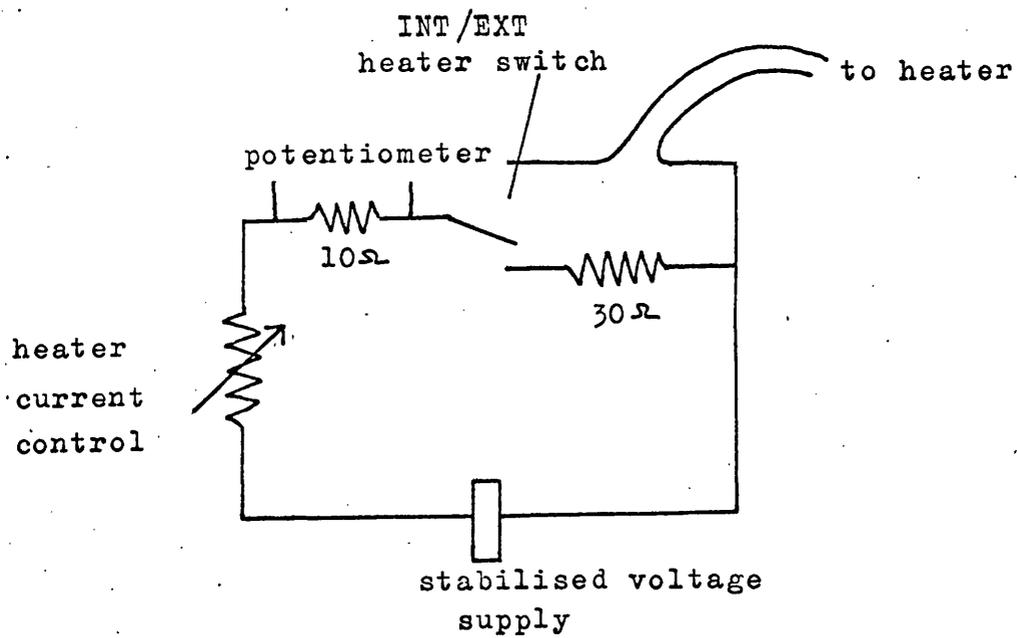
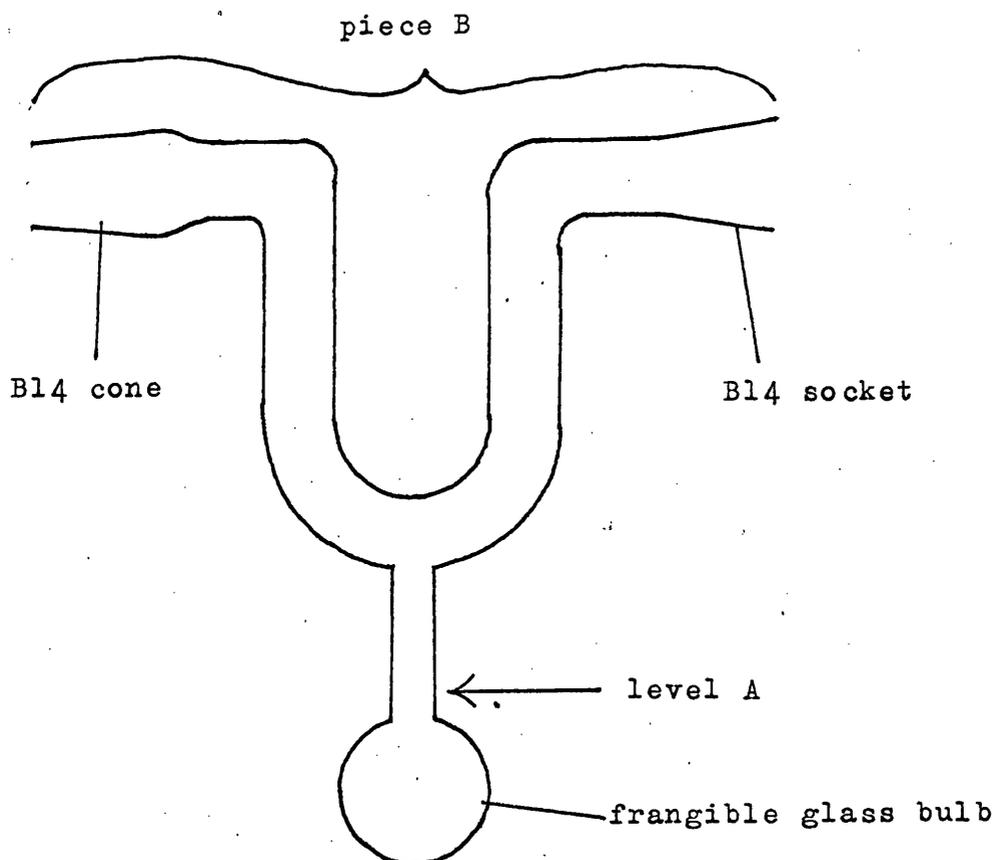


FIGURE 2.3.5. U-tube for Filling Bulbs with Volatile Samples.



the hydrolysis solution contained in the calorimeter. The temperature change of the contents of the calorimeter was followed using the thermistor whose changing resistance was monitored on the Kipp recorder. The recorder was then calibrated by supplying a known amount of heat into the calorimeter through the heater.

(b) Detailed Procedure.

The compounds considered were all extremely moisture sensitive so that moisture-free techniques were necessary for the introduction of the samples into the frangible glass bulbs. The particular technique used was dependent on the volatility of the sample.

) With volatile samples, the bulb was made up with a U-tube (Figure 2.3.5). The volume of the bulb to A was measured (to 0.1ml accuracy) before the whole piece (B) was washed and dried to constant mass. A set of bulbs was assembled on a vacuum line (Figure 2.3.5(a)) with an ampoule (C) containing the compound being considered. The apparatus was evacuated for several days and flamed out before the break-seal (D) was broken and part of the sample distilled into bulb 1 (at -196°C). Whilst at -196°C , bulb 1 was sealed off at A. The procedure was repeated with the other bulbs and any excess sample was distilled into trap E which was then also sealed off. As a precaution against impurities the first and last portions of the distillate were discarded. On completion of the filling procedure the U-tubes were washed and dried. The mass of each U-tube and bulb was determined (to constant mass). The bulbs were kept at -30°C until required.

For non-volatile samples it was necessary to fill the bulbs in a dry box (see Section 5.1.2(c)). Each frangible bulb was fitted with a B7 'Quickfit' cone (piece B in Figure 2.3.6.). The volume of each bulb (to A) was measured before it was washed and dried to constant mass. The bulbs were attached to piece C. The whole piece D was evacuated for several days and flamed out before being introduced into the dry box. A sample of the compound being considered was introduced into each bulb before the whole piece D was removed from the dry box and evacuated. Each bulb was sealed off at A. After the cones had been washed and dried the mass of each bulb and cone was determined (to constant mass).

The bulb, containing a known mass of a sample, was sealed on to the glass stirrer of the calorimeter. With volatile compounds it was necessary to cool the bulb to -196°C during this operation. Approximately 150ml of sodium hydroxide solution or sodium hydroxide and sodium hypochlorite solution was poured into the Dewar flask of the calorimeter. The calorimeter was assembled, immersed in the constant temperature water bath (25°C) and allowed to equilibrate for at least twelve hours. The stirrer was rotated at constant speed and the Kipp recorder and the galvanometer attached to the potentiometer were switched on. A further three to four hours were allowed for the system to come to equilibrium.

After the recorder pen had been activated for at least five minutes, the glass stirrer was depressed, causing the frangible bulb to be smashed on the steel spike. The

hydrolysis was recorded as a deflection on the Kipp recorder. A cooling curve was plotted on the recorder for about twenty minutes after the completed hydrolysis (Figure 2.3.7(a)). The deflection due to hydrolysis was measured.

The recorder was then calibrated by introducing a known quantity of heat into the calorimeter by means of the heater. The heater resistance had previously been accurately measured. The recorder pen was activated for five minutes. The heater current was switched into the heater circuit for a known length of time (measured to 0.1s on a Junghans stopwatch). This heating of the calorimeter contents was recorded on the Kipp recorder. During the heating, the heater current was measured as in Section 2.3.1. After the completion of heating a cooling curve was plotted on the recorder so that an accurate recorder deflection could be obtained (Figure 2.3.7(b)). Several heating calibrations were carried out in connection with each hydrolysis determination.

FIGURE 2.3.5(a). Apparatus for Filling Bulbs with Volatile Samples.

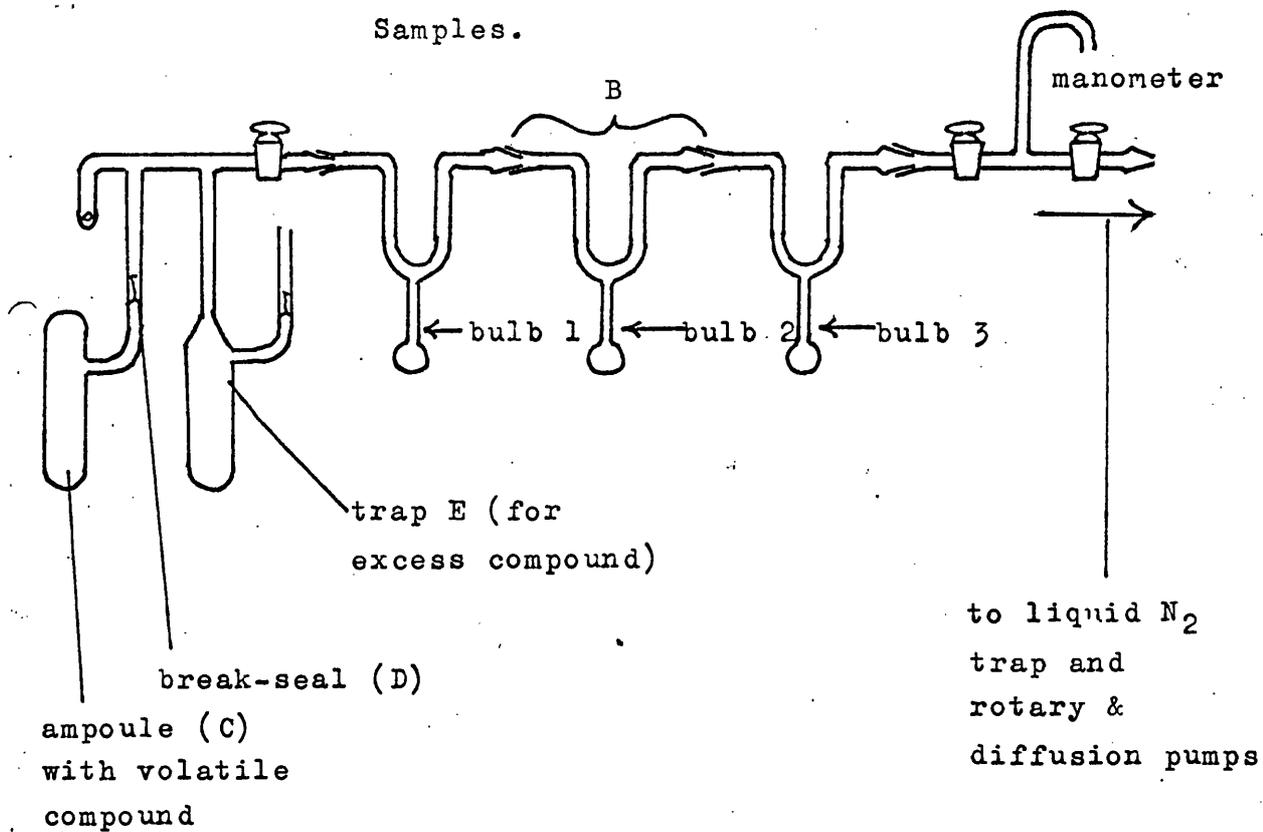


FIGURE 2.3.6. Apparatus for Filling Bulbs with Non Volatile Samples.

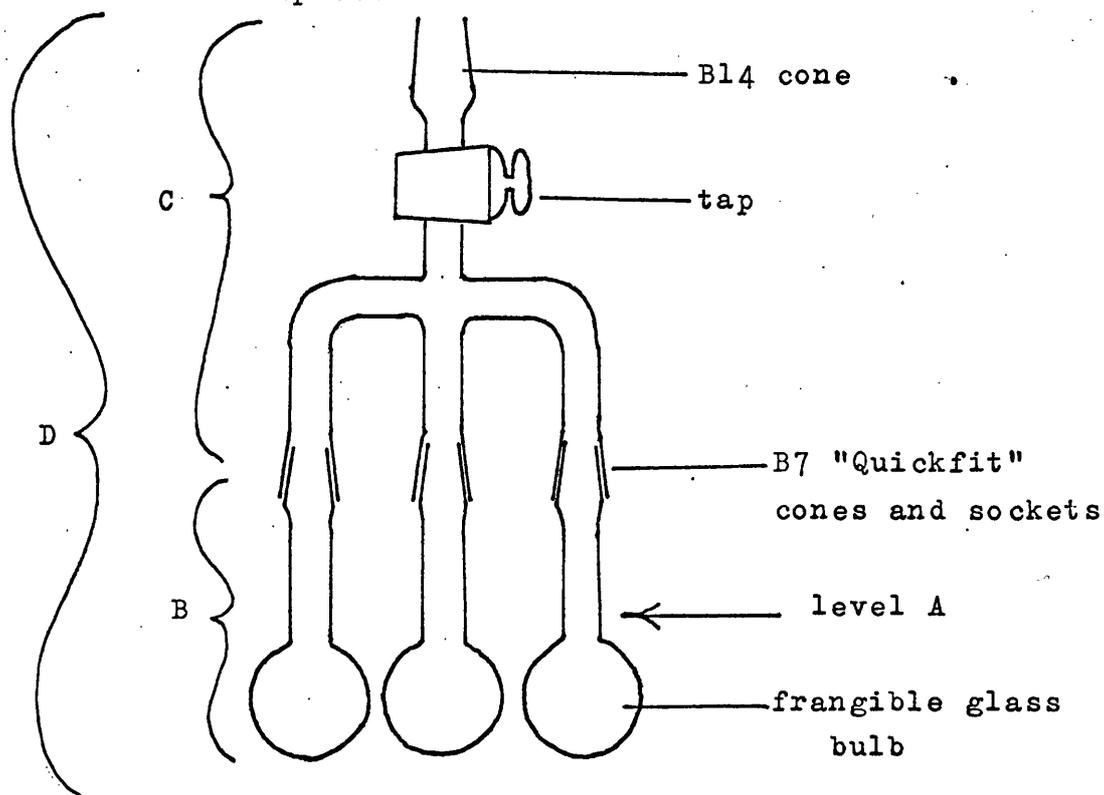
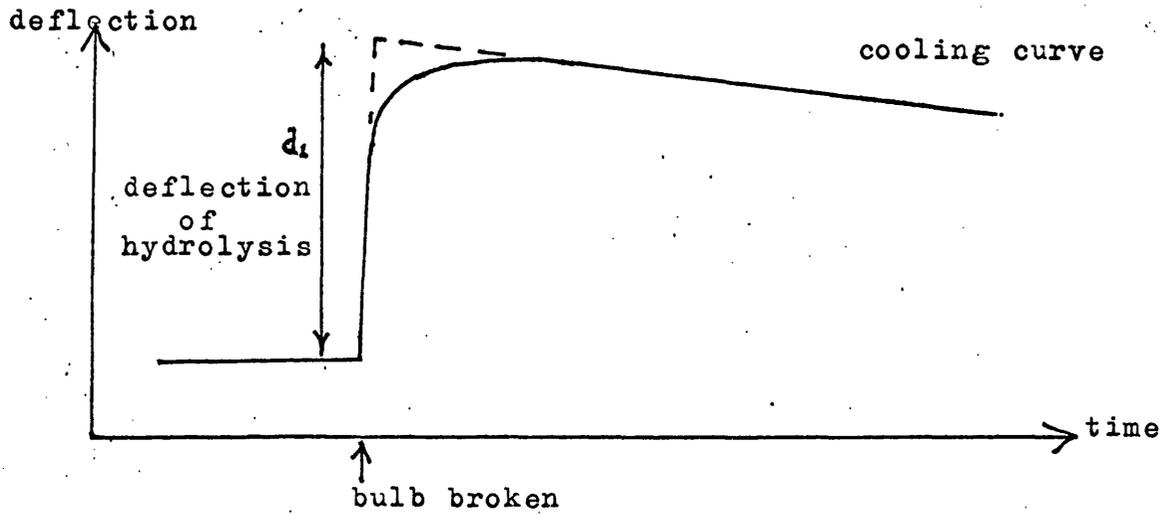
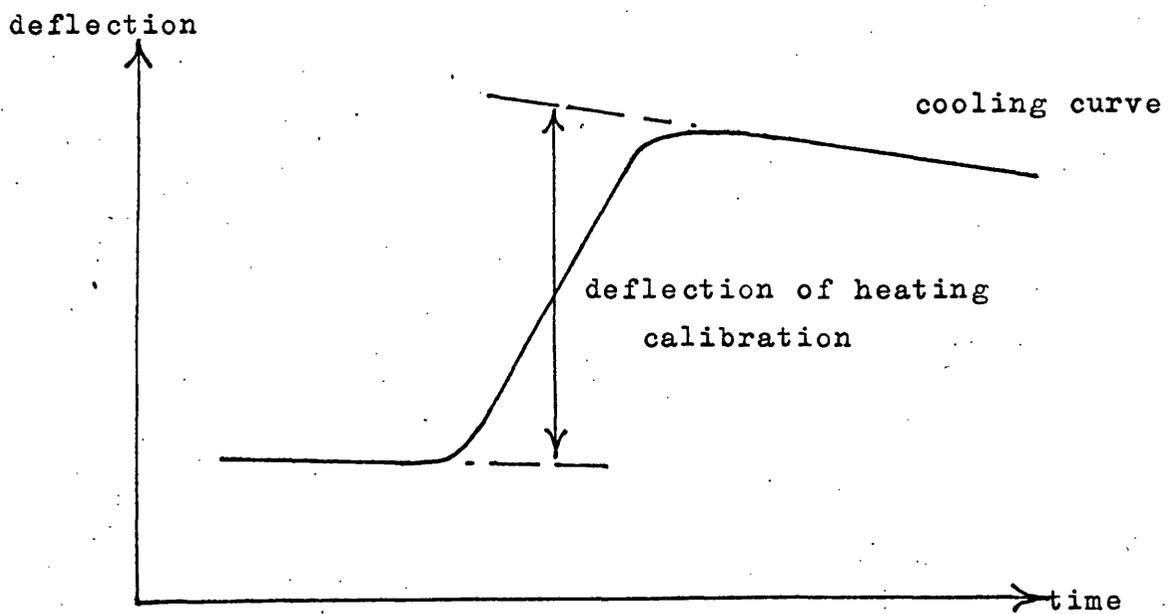


FIGURE 2.3.7. Recording of the Temperature Changes on the Kipp Recorder.

(a) The hydrolysis.



(b) The heating calibration.



(c) A Typical Experiment.

If the volume of the bulb is V (ml), the mass of the bulb empty is W_1 (g), the mass of the bulb filled is W_2 (g) and the density of air at room temperature²² is ρ , then the actual mass of the sample, W (g), is given by

$$W = (W_2 - W_1) + \rho V \quad (\text{g})$$

If for the hydrolysis of this sample:-

Recorder deflection for hydrolysis reaction	=	A (mm)
Recorder deflection for heater calibration	=	B (mm)
Heater resistance	=	R (ohm)
Heater current	=	I (A)
Time of passing current through heater	=	T (s)
Molecular weight of compound	=	M

Then

$$\begin{aligned} \text{Heat introduced into calorimeter by heater} &= I^2 RT \text{ joule} \\ &= \frac{I^2 RT}{4.1840} \text{ cal.} \end{aligned}$$

$$\therefore \text{Heat liberated during the hydrolysis} = \frac{I^2 RT}{4.1840} \cdot \frac{A}{B} \text{ cal.}^*$$

Then the heat (enthalpy) of hydrolysis of the compound in the solution used is

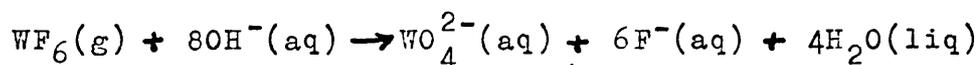
$$\frac{I^2 RT}{4.1840} \cdot \frac{A \cdot M}{B \cdot W} \text{ calorie mol}^{-1}.$$

The enthalpy of formation can be calculated from this enthalpy of hydrolysis with a knowledge of the hydrolysis reaction and the standard enthalpies of formation of the

Footnote *

see Section 2.3.3

other species involved. For example, the hydrolysis of gaseous tungsten hexafluoride in dilute sodium hydroxide proceeds according to the equation



Then if ΔH_{hyd} is the enthalpy of hydrolysis of the reaction and $\Delta H_f^\circ(\text{OH}^-)$, $\Delta H_f^\circ(\text{WO}_4^{2-})$, $\Delta H_f^\circ(\text{F}^-)$ and $\Delta H_f^\circ(\text{H}_2\text{O})$ are the standard enthalpies of formation of $\text{OH}^-(\text{aq})$, $\text{WO}_4^{2-}(\text{aq})$, $\text{F}^-(\text{aq})$ and $\text{H}_2\text{O}(\text{liq})$ respectively; the enthalpy of formation of gaseous tungsten hexafluoride, $\Delta H_f^\circ(\text{WF}_6)$, is given by

$$\Delta H_f^\circ(\text{WF}_6) = \Delta H_f^\circ(\text{WO}_4^{2-}) + 6\Delta H_f^\circ(\text{F}^-) + 4\Delta H_f^\circ(\text{H}_2\text{O}) - 8\Delta H_f^\circ(\text{OH}^-) - \Delta H_{\text{hyd}}$$

2.3.3. Expression of the Results.

(a) Units.

The thermochemical results in this thesis have been expressed in terms of the thermochemical 'defined' calorie (4.1840 absolute joule).

(b) Mean Values and Standard Deviations.

In the determination of any enthalpy, x , a series of n measurements, x_i , of the enthalpy have been obtained.

The mean value, \bar{x} , defined as

$$\bar{x} = \frac{1}{n} \sum_{i=1}^{i=n} x_i, \text{ has been quoted as the}$$

enthalpy. A standard deviation, s , defined by

$$s^2 = \frac{1}{n} \sum_{i=1}^{i=n} (x_i - \bar{x})^2, \text{ follows each enthalpy}$$

so that the enthalpy is quoted thus:-

The enthalpy, x , of a given change = $\bar{x} \pm s$.

2.3.4. Reliability of the Apparatus.

The reliability of the apparatus was tested by repeating the previously investigated calorimetric studies of the precipitation of silver chloride, the solution of tris (hydroxymethyl) methylamine, and the alkaline hydrolysis of tungsten hexafluoride.

The precipitation of silver chloride involved the reaction of a known mass of a known strength of potassium chloride solution (in the frangible bulb) with an excess of dilute silver nitrate solution (in the calorimeter). The enthalpy of precipitation of silver chloride was measured directly. The values obtained (see Table 2.3.4(a)) were consistent with the literature values^{23,24}.

The enthalpy of solution of a known mass (approx. 0.7g) of tris (hydroxymethyl) methylamine (known as TRIS or THAM) was measured directly in 0.1N hydrochloric acid. The values obtained (Table 2.3.4(b)) were consistent with the literature values^{25,26}.

The enthalpy of hydrolysis of gaseous tungsten hexafluoride in sodium hydroxide solution (0.1 and 1.0N) was measured directly and the values obtained (Table 2.5.1(a)) were consistent with the values obtained for the hydrolysis of liquid tungsten hexafluoride¹³ taking into consideration the enthalpy of vaporisation of tungsten hexafluoride⁸.

TABLE 2.3.4

(a) Enthalpy of precipitation of silver chloride.

Sample No.	Mass of KCl solution(g)	Strength of KCl solution	Calorimeter solution	Enthalpy of precipitation (kcal mol ⁻¹)
1	0.6353	18.2636g in 260.50g soln	150ml $\frac{N}{10}$ AgNO ₃	-15.68
3	1.0798	"	"	-15.77

Enthalpy of precipitation of silver chloride = -15.72kcal mol⁻¹Literature values are -15.70²³ and -15.74²⁴ kcal mol⁻¹.

(b) Enthalpy of solution of TRIS.

Sample No.	Mass of TRIS(g)	Calorimeter solution	Enthalpy of solution (cal mol ⁻¹)
1	0.7034	150ml 0.1N HCl	-6991
3	0.7578	"	-6989

Enthalpy of solution of TRIS = -6990 cal mol⁻¹.Literature values are -7104²⁵ and -7111²⁶ cal mol⁻¹.

2.4. Experimental Accuracy.

2.4.1. Accuracy of the Enthalpies of Hydrolysis.

The accuracy of an enthalpy of hydrolysis is dependent on the accuracy of the calorimetric apparatus and the purity of the sample used.

(a) Accuracy of the Apparatus.

In considering the accuracy of the apparatus several factors must be considered:

(i) Consistency of Stirring.

Stirring of the solution in the calorimeter was achieved with a glass stirring rod attached to an electrical stirring device whose speed was governed by a variable rheostat.

The correct rate of stirring, set at the beginning of each experiment, was sufficient to ensure the desired uniformity of temperature but not high enough to produce excessive amounts of heat. The rate of stirring was kept constant throughout each experiment so that the small amount of heat produced by stirring was compensated for in the measurement of the recorder deflections.

(ii) Accuracy of the Thermistor Circuit.

The temperature increases in the calorimeter were monitored using a thermistor inserted into the calorimeter. The thermistor was particularly suitable for these measurements being compact and having a low heat capacity.

Although the error resulting from the use of a thermistor would be small, the circuit incorporating the thermistor (Figure 2.3.2) might cause an error in the deflection produced on the Kipp recorder of the order of 1%.

(iii) Accuracy of the Measurement of the
Deflections.

The value of the deflection of the hydrolysis was obtained, on the recorder, as d_1 , by extrapolating back the cooling curve (Figure 2.3.7) to the time of initiation of the hydrolysis.

Using this method of measurement with the fast hydrolysis reactions the loss of accuracy was very small ($< \frac{1}{2}\%$). With the electrical heating calibrations the deflection was taken at the mid time of passage of current and the error was again small.

(iv) The Heater Current.

At the mid point in the time of passage of the heating current, a potentiometer was used to measure the potential difference across a standard ten ohm resistance incorporated in the heater circuit (Figure 2.3.4.). The heating current was calculated from this potential difference. The current was normally of the order of 0.1 to 0.15A, measured to an accuracy of 0.0001A, and varied less than 0.0005A during the period over which it was passed.

(v) The Timing of the Heating.

The time over which the current was passed was measured using a Junghans stopwatch. Since the stopwatch and current switch were operated manually, and not electronically connected, a small 'operator' error might have occurred.

(vi) The Resistance of the Heater.

The resistance of the heater was of the order of 30 ohm and was measured, before insertion into the calorimeter, on a

Wheatstone bridge to an accuracy of 0.01 ohm. It was necessary to measure the resistance of the heater with its connecting leads and also to measure the resistance of the equivalent leads in order to obtain the true resistance of the heating coil.

(vii) Thermostatic Control of the Water Bath.

The enthalpies of hydrolysis were all measured at 25°C and are quoted at this temperature. Since the enthalpies vary with temperature, any variation in the temperature of the thermostatically controlled water bath would lead to an error in the resultant enthalpy of hydrolysis. In the system used (Section 2.3.1) the variation in the temperature of the water bath was very small ($<0.1^{\circ}\text{C}$) and the resultant errors in the enthalpies of hydrolysis were negligible.

(b) Purity of the Compounds.

The hydrolyses were carried out on as pure samples as could be obtained. In all cases, except the non-volatile solids, the compounds were purified by successive vacuum distillations. In the case of rhenium hexafluoride further purification was also carried out by passing the gaseous hexafluoride over heated rhenium metal (Section 5.2.2.). Analyses were carried out (Chapter 5) and in some cases X-ray powder photographs were also obtained as a check on the purity of the (solid) compounds. Only in the case of the non-volatile solids (KWF_6 , KMoF_6 and K_2WCl_6) might the impurity levels be expected to cause noticeable errors.

However, there is no evidence for significant errors in these samples.

Moisture is released during the sealing-off process of pyrex glass. Therefore, the use of frangible glass bulbs for containing the samples might be expected to lead to a reduction in the purity of the samples. However, with the rigorous drying of the bulbs before the introduction of the samples, this effect, and the subsequent error, would be expected to be small.

2.4.2. Accuracy of the Enthalpies of Formation.

The enthalpies of formation of hydrolysed compounds are determined using the equation of hydrolysis, the enthalpy of hydrolysis and the standard enthalpies of formation of the other species in the equation of hydrolysis. Therefore, the accuracy of the calculated enthalpy of formation of a compound is dependent on the stoichiometry of the hydrolysis reaction, the accuracy of the enthalpy of hydrolysis (Section 2.4.1.) and the accuracy of the other known enthalpies of formation.

(a) Stoichiometry of the Hydrolysis Reaction.

If the hydrolysis reaction is entirely the expected reaction then the measured enthalpy of hydrolysis can be used with the equation of hydrolysis to determine the standard enthalpy of formation of the compound. However, if side reactions occur in the hydrolysis, the measured enthalpy of hydrolysis cannot give a true enthalpy of formation for the compound. The only hydrolysis, studied in

this thesis, giving a significant side hydrolysis reaction is the oxidative hydrolysis of osmium hexafluoride. In this case, since the formation of a certain amount of the species $\text{OsF}_6^{2-}(\text{aq})$ was indicated⁴, the consistent values for the enthalpy of hydrolysis could not be used to determine the enthalpy of formation of osmium hexafluoride. Side hydrolysis reactions do not occur to any appreciable extent in the other compounds considered in this thesis. Therefore, the enthalpies of hydrolysis can be used to give reasonably accurate standard enthalpies of formation.

By making a comparison of the standard enthalpies of formation of compounds obtained by different methods, it is possible to judge the accuracy of these methods.

The enthalpies of formation of $\text{MoF}_6(\text{g})$, $\text{WF}_6(\text{g})$ and $\text{WF}_5(\text{s})$ which have been obtained by hydrolysis are the same (within experimental error) as those obtained by the direct and accurate fluorine bomb calorimetry method (Table 2.4.2(a)) suggesting that the hydrolysis calorimetry is reliable and accurate within the limits shown.

(b) Accuracy of the other known Standard Enthalpies of Formation.

In the determination of the standard enthalpies of formation of compounds from their enthalpies of hydrolysis, it has been necessary to use the standard enthalpies of formation of the following species: $\text{OH}^-(\text{aq})$, $\text{H}_2\text{O}(\text{l})$, $\text{F}^-(\text{aq})$, $\text{Cl}^-(\text{aq})$, $\text{OCl}^-(\text{aq})$, $\text{WO}_4^{2-}(\text{aq})$, $\text{MoO}_4^{2-}(\text{aq})$, $\text{ReO}_4^-(\text{aq})$, $\text{OsO}_4(\text{aq})$ and $\text{K}^+(\text{aq})$. Table 2.4.2(b) shows the values of the enthalpies

TABLE 2.4.2 (a).

Compound	Standard enthalpy of formation (kcal mol ⁻¹)			
	Obtained by hydrolysis		Obtained by fluorine bomb calorimetry.	
	This thesis	Myers & * Brady ¹³	Hubbard ^{14,27}	Schröder & Sieben ²⁸
MoF ₆ (gas)	-374.8±2.5	-387.4±4	-372.3±0.2	—
WF ₆ (gas)	-411.8 ₅ ±1.4	-411.2±4	-411.5±0.4	-411.7±0.5
WF ₅ (solid)	-349.9±3.5	—	—	-346.1± _{1.0} ^{2.6}

* these enthalpies of formation have been recalculated using the heats of hydrolysis of Myers & Brady with the more recent enthalpies of formation of Table 2.4.2(b).

TABLE 2.4.2(b)

Species	Standard enthalpy of formation(kcal mol ⁻¹)	Source	Ref
OH ⁻ (aq)	-54.97	NBS 270-3	29
H ₂ O(liq)	-68.315	NBS 270-3	29
F ⁻ (aq)	-79.50	NBS 270-3	29
Cl ⁻ (aq)	-39.952	NBS 270-3	29
OCl ⁻ (aq)	-26.2	McDonald et al	30
WO ₄ ²⁻ (aq)	-257.1	NBS 270-4	31
MoO ₄ ²⁻ (aq)	-238.2	Graham & Hepler	32
ReO ₄ ⁻ (aq)	-189.2	Boyd et al	33
K ⁺ (aq)	-60.32	NBS 270-3	29
OsO ₄ (aq)	-90.4	NBS 270-4	31

which have been used in this thesis and the sources from which they have been obtained.

Although these are the most recent and reliable values which are available at present, it is possible that any of the values may be revised at some future date. Any such revision will necessitate the revision of those enthalpies of formation whose calculation involved the use of the enthalpy being revised.

In all the hydrolyses it was necessary to use a large excess of the hydrolysing agent (and, if used, the oxidising agent) so that the change in dilution of these reagents was minimised. It was then possible to use constant enthalpies of formation for the reagents ($\text{OH}^-(\text{aq})$ and $\text{OCl}^-(\text{aq})$) without introducing errors due to the enthalpies of dilution of the reagents. Although the enthalpy values used (Table 2.4.2(b)) for these reagents were those at infinite dilution, the error due to the actual concentration of the reagents was negligible.

2.5 Enthalpies of Formation of Hexafluorides.

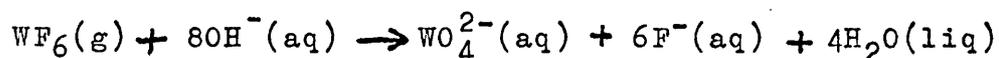
2.5.1. Tungsten and Molybdenum Hexafluorides.

In this thesis the enthalpies of formation of gaseous tungsten and molybdenum hexafluorides have been determined via their enthalpies of hydrolysis.

(a) Enthalpy of formation of gaseous tungsten hexafluoride.

Tungsten hexafluoride was prepared, purified and analysed as described in Sections 5.2.1 and 5.3. The enthalpy of hydrolysis of gaseous tungsten hexafluoride was measured using the calorimetric procedure described previously (Section 2.3.). The calorimetric measurements were carried out on four samples (from three separate preparations) of gaseous tungsten hexafluoride each being hydrolysed in an excess of sodium hydroxide solution (either 0.1N or 1N). The four consistent results obtained (Table 2.5.1(a).) gave an average value for the enthalpy of hydrolysis of gaseous tungsten hexafluoride of $-155.75 \pm 1.4 \text{ kcal mol}^{-1}$. The enthalpy of hydrolysis of liquid tungsten hexafluoride has previously been measured by Myers and Brady¹³ as $-150.1 \pm 4 \text{ kcal mol}^{-1}$. Since the enthalpy of ~~vaporisation~~^{8,34} of tungsten hexafluoride is $6.15 \text{ kcal mol}^{-1}$ these two enthalpies of hydrolysis are found to be in close agreement.

The hydrolysis of tungsten hexafluoride in an excess of a sodium hydroxide solution proceeds according to the equation:-



Using the standard enthalpies of formation of the species $\text{OH}^-(\text{aq})$, $\text{WO}_4^{2-}(\text{aq})$, $\text{F}^-(\text{aq})$ and $\text{H}_2\text{O}(\text{liq})$, (Table 2.4.2(b)) and the measured enthalpy of hydrolysis, the standard enthalpy of formation of gaseous tungsten hexafluoride has been calculated to be $-411.85 \pm 1.4 \text{ kcal mol}^{-1}$. This value is in close agreement with the values of $-411.5 \pm 0.4 \text{ kcal mol}^{-1}$ ¹⁴ and $-411.7 \pm 0.5 \text{ kcal mol}^{-1}$ ²⁸ obtained by fluorine bomb calorimetry.

(b) Enthalpy of formation of gaseous molybdenum hexafluoride.

The enthalpy of hydrolysis of gaseous molybdenum hexafluoride (prepared, purified and analysed as described in Sections 5.2.1 and 5.3) was measured using the calorimetric procedure described previously (Section 2.3).

The calorimetric measurements were carried out on five samples (from two separate preparations) of gaseous molybdenum hexafluoride each being hydrolysed in an excess of sodium hydroxide solution (either 0.1N or 1N). The five consistent values obtained (Table 2.5.1(b)) gave a value for the enthalpy of hydrolysis of gaseous molybdenum hexafluoride of $-173.9 \pm 2.5 \text{ kcal mol}^{-1}$. The enthalpy of hydrolysis of liquid molybdenum hexafluoride has previously been measured by Myers and Brady¹³ as $-154.7 \pm 4 \text{ kcal mol}^{-1}$. However, since the enthalpy of vaporisation of molybdenum hexafluoride is only $6.63 \text{ kcal mol}^{-1}$ ³⁵ (or $6.85 \text{ kcal mol}^{-1}$ ^{8,34}) it can be seen that the two enthalpies of hydrolysis are not in agreement.

The hydrolysis of molybdenum hexafluoride in an excess of sodium hydroxide solution proceeds according to the equation:-

TABLE 2.5.1

(a) Enthalpy of hydrolysis of gaseous tungsten hexafluoride.

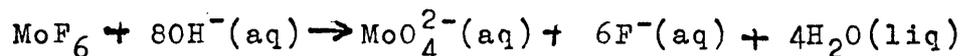
Set No.	Sample No.	Mass of sample(g)	Hydrolysing Agent	Enthalpy of hydrolysis (kcal mol ⁻¹)
1	2	0.1284	150ml N NaOH	-154.6 ₅
2	2	0.3750	150ml N NaOH	-155.1
3	1	0.0945	150ml $\frac{N}{10}$ NaOH	-155.1
3	2	0.2103	150ml N NaOH	-158.1 ₅

Enthalpy of hydrolysis of $WF_6(\text{gas}) = -155.75 \pm 1.4 \text{ kcal mol}^{-1}$.

(b) Enthalpy of hydrolysis of gaseous molybdenum hexafluoride.

Set No.	Sample No.	Mass of sample(g)	Hydrolysing Agent	Enthalpy of hydrolysis (kcal mol ⁻¹)
1	3	0.1081	150ml N NaOH	-173.5
1	5	0.0192	150ml $\frac{N}{10}$ NaOH	-169.3
2	1	0.0903	150ml N NaOH	-176.0
2	2	0.1511	150ml N NaOH	-175.8
2	3	0.1029	150ml $\frac{N}{10}$ NaOH	-174.9

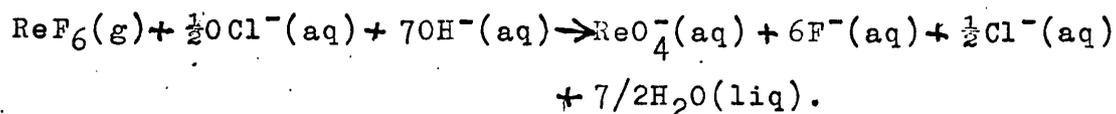
Enthalpy of hydrolysis of $MoF_6(\text{g}) = -173.9 \pm 2.5 \text{ kcal mol}^{-1}$.



Using the standard enthalpies of formation of the species $\text{OH}^-(\text{aq})$, $\text{MoO}_4^{2-}(\text{aq})$, $\text{F}^-(\text{aq})$ and $\text{H}_2\text{O}(\text{liq})$ (Table 2.4.2(b)) and the measured enthalpy of hydrolysis, the standard enthalpy of formation of gaseous molybdenum hexafluoride is calculated to be $-374.8 \pm 2.5 \text{ kcal mol}^{-1}$. There is reasonable agreement between this value and the value of $-372.3 \pm 0.2 \text{ kcal mol}^{-1}$ obtained by fluorine bomb calorimetry.²⁷

2.5.2. Rhenium Hexafluoride.

The enthalpy of oxidative hydrolysis of gaseous rhenium hexafluoride (prepared, purified and analysed as described in Sections 5.2.1, 5.2.2 and 5.3) has been measured using the usual calorimetric procedure (Section 2.3). The calorimetric measurements were carried out on ten samples (from three separate preparations) of gaseous rhenium hexafluoride each being hydrolysed in an excess of a solution of sodium hydroxide (0.1N or 1N) and sodium hypochlorite (~1.5 to 2.5%). The ten consistent values obtained (Table 2.5.2) gave a value of $-204.8 \pm 3.2 \text{ kcal mol}^{-1}$ for the enthalpy of oxidative hydrolysis of gaseous rhenium hexafluoride. The hydrolysis under consideration proceeds according to the equation:-



Using the standard enthalpies of formation of $\text{OCl}^-(\text{aq})$,

TABLE 25.2

Enthalpy of hydrolysis of gaseous rhenium hexafluoride.

Set No.	Sample No.	Mass of sample(g)	Hydrolysing Agents	Enthalpy of Hydrolysis(kcal mol ⁻¹)
1	2	0.0665	130ml $\frac{N}{10}$ NaOH & 20ml 12% NaOCl	-202.07
2	2	0.0368	120ml $\frac{N}{10}$ NaOH & 30ml 12% NaOCl	-201.01
3	1	0.0522	120ml $\frac{N}{10}$ NaOH & 30ml 12% NaOCl	-202.53
3	2	0.0769	120ml $\frac{N}{10}$ NaOH & 30ml 12% NaOCl	-201.02
3	3	0.0955	120ml $\frac{N}{10}$ NaOH & 30ml 12% NaOCl	-206.08
4	1	0.0758	130ml $\frac{N}{10}$ NaOH & 20ml 12% NaOCl	-204.60
4	2	0.1166	120ml N NaOH & 30ml 12% NaOCl	-209.72
4	3	0.0498	130ml $\frac{N}{10}$ NaOH & 20ml 12% NaOCl	-208.95
5	1	0.0503	120ml N NaOH & 30ml 12% NaOCl	-208.19
5	3	0.0382	120ml N NaOH & 30ml 12% NaOCl	-203.50

Enthalpy of hydrolysis of $\text{ReF}_6(\text{g}) = -204.76 \pm 3.2 \text{ kcal. mol}^{-1}$

$\text{OH}^-(\text{aq})$, $\text{ReO}_4^-(\text{aq})$, $\text{F}^-(\text{aq})$, $\text{Cl}^-(\text{aq})$ and $\text{H}_2\text{O}(\text{liq})$ (Table 2.4.2(b)) and the measured enthalpy of hydrolysis, the standard enthalpy of formation of gaseous rhenium hexafluoride is calculated to be $-322.6 \pm 3.2 \text{ kcal mol}^{-1}$.

When Ruff and co-workers first investigated rhenium hexafluoride^{5,19,36} they obtained a value of $-275 \text{ kcal mol}^{-1}$ for the enthalpy of formation of gaseous rhenium hexafluoride⁵. However, Malm and Selig¹⁸ suggest that, judging by vapour pressure data, Ruff's material contained a considerable amount of rhenium heptafluoride. The material used in this thesis was shown to be pure by analysis. Thus it is concluded that the new value quoted here is correct.

2.5.3. Osmium Hexafluoride.

The enthalpy of oxidative hydrolysis of gaseous osmium hexafluoride (prepared and purified as described in Section 5.2.1.) has been measured using the usual calorimetric procedure (Section 2.3). The calorimetric measurements were carried out on eight samples (from three separate preparations) of gaseous osmium hexafluoride, each being hydrolysed in an excess of a solution of sodium hydroxide ($\frac{\text{N}}{10}$) and sodium hypochlorite (~ 1.5 to 2.5%). The seven consistent values obtained (Table 2.5.3.) gave a value of $-97.5 \pm 4.3 \text{ kcal mol}^{-1}$ for the enthalpy of oxidative hydrolysis of gaseous osmium hexafluoride.

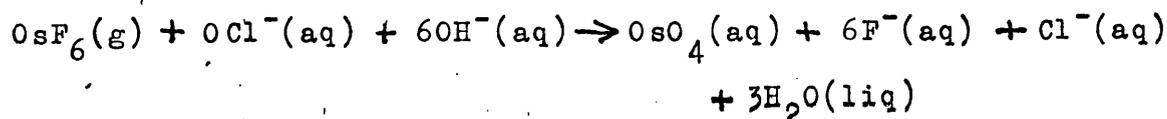
In order to estimate the standard enthalpy of formation of osmium hexafluoride it is necessary to assume that the hydrolysis proceeds according to the equation:-

TABLE 2.5.3

Enthalpy of hydrolysis of gaseous osmium hexafluoride.

Set No.	Sample No.	Mass of sample(g)	Hydrolysing Agents	Enthalpy of Hydrolysis(kcal mol ⁻¹)
1	2	0.0255	130ml $\frac{N}{10}$ NaOH & 20ml 12% NaOCl	-106.80
1	3	0.0499	120ml $\frac{N}{10}$ NaOH & 30ml 12% NaOCl	-97.80
2	1	0.0392	"	-96.13
2	2	0.0392	"	-94.58
2	3	0.0260	"	-95.12
3	1	0.0192	"	-99.10
3	2	0.0439	"	-92.90

Enthalpy of hydrolysis of $\text{OsF}_6(\text{g}) = -97.5 \pm 4.3 \text{ kcal. mol}^{-1}$



Then using the known standard enthalpies of formation of $\text{OCl}^-(\text{aq})$, $\text{OH}^-(\text{aq})$, $\text{OsO}_4(\text{aq})$, $\text{F}^-(\text{aq})$, $\text{Cl}^-(\text{aq})$ and $\text{H}_2\text{O}(\text{liq})$ (Table 2.4.2(b)) and the measured enthalpy of hydrolysis, ^{standard} the Δ enthalpy of formation of gaseous osmium hexafluoride is estimated to be $-358.8 \pm 4.3 \text{ kcal mol}^{-1}$. However, this enthalpy of formation will be incorrect since a certain amount of the stable species $\text{OsF}_6^{2-}(\text{aq})$ will also be formed in the hydrolysis.⁴

2.6. Enthalpies of Formation of Pentafluorides.

2.6.1. Enthalpy of Formation of Tungsten Pentafluoride.

The enthalpy of oxidative hydrolysis of solid tungsten pentafluoride (prepared and analysed as described in Sections 5.2.3 and 5.3) has been measured using the usual calorimetric procedure (Section 2.3). The calorimetric measurements were carried out on four samples of solid tungsten pentafluoride, each being hydrolysed in an excess of a solution of sodium hydroxide (0.1N or 1N) and sodium hypochlorite (~1.3 to 2%). The four consistent values obtained (Table 2.6.1) gave a value of $-165.9 \pm 3.5 \text{ kcal mol}^{-1}$ for the enthalpy of oxidative hydrolysis of solid tungsten pentafluoride.

The oxidative hydrolysis proceeds according to the equation:-

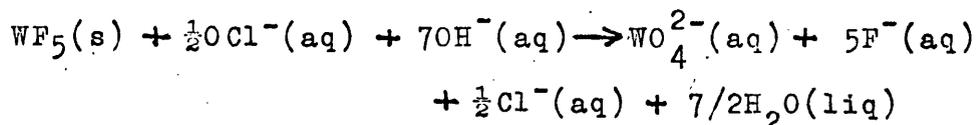


TABLE 2.6.1

Enthalpy of hydrolysis of solid tungsten pentafluoride.

Set No.	Sample No.	Mass of sample(g)	Hydrolysing Agents	Enthalpy of hydrolysis(kcal mol ⁻¹)
1	1	0.2671	70ml N NaOH, 30ml 10% NaOCl & 50ml H ₂ O.	-170.48
2	1	0.0872	130ml $\frac{N}{10}$ NaOH, & 20ml 10% NaOCl	-160.72
2	2	0.1762	120ml N NaOH & 30ml 10% NaOCl	-166.22
2	3	0.2039	120ml N NaOH & 30ml 10% NaOCl	-166.18

Enthalpy of hydrolysis of WF₅(solid) = -165.9 ± 3.5 kcal. mol⁻¹

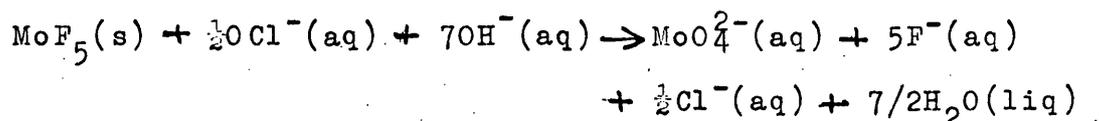
Using the standard enthalpies of formation of $\text{OCl}^-(\text{aq})$, $\text{OH}^-(\text{aq})$, $\text{WO}_4^{2-}(\text{aq})$, $\text{F}^-(\text{aq})$, $\text{Cl}^-(\text{aq})$ and $\text{H}_2\text{O}(\text{liq})$. (Table 2.4.2(b)) and the measured enthalpy of hydrolysis, the standard enthalpy of formation of solid tungsten pentafluoride is calculated to be $-349.9 \pm 3.5 \text{ kcal mol}^{-1}$. This value is in agreement with the value, of $346.1 - 1.0 \text{ kcal mol}^{-1}$,^{+ 2.6} which has previously been obtained by Schröder and Sieben²⁸ using fluorine bomb calorimetry.

2.6.2. Enthalpy of Formation of Molybdenum Pentafluoride

The enthalpy of oxidative hydrolysis of solid molybdenum pentafluoride (prepared, purified and analysed as in Sections 5.2.4(a) and 5.3.) has been measured using the usual calorimetric procedure (Section 2.3).

The calorimetric measurements were carried out on six samples of solid molybdenum pentafluoride, each being hydrolysed in an excess of a solution of sodium hydroxide (0.1N or 1N) and sodium hypochlorite (~ 1.5 to 2.5%). The six consistent values obtained (Table 2.6.2) gave a value of $-165.46 \pm 1.3 \text{ kcal mol}^{-1}$ for the enthalpy of oxidative hydrolysis of solid molybdenum pentafluoride.

The oxidative hydrolysis proceeds according to the equation:-



Then, using the standard enthalpies of formation of $\text{OCl}^-(\text{aq})$, $\text{OH}^-(\text{aq})$, $\text{MoO}_4^{2-}(\text{aq})$, $\text{F}^-(\text{aq})$, $\text{Cl}^-(\text{aq})$ and $\text{H}_2\text{O}(\text{liq})$ (Table 2.4.2(b)) and the measured enthalpy of oxidative hydrolysis, the standard enthalpy of formation of solid molybdenum pentafluoride is calculated to be $-331.42 \pm 1.3 \text{ kcal mol}^{-1}$.

TABLE 2.6.2

Enthalpy of hydrolysis of solid molybdenum pentafluoride.

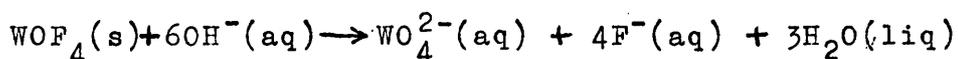
Set No.	Sample No.	Mass of sample(g)	Hydrolysing Agents	Enthalpy of hydrolysis(kcal mol ⁻¹)
1	1	0.2657	120ml N NaOH & 30ml 12% NaOCl	-166.11
1	2	0.2125	"	-167.31
1	3	0.1857	"	-166.55
1	4	0.1829	"	-164.90
1	5	0.1109	130ml $\frac{N}{10}$ NaOH & 20ml 12% NaOCl	-164.16
1	6	0.2195	120ml N NaOH & 30ml 12% NaOCl	-163.74

Enthalpy of hydrolysis of MoF₅(solid) = -165.46 ± 1.3 kcal. mol⁻¹

2.7. Enthalpies of Formation of Oxytetrafluorides.

2.7.1. Enthalpy of Formation of Tungsten Oxytetrafluoride.

The enthalpy of hydrolysis of solid tungsten oxytetrafluoride (prepared, purified and analysed as described in Sections 5.2.5 and 5.3.) has been measured using the usual calorimetric procedure (Section 2.3.). The calorimetric measurements were carried out on eleven samples (from five separate preparations) of solid tungsten oxytetrafluoride, each being hydrolysed in an excess of a solution of sodium hydroxide (0.1N or 1N). The ten consistent values obtained (Table 2.7.1.) gave a value of $-91.7_3 \pm 2.2 \text{kcal mol}^{-1}$ for the enthalpy of hydrolysis of solid tungsten oxytetrafluoride. The hydrolysis proceeds thus:



Using the standard enthalpies of formation of $\text{OH}^-(\text{aq})$, $\text{WO}_4^{2-}(\text{aq})$, $\text{F}^-(\text{aq})$ and $\text{H}_2\text{O}(\text{liq})$ (Table 2.4.2(b)) and the measured enthalpy of hydrolysis, the standard enthalpy of formation of solid tungsten oxytetrafluoride is calculated to be $-358.5 \pm 2.2 \text{kcal mol}^{-1}$.

The standard enthalpy of sublimation of tungsten oxytetrafluoride has been estimated³⁷, from vapour pressure determinations, to be $16.49 \text{kcal mol}^{-1}$ and the structure of the gaseous tungsten oxytetrafluoride has been shown, by infra-red studies, to be monomeric³⁸⁻⁴¹. Therefore, the enthalpy of formation of gaseous monomeric tungsten oxytetrafluoride is estimated to be $-342.0 \pm 2.2 \text{kcal mol}^{-1}$. The

TABLE 2.7.1

Enthalpy of hydrolysis of solid tungsten oxytetrafluoride

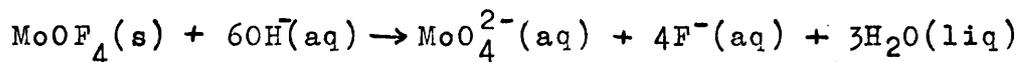
Set No.	Sample No.	Mass of sample(g)	Hydrolysing Agent	Enthalpy of hydrolysis(kcal mol ⁻¹)
1	2	0.1045	150ml $\frac{N}{10}$ NaOH	-90.36
1	3	0.0707	"	-94.78
2	3	0.0877	"	-88.20
3	2	0.0840	"	-88.86
4	1	0.3071	150ml N NaOH	-92.38
4	2	0.2237	150ml $\frac{N}{10}$ NaOH	-91.30
4	3	0.2488	"	-94.12
5	1	0.1224	"	-93.25
5	2	0.1477	"	-90.24
5	3	0.1914	"	-93.80

Enthalpy of hydrolysis of WO_4 (solid) = $-91.7_3 \pm 2.2$ kcal.mol⁻¹

standard enthalpy of formation of gaseous monomeric tungsten oxytetrafluoride has previously been estimated, from mass spectrometric studies, to be $-316 \pm 10 \text{ kcal mol}^{-1}$ ¹⁵. These workers had previously reported⁴² a standard enthalpy of formation of gaseous tungsten oxytetrafluoride of $-338.4 \pm 6 \text{ kcal mol}^{-1}$.

2.7.2. Enthalpy of Formation of Molybdenum Oxytetrafluoride.

The enthalpy of hydrolysis of solid molybdenum oxytetrafluoride (prepared, purified and analysed as described in Sections 5.2.5 and 5.3) has been measured using the usual calorimetric procedure (Section 2.3). The calorimetric measurements were carried out on four samples (from two separate preparations) of solid molybdenum oxytetrafluoride, each being hydrolysed in an excess of a solution of sodium hydroxide (0.1N). The four consistent values obtained (Table 2.7.2) gave a value of $-101.6 \pm 1.2 \text{ kcal mol}^{-1}$ for the enthalpy of hydrolysis of solid molybdenum oxytetrafluoride. The hydrolysis proceeds according to the equation:-



Using the standard enthalpies of formation of $\text{OH}^-(\text{aq})$, $\text{MoO}_4^{2-}(\text{aq})$, $\text{F}^-(\text{aq})$ and $\text{H}_2\text{O}(\text{liq})$ (Table 2.4.2(b)) and the measured enthalpy of hydrolysis, the standard enthalpy of formation of solid molybdenum oxytetrafluoride is calculated to be $-329.8 \pm 1.2 \text{ kcal mol}^{-1}$.

TABLE 2.7.2.

Enthalpy of hydrolysis of solid molybdenum oxytetrafluoride

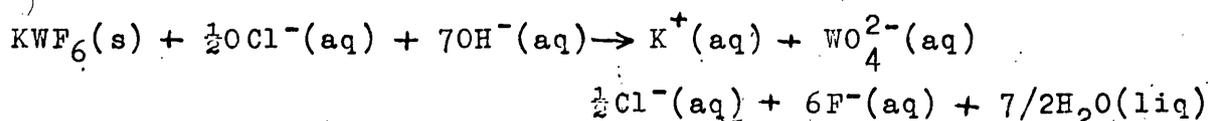
Set No.	Sample No.	Mass of sample (g)	Hydrolysing Agent	Enthalpy of hydrolysis (kcal mol ⁻¹)
1	1	0.0399	150ml $\frac{N}{10}$ NaOH	-99.85
1	2	0.0397	"	-101.83
1	3	0.0276	"	-103.09
2	3	0.0325	"	-101.48

Enthalpy of hydrolysis of MoOF_4 (solid) = $-101.56 \pm 1.2 \text{ kcal. mol}^{-1}$

2.8. Enthalpies of Formation of some Salts of Hexahalides.

2.8.1. Enthalpy of Formation of Potassium hexafluorotungstate (V).

The enthalpy of oxidative hydrolysis of solid potassium hexafluorotungstate(V) (prepared and analysed as described in Sections 5.2.6 and 5.3) has been measured using the usual calorimetric procedure (Section 2.3.). The calorimetric measurements were carried out on six samples (from three separate preparations) of solid potassium hexafluorotungstate(V), each being hydrolysed in an excess of a solution of sodium hydroxide (0.1N) and sodium hypochlorite (~1.5 to 2.5%). The six consistent values obtained (Table 2.8.1) gave a value of $123.6 \pm 2.6 \text{ kcal mol}^{-1}$ for the enthalpy of oxidative hydrolysis. The hydrolysis proceeds according to the equation:-



Using the standard enthalpies of formation of $\text{OCl}^-(\text{aq})$, $\text{OH}^-(\text{aq})$, $\text{K}^+(\text{aq})$, $\text{WO}_4^{2-}(\text{aq})$, $\text{Cl}^-(\text{aq})$, $\text{F}^-(\text{aq})$ and $\text{H}_2\text{O}(\text{liq})$ (Table 2.4.2(b)) and the measured enthalpy of oxidative hydrolysis, the standard enthalpy of formation of solid potassium hexafluorotungstate(V) is calculated to be $-532.0 \pm 2.6 \text{ kcal mol}^{-1}$.

2.8.2. Enthalpy of Formation of Potassium Hexafluoromolybdate(V).

The enthalpy of oxidative hydrolysis of solid potassium hexafluoromolybdate(V) (prepared and analysed as described in Sections 5.2.6 and 5.3) has been measured using the

TABLE 2.8.1

Enthalpy of hydrolysis of solid potassium hexafluoro-
tungstate (V).

Set No.	Sample No.	Mass of sample(g)	Hydrolysing Agents	Enthalpy of hydrolysis(kcal mol ⁻¹)
2	2	0.0544	130ml $\frac{N}{10}$ NaOH & 20ml 12% NaOCl	-120.34
4	1	0.0455	"	-125.94
4	2	0.0592	"	-125.88
4	3	0.0960	120ml $\frac{N}{10}$ NaOH & 30ml 12% NaOCl	-126.82
5	1	0.0829	130ml $\frac{N}{10}$ NaOH & 20ml 12% NaOCl	-121.71
5	3	0.0967	"	-120.90

Enthalpy of hydrolysis of KWF_6 (solid) = -123.6 ± 2.6 kcal.mol⁻¹

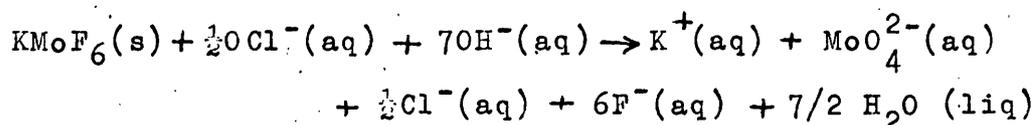
TABLE 2.8.2

Enthalpy of hydrolysis of solid potassium
hexafluoromolybdate(V).

Set No.	Sample No.	Mass of sample(g)	Hydrolysing Agents	Enthalpy of hydrolysis(kcal mol ⁻¹)
1	1	0.0879	130ml $\frac{N}{10}$ NaOH & 20ml 12% NaOCl	-141.03
1	3	0.1041	120ml N NaOH & 30ml 12% NaOCl	-144.31
3	1	0.0769	130ml $\frac{N}{10}$ NaOH & 20ml 12% NaOCl	-146.45
3	2	0.0799	125ml $\frac{N}{10}$ NaOH & 25ml 12% NaOCl	-141.88
3	3	0.1199	120ml N NaOH & 30ml 12% NaOCl	-145.60
3	4	0.0662	130ml $\frac{N}{10}$ NaOH & 20ml 12% NaOCl	-142.65
3	5	0.1153	120ml N NaOH & 30ml 12% NaOCl	-142.26

Enthalpy of hydrolysis of KMoF_6 (solid) = $-143.45 \pm 1.9 \text{ kcal mol}^{-1}$

usual calorimetric procedure (Section 2.3). The calorimetric measurements were carried out on nine samples (from three separate preparations) of solid potassium hexafluoromolybdate(V), each being hydrolysed in an excess of solution of sodium hydroxide (0.1N or 1N) and sodium hypochlorite (~ 1.5 to 2.5%). The seven consistent values obtained (Table 2.8.2) gave a value of $-143.4_5 \pm 1.9 \text{ kcal mol}^{-1}$ for the enthalpy of oxidative hydrolysis. The hydrolysis proceeds according to the equation:-



Using the standard enthalpies of formation of $\text{OCl}^-(\text{aq})$, $\text{OH}^-(\text{aq})$, $\text{K}^+(\text{aq})$, $\text{MoO}_4^{2-}(\text{aq})$, $\text{Cl}^-(\text{aq})$, $\text{F}^-(\text{aq})$ and $\text{H}_2\text{O}(\text{liq})$ (Table 2.4.2(b)) and the measured enthalpy of oxidative hydrolysis, the standard enthalpy of formation of solid potassium hexafluoromolybdate(V) is calculated to be $-493.2_5 \pm 1.9 \text{ kcal mol}^{-1}$.

2.8.3. Enthalpy of Formation of Potassium

Hexachlorotungstate(IV).

The enthalpy of oxidative hydrolysis of solid potassium hexachlorotungstate(IV) (prepared as described in Section 5.2.7) has been measured using the usual calorimetric procedure. The calorimetric measurements were carried out on six samples (from two separate preparations) of solid potassium hexachlorotungstate(IV), each being hydrolysed in an excess of a solution of sodium hydroxide (N) and sodium hypochlorite ($\sim 1.4\%$). The six consistent values obtained (Table 2.8.3.) gave a value of $-176.4 \pm 1.8 \text{ kcal mol}^{-1}$ for the

TABLE 2.8.3

Enthalpy of hydrolysis of solid potassium
hexachlorotungstate(IV). ‡

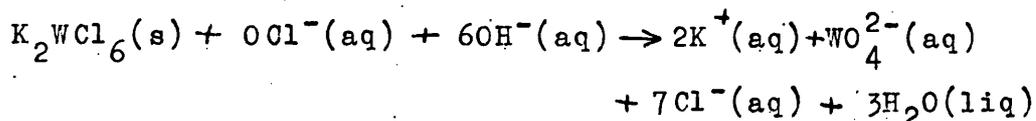
Set No.	Sample No.	Mass of sample(g)	Hydrolysing Agents	Enthalpy of hydrolysis(kcal mol ⁻¹)
1	1	0.0786	120ml N NaOH & 20ml 10% NaOCl	-176.55
1	2	0.0934	"	-174.05
1	3	0.0973	"	-173.85
2	1	0.3253	"	-178.10
2	2	0.4598	"	-178.55
2	3	0.4280	"	-177.20

Enthalpy of hydrolysis of K_2WCl_6 (solid) = -176.4 ± 1.8 kcal. mol⁻¹

Footnote. ‡

Measurements made by undergraduate students as part of a supervised project.

enthalpy of oxidative hydrolysis. The hydrolysis proceeds according to the equation:-



Using the standard enthalpies of formation of $\text{OCl}^-(\text{aq})$, $\text{OH}^-(\text{aq})$, $\text{K}^+(\text{aq})$, $\text{WO}_4^{2-}(\text{aq})$, $\text{Cl}^-(\text{aq})$ and $\text{H}_2\text{O}(\text{liq})$ (Table 2.4.2(b)) and the measured enthalpy of oxidative hydrolysis, the standard enthalpy of formation of potassium hexachlorotungstate(IV) is calculated to be $-329.9 \pm 1.8 \text{ kcal mol}^{-1}$.

The enthalpy of formation has recently been determined,⁴³ via the enthalpy of combustion; to be $324.8 \pm 6.3 \text{ kcal mol}^{-1}$.

2.9. Trends in the Enthalpies of Formation and the Bond Strengths of Binary Metal Halides.

2.9.1. Trends in the Enthalpies of Formation.

Table 2.9.1 shows the measured enthalpies of formation of the fluorides and chlorides of the second and third row transition elements in their +5 and +6 oxidation states. The graphs of the enthalpy of formation against molecular weight (Graphs 2.9.1(a) to (c)) clearly show the general trend of a decreasing enthalpy of formation⁺ with increasing molecular weight for each type of compound.

From the graphs it is possible to make rough estimates of some unknown enthalpies of formation: $\Delta H_f^\circ(\text{TcF}_5(\text{s})) \approx -260 \text{ kcal mol}^{-1}$; and $\Delta H_f^\circ(\text{OsF}_6(\text{g})) \approx -190 \text{ kcal mol}^{-1}$.

Footnote †

decreasing magnitude of the negative enthalpies of formation.

Table 2.9.1.1. - Known enthalpies of formation of fluorides and chlorides of the +5 and +6 oxidation states of the refractory metals.

Halide Type	Transition Series	Species	ΔH_f° (kcalmol ⁻¹)	Source	Ref
	2nd Row	MoF ₆ (g)	-372.3 ± 0.2 *	Settle, Feder and Hubbard	27
			-374.8 ± 2.5	this thesis (Section 2.5.1)	
			-411.5 ± 0.4 *	O'Hare and Hubbard	14
		WF ₆ (g)	-411.7 ± 0.5	Schröder and Sieben	28
			-411.8 ± 1.4	this thesis (Section 2.5.1)	
Hexafluoride	3rd Row	ReF ₆ (g)	-322.6 ± 3.2	this thesis (Section 2.5.2)	
		IrF ₆ (g)	-130	NBS Tech Note 270-4	31
			-140 †	Shchukarev et al	16 44
Hexachloride	3rd Row	WCl ₆ (g)	-122.8	NBS Tech Note 270-4	31
			-118.0 ± 6 *	JANAF Thermochemical Tables	45

TABLE 2.9.1. CONTINUED.

Halide Type	Transition Series	Species	ΔH_f^{298} (kcal mol ⁻¹)	Source	Ref.
Pentafluoride	2nd Row	NbF ₅ (s)	-432	Myers and Brady	13
		MoF ₅ (s)	-433.5 ± 0.15*	Greenberg, Natke & Hubbard this thesis (Section 2.6.2)	46
Iuoride	3rd Row	RuF ₅ (s)	-331.4 ± 1.3	Porte, Greenberg & Hubbard	47
		TaF ₅ (s)	-213.4 ± 0.35	Greenberg, Natke & Hubbard	46
		WF ₅ (s)	-346.1 ± 2.6* -1.0	Schröder and Sieben	28
			-349.9 ± 3.5	this thesis (Section 2.6.1)	
Pentachloride	2nd Row	NbCl ₅ (s)	-188.0	Schafer & Kahlenberg	48
			-190.5	Tarassenkow & Komandin	49
			-190.6	i) Amosov. ii) Gross et al. iii) NBS Tech Note 270-5	50, 51, 52
			-190.65 *	Reznitskii	53
			-193.7	Shchukarev et al	54
		MoCl ₅ (s)	-126.6	Shchukarev et al	16, 55, 56
			-126.0 *	i) NBS Tech. Note 270-4. ii) JANAF Thermochemical Tables	31, 45

TABLE 2.9.1. CONTINUED.

Halide Type	Transition Series	Species	ΔH_f^{298} (kcal mol ⁻¹)	Source	Ref.
Pentachloride	3rd Row	TaCl ₅ (s)	-205.0	i) Schafer et al. ii) Amosov	48, 50
			-205.22 *	Gal'chenko et al	57
			-205.3	NBS Tech. Note 270-5	52
			-205.5	i) Gross et al. ii) Schafer et al.	51, 58
			-206.0	Shchukarev et al.	59
		WCl ₅ (s)	-137	Shchukarev et al.	16
			-118.6	NBS Tech. Note 270-4	31
			-122.6 ± 10*	JANAF Thermochemical Tables	45
		ReCl ₅ (s)	-86 ± 5 *	Fraser	60
			-89	NBS Tech. Note 270-4	31

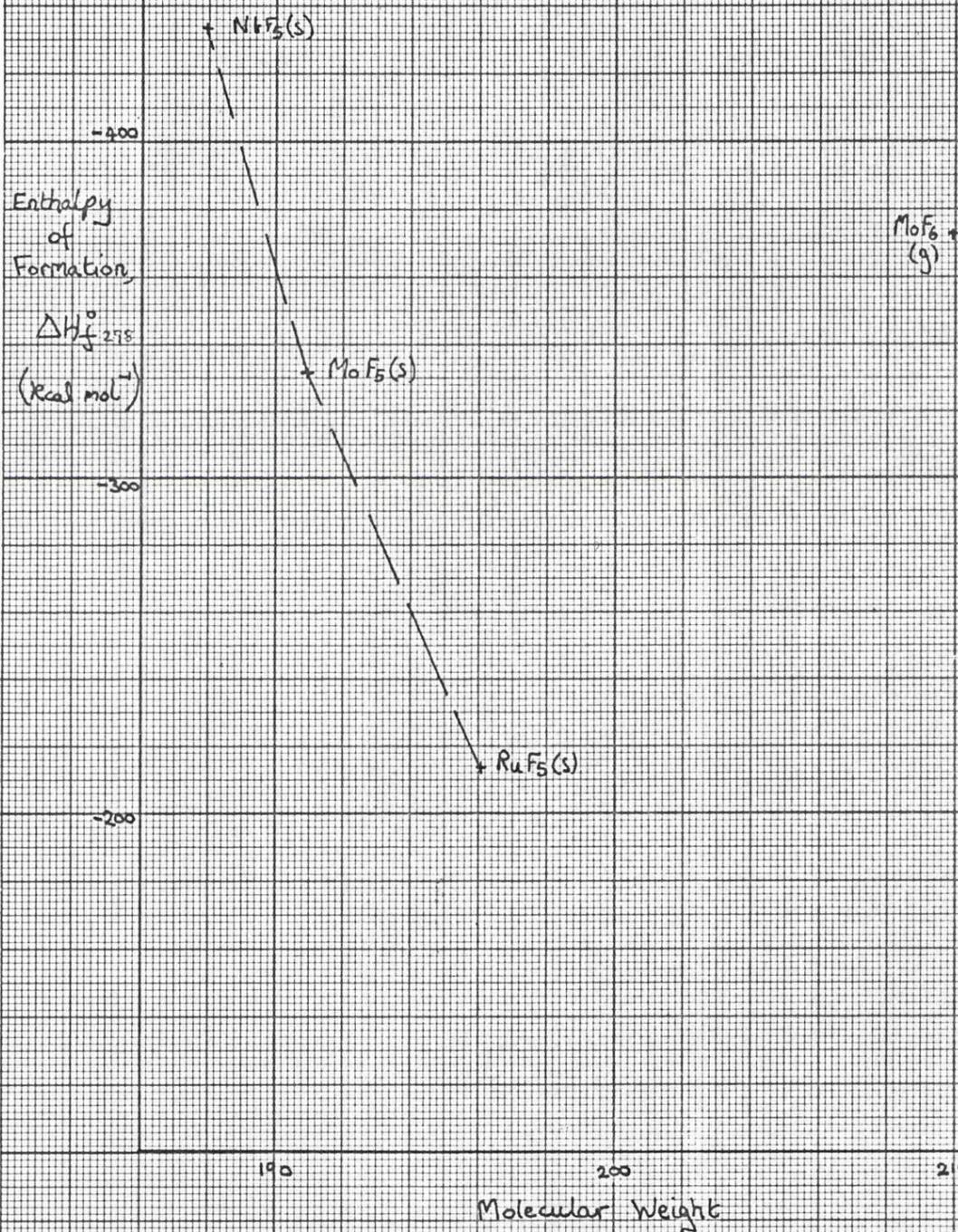
FOOTNOTES (for Table 2.9.1.) SEE OVER PAGE.

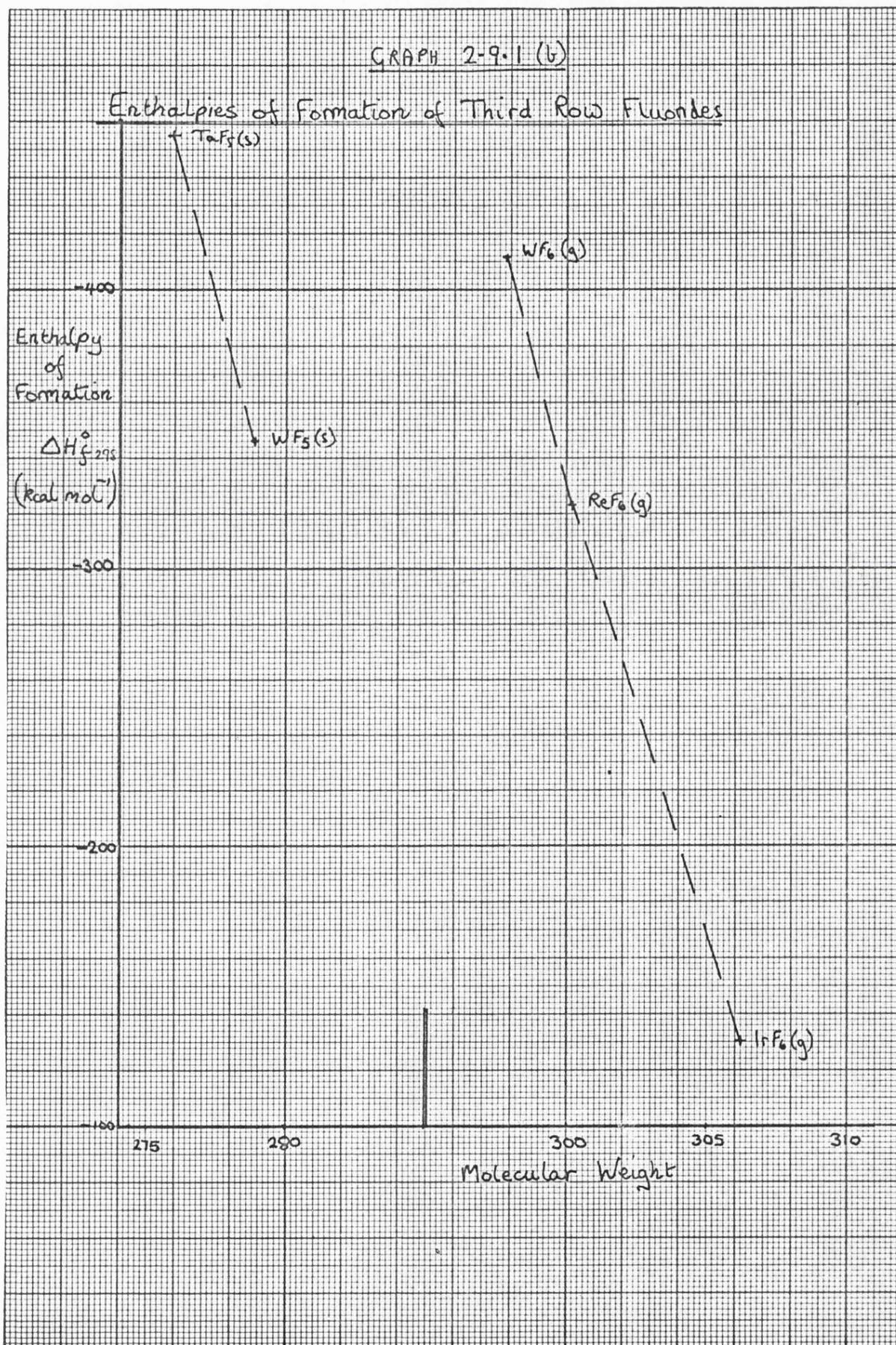
FOOTNOTES TABLE 2.9.1.

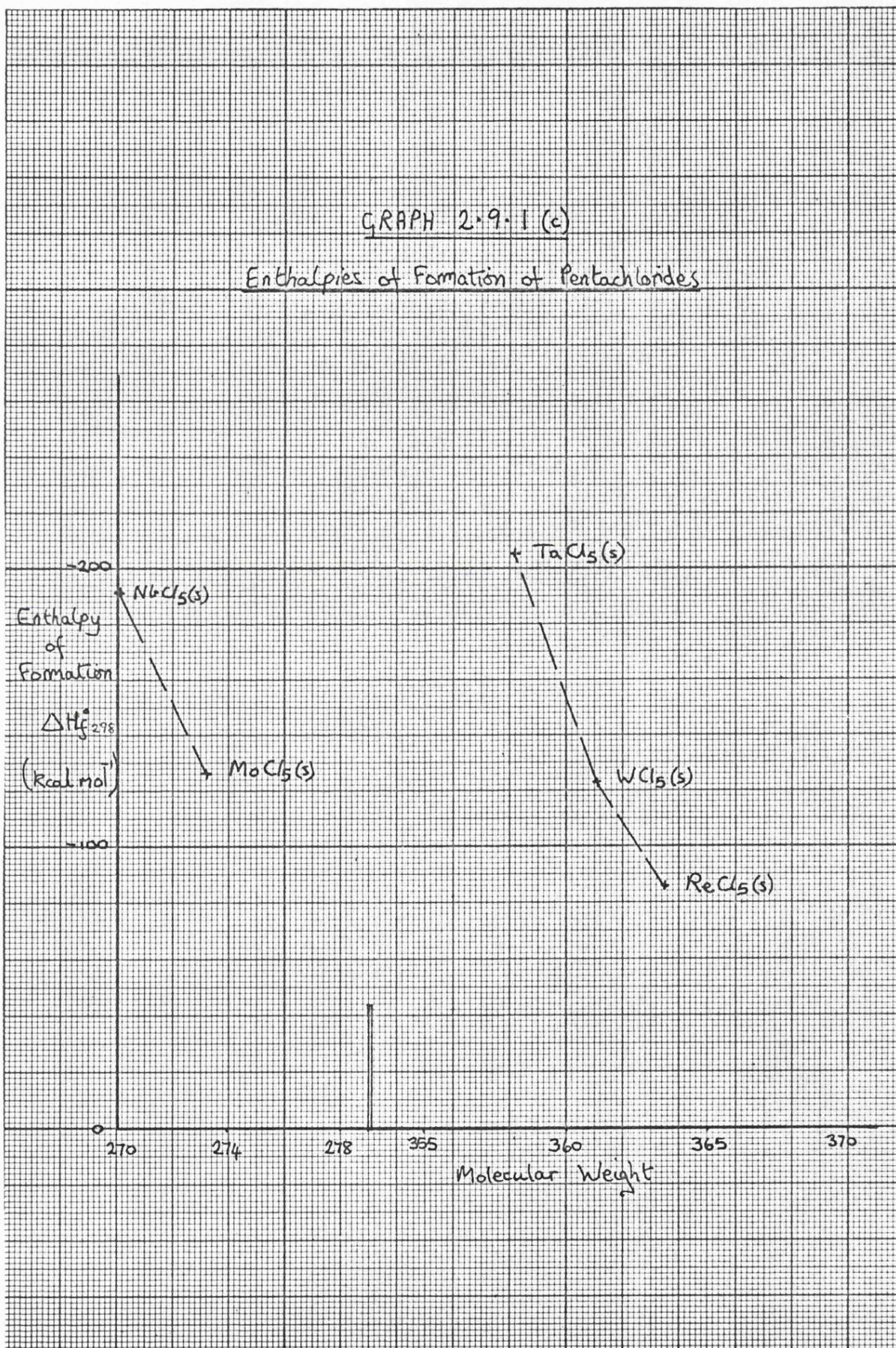
- * Where more than one value is shown the one which has been used in the later bond strength calculations has been marked thus *. When available, values obtained by bomb calorimetry have been used. In the absence of deciding factors the most recent value has been used.
- † Shchukarev has determined the enthalpy of formation of tungsten hexachloride using the enthalpy of hydrolysis. His values have not been corrected with the more recent enthalpies of formation of $WO_4^{2-}(aq)$, $OH^-(aq)$, $Cl^-(aq)$ and $H_2O(liq)$. The enthalpy of formation of tungsten pentachloride given by Shchukarev is determined from his enthalpy of formation for the hexachloride.

GRAPH 2.9.1 (a)

Enthalpies of Formation of Second Row Fluorides



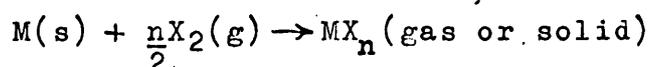




2.9.2. Use of Bond Strengths.

(a) Inadequacies of comparisons of enthalpies of formation

The enthalpy of formation of a compound is defined as the energy absorbed when the compound in its standard state is formed from its elements in their standard states. In the case of the transition metal fluorides and chlorides, the enthalpy of formation is the energy absorbed in the reaction:-



Therefore, a comparison of the enthalpies of formation does not take into account changes in the lattice energy of the metal, the dissociation energy of the halogen or the state of the halide. A better comparison with thermal stabilities and chemical reactivities can be obtained by considering either the enthalpy of reaction $MX_n(g) \rightarrow M(g) + nX(g)$ (called the enthalpy of atomisation) or the average metal halide bond strength in the compound.

(b) Definition and derivation of bond strength.

Bond strength is defined as the enthalpy change associated with the reaction in which one mol. of the bond is homolytically broken[†], the reactants and products being in the ideal gas state at 25°C and 1 atmosphere pressure.

For a compound, MX_n , the average metal halide bond strength, $\Delta H(M-X)$, is derived from the thermochemical cycles (Figure 2.9.2.). Where the enthalpy of formation of the gaseous metal halide is known, the average metal halide bond strength, obtained using cycle (a), is given by:-

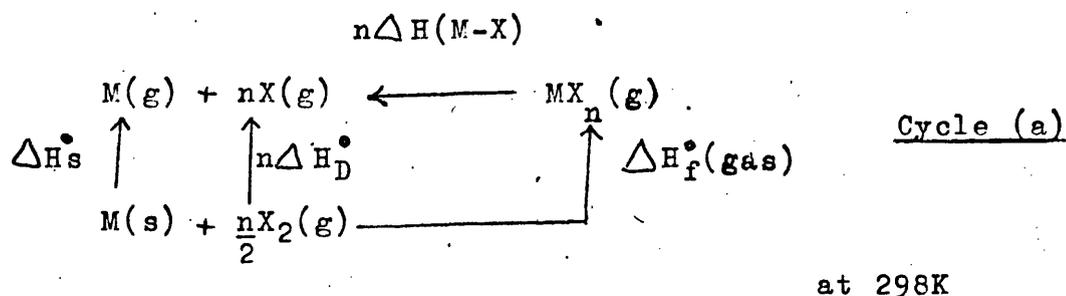
Footnote.

[†] Gives positive bond strengths to stable bonds

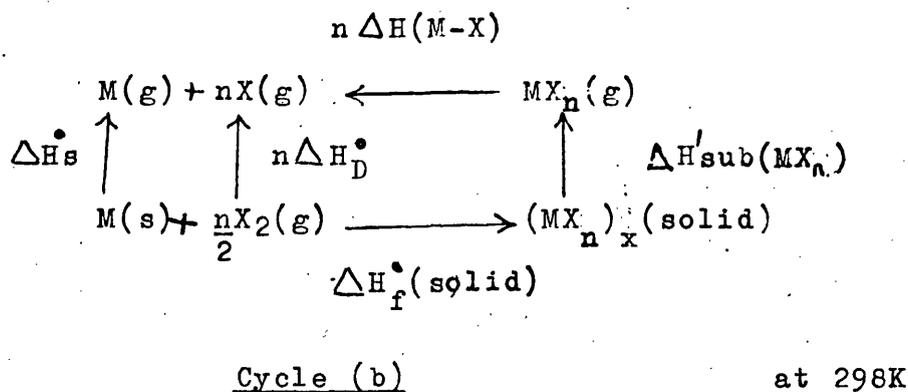
$$\Delta H(M-X) = \frac{\Delta H_s^\bullet + n\Delta H_D^\bullet - \Delta H_f^\bullet(\text{gas})}{n} \quad \text{Eq. 2.9.2(a).}$$

Figure 2.9.2. - Bond Strengths from thermochemical cycles.

(a) for gaseous metal halides.



(b) for solid metal halides.



Where

ΔH_s^\bullet is the enthalpy of sublimation of the metal (and is equal to the enthalpy of formation of the gaseous metal)

ΔH_D^\bullet is the enthalpy of formation of one halogen atom (or half the dissociation energy of one halogen molecule)

$\Delta H_f^\bullet(\text{gas})$ is the enthalpy of formation of the gaseous metal halide.

$\Delta H_f^\circ(\text{solid})$ is the enthalpy of formation of the solid metal halide.

$\Delta H'_{\text{sub}}(\text{MX}_n)$ is the enthalpy of sublimation of the metal halide (including, if necessary, the dissociation to the monomeric vapour)

When the enthalpy of the solid metal halide is known, the average metal halogen bond strength, obtained using cycle(b), is given by:-

$$\Delta H(\text{M-X}) = \frac{\Delta H_s^\circ + n\Delta H_D^\circ - \Delta H_f^\circ(\text{solid}) - \Delta H'_{\text{sub}}(\text{MX}_n)}{n} \quad \text{Eq 2.9.2(b)}$$

2.9.3. Trends in the Bond Strengths of Metal Halides.

(a) Bond Strengths in Hexahalides.

Values of the average metal halogen bond strengths in the metal hexahalides have been calculated using equation 2.9.2(a) and the data shown in Tables 2.9.1 (enthalpies of formation of the gaseous hexahalides), 2.9.3(a) (enthalpies of formation of the gaseous atomic halogens) and 2.9.3(b) (enthalpies of formation of the metals in their gaseous states). The metal-halogen bond strengths of the hexahalides are given in Table 2.9.3(d).

(b) Bond Strengths in Pentahalides.

Values of the average metal-halogen bond strengths in the metal pentahalides have been calculated using equation 2.9.2(b). The data shown in the Tables 2.9.1, 2.9.3(a) and 2.9.3(b) have been used directly.

However, equation 2.9.2(b) requires the use of the

enthalpy of sublimation giving the monomeric ^{halide} vapour at 298K. In the case of the pentachlorides, the measured enthalpies of sublimation (Table 2.9.3(c)) are known to refer to sublimation to the monomers. Since all these known enthalpies of sublimation of the pentachlorides are $\sim 20 \text{kcal mol}^{-1}$, the unknown enthalpies of the sublimation of pentachlorides have been taken as 20kcal mol^{-1} .

In the case of tungsten pentafluoride, Schröder has shown that his enthalpy of sublimation ($23.4 \text{kcal mol}^{-1}$)⁶ is for the reaction $(\text{WF}_5)_4(\text{solid}) \rightarrow (\text{WF}_5)_4(\text{vapour})$. However, he has also estimated the enthalpy of sublimation to the monomeric vapour to be $16 \pm 2 \text{kcal mol}^{-1}$ ²⁸. Junkins et al⁶¹ have estimated the enthalpy of sublimation of niobium pentafluoride to be $22.4 \text{kcal mol}^{-1}$. This is assumed to refer to sublimation to the monomer. The unknown enthalpies of sublimation of the pentafluorides ($\text{MF}_5(\text{s}) \rightarrow \text{MF}_5(\text{monomeric vapour})$) have been taken as 20kcal mol^{-1} .

The calculated metal-halogen bond strengths are shown in Table 2.9.3(d) and on Graphs 2.9.3. (a) to (c)

(c) Trends in the Bond Strengths.

The graphs (2.9.3 (a) to (c)) clearly show the decreasing bond strength (in a particular compound type) with increasing molecular weight. It was suggested earlier (Section 2.9.2) that the variation in the bond strength gives a better indication of thermal stability and chemical reactivity trends within a series of compounds than do the variations in the enthalpies of formation.

Table 2.9.3(a) - Enthalpies of Formation of the Halogens and Oxygen in the Gaseous Atomic State.

Species	Enthalpy of formation ΔH_{f298}° (kcal mol ⁻¹)	Source	Ref.
F(gas)	18.88	NBS Tech. Note 270-3(1968)	29
Cl(gas)	29.082	"	"
Br(gas)	26.741	"	"
I (gas)	25.535	"	"
O (gas)	59.553	"	"

Table 2.9.3(b) - Enthalpies of Formation of some Transition Metals in the Gaseous State (from N.B.S. Technical Notes).

Metal Species	Enthalpy of formation ΔH_{f298}° (kcal mol ⁻¹)	Source*	Ref.
Nb(gas)	173.5	NBS Tech Note 270-5(1971)	52
Mo(gas)	157.3	NBS Tech Note 270-4(1969)	31
Tc(gas)	162	"	"
Ru(gas)	153.6	"	"
Rh(gas)	133.1	"	"
Pd(gas)	90.4	"	"
Ta(gas)	186.9	NBS Tech Note 270-5(1971)	52
W(gas)	203.0	NBS Tech Note 270-4(1969)	31
Re(gas)	184.0	"	"
Os(gas)	189.0	"	"
Ir(gas)	159.0	"	"
Pt(gas)	135.1	"	"

* In general there are several similar values for each of these enthalpies. The values from the N.B.S. Technical Notes have been used throughout for consistency. A good review of the thermochemistry of the platinum group of metals is given by Goldberg and Hepler⁶². Close agreement exists between this review and N.B.S. Tech. Note 270-4.

Table 2.9.3(c) - Known Enthalpies of Sublimation of Metal Pentahalides.

Halide	Enthalpy of sublimation [†] $\Delta H'_{\text{sub}298}$ (kcal mol ⁻¹)	Source	Ref.
NbF ₅	23.0 (22.4 at M.Pt)	Junkins et al (1952) corrected by Kubaschewski et al (1967)	61 34
NbCl ₅	22.42 ± 0.06	Keneshea et al (1968)	63
MoCl ₅	18.8	Saeki & Matsuzaki (1965) & JANAF Thermochemical Tables (1971)	64 45
TaCl ₅	21.63	Saeki et al (1968)	65
WF ₅	23.4* 16 +	Schröder and Grewe (1970)	6
		Schröder and Sieben (1970)	28
WCl ₅	24	Shchukarev et al (1959) & JANAF Thermochemical Tables (1971)	66 45

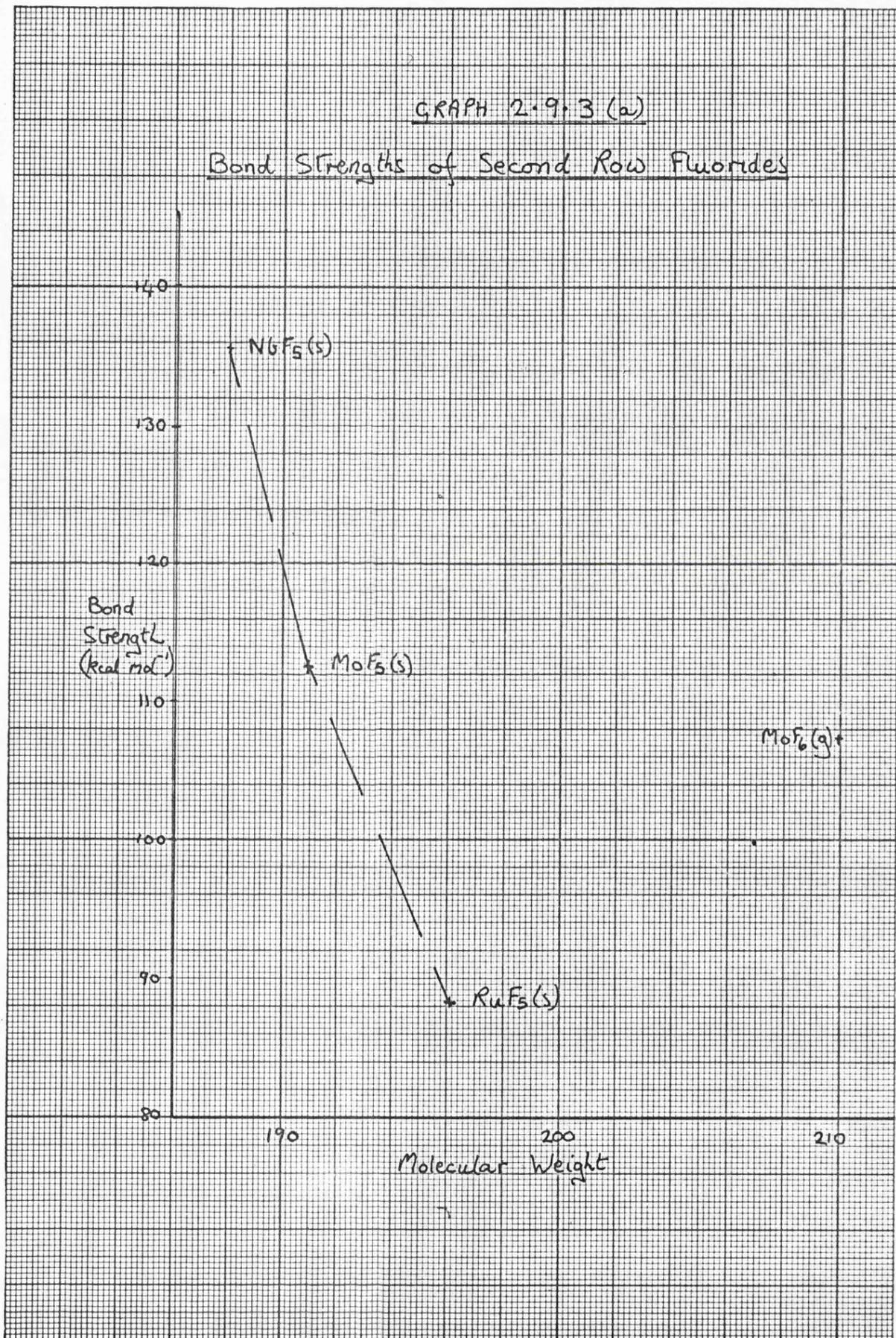
* 23.4 kcal per mole of tetrameric vapour formed

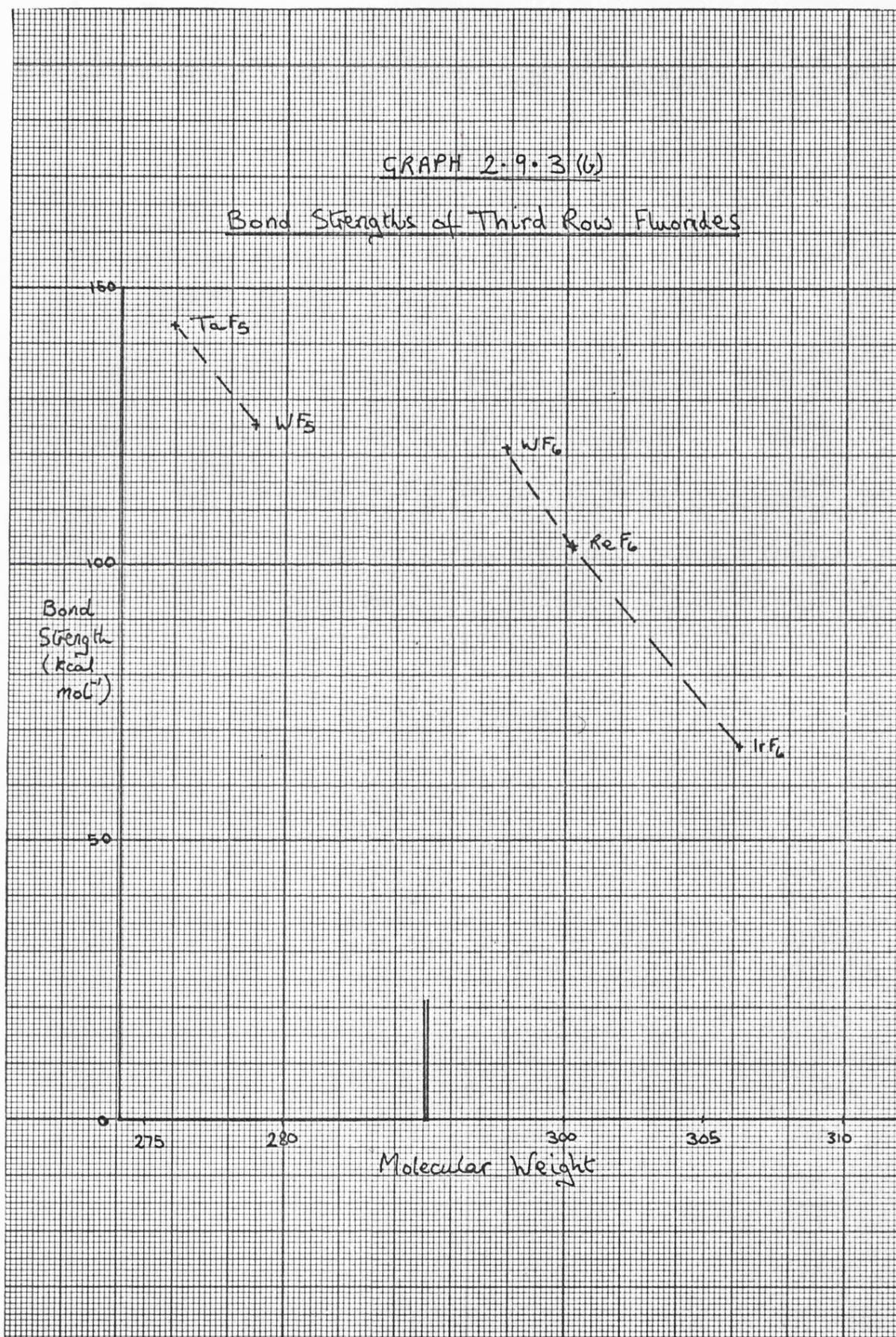
+ 16 kcal per mole of monomeric vapour formed

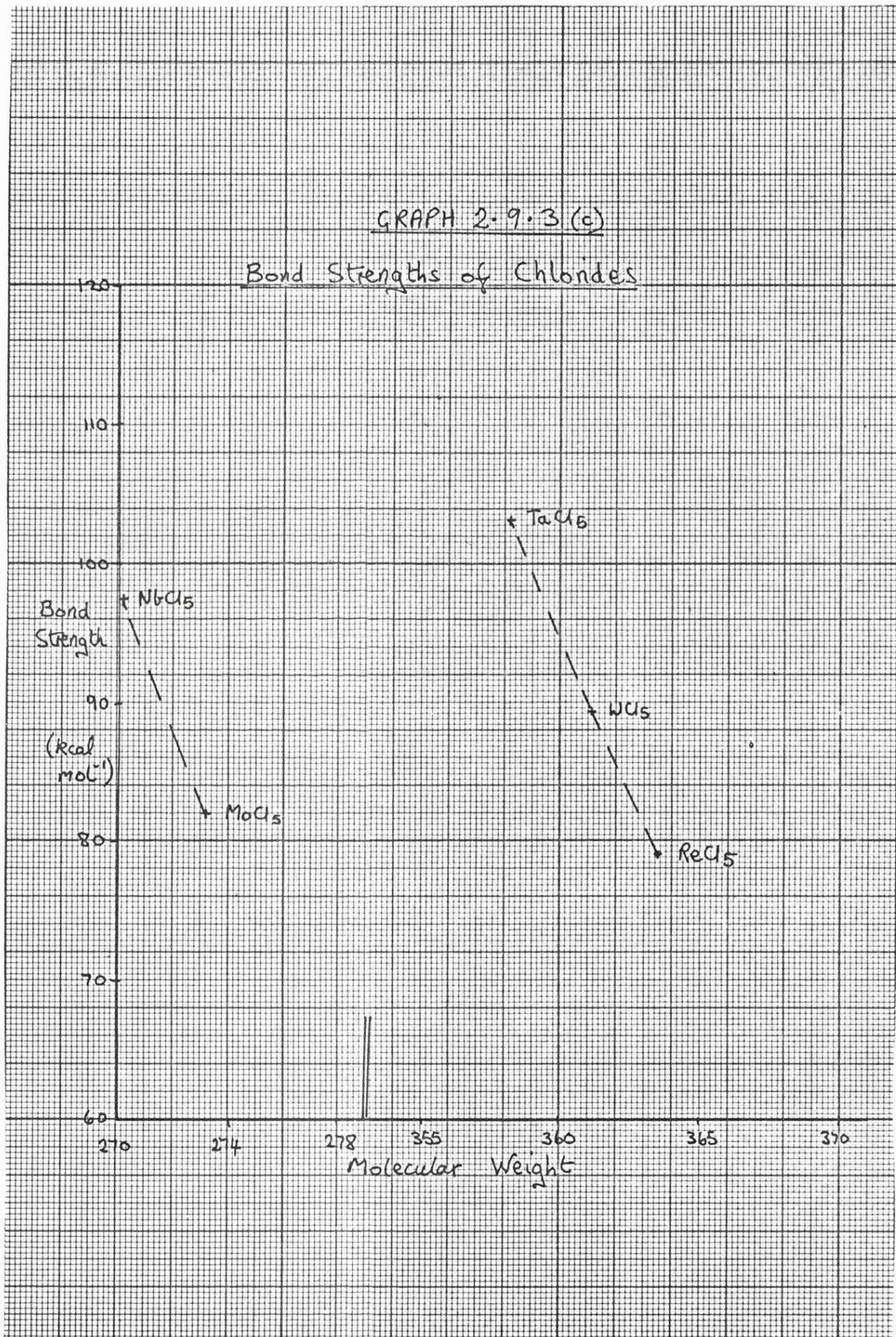
† The enthalpies of sublimation of the pentachlorides shown are known to refer to sublimation to the monomer. NbF₅ is assumed to refer to sublimation to the monomer.

Table 2.9.3(d) - Bond Strengths in Halides.

Halide Type	Transition Series	Halide	Calculated Ave. Metal-Halogen Bond Strength(kcal mol ⁻¹ bond ⁻¹)
Hexafluoride	2nd Row	MoF ₆	107.15
	3rd Row	WF ₆	121.3
		ReF ₆	103.3
		IrF ₆	67.05
Hexachloride	3rd Row	WCl ₆	82.58
Pentafluoride	2nd Row	NbF ₅	135.6
		MoF ₅	112.6
		RuF ₅	88.3
	3rd Row	TaF ₅	143.26
		WF ₅	125.5
Pentachloride	2nd Row	NbCl ₅	97.43
		MoCl ₅	82.0
	3rd Row	TaCl ₅	103.18
		WCl ₅	89.4
		ReCl ₅	79.08







(d) A Previous Demonstration of Bond Strength Trends.

In their review article, Canterford, Colton and O'Donnell¹¹ have suggested that the $a_{1g}(\nu)$ mode of the vapour phase spectrum of an hexafluoride may be taken as a measure of the bond strength since it is ^acompletely symmetrical vibration which does not change the symmetry of the molecule or involve any movement of the central atom. Graphs of the a_{1g} frequencies against molecular weight clearly follow the decreasing bond strength with increasing molecular weight for both transition series. (Table 2.9.3(e) shows data on the third row hexafluorides).

(e) Explanation of Bond Strength Trends.

The decreasing bond strength along a series (for a particular compound type) can be explained by a consideration of the molecular orbitals in that compound. The 2nd row hexafluorides are considered in detail.

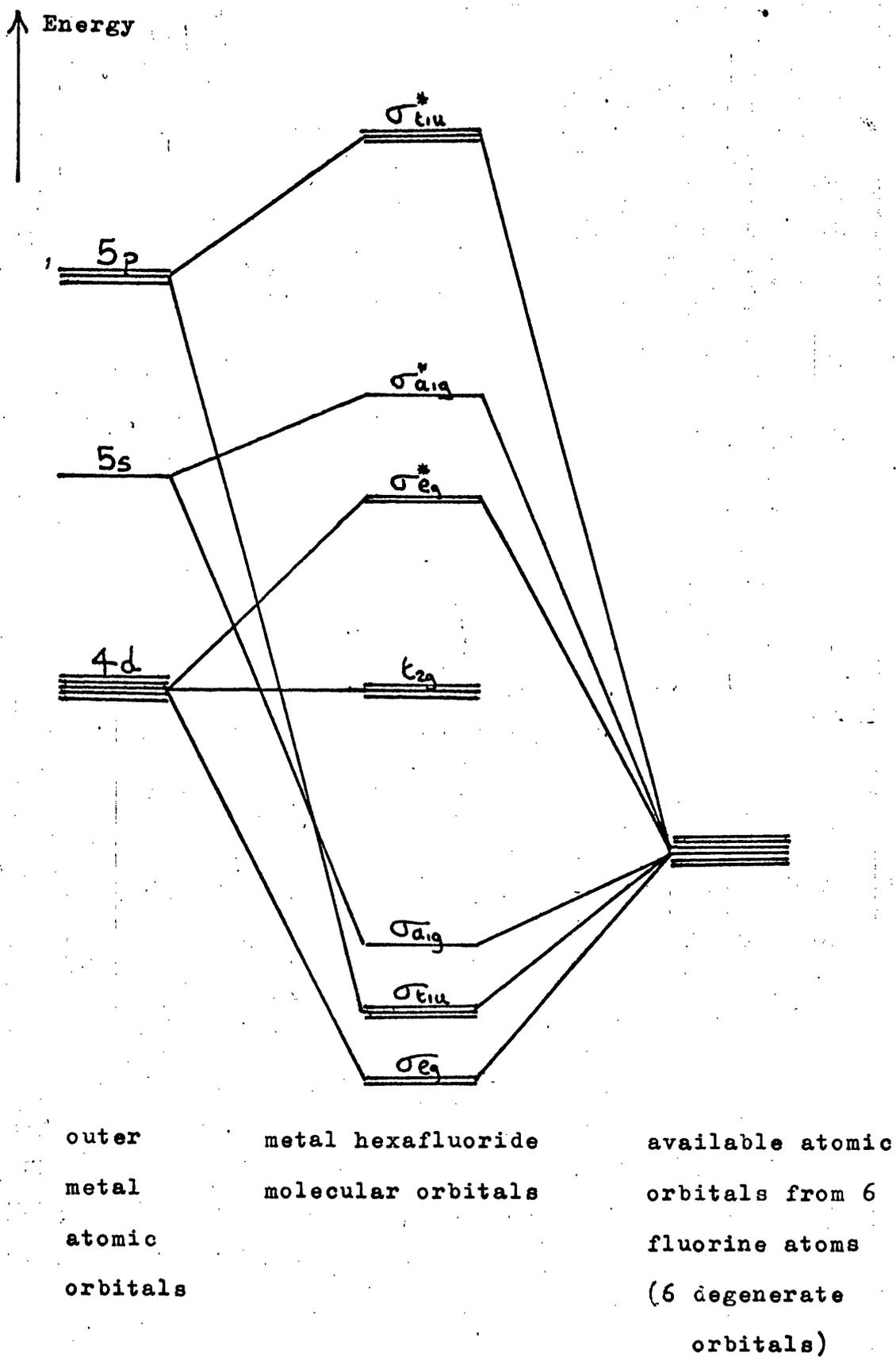
In a simple σ bonding treatment of a hexafluoride, the molecular orbitals are made up as shown in Figure 2.9.3(a). The $\sigma_{a_{1g}}$, $\sigma_{t_{1u}}$ and σ_{e_g} are bonding orbitals, the t_{2g} are non-bonding orbitals and the $\sigma_{e_g}^*$, $\sigma_{a_{1g}}^*$, and $\sigma_{t_{1u}}^*$ are anti-bonding orbitals.

Each of the six available ligand σ orbitals contains one electron. Since the outer atomic structure of molybdenum is $5s^1 4d^5$, there are twelve electrons available for the σ orbitals of MoF_6 . Therefore, only the 6 σ bonding orbitals will be filled. Proceeding along the period (to TcF_6 , RuF_6 , RhF_6 and PdF_6) electrons are added to the t_{2g} non-bonding orbitals and the number of σ bonding electrons is unchanged.

Table 2.9.3(e) 3rd Row Hexafluoride Bond Strengths and $\nu_1(a_{1g})$ vibrational frequencies.

Hexafluoride	$\nu_1(a_{1g})$ vibration ⁶⁷ frequency(cm^{-1})	Bond Strength ($\text{kcal mol}^{-1} \text{ bond}^{-1}$)
WF ₆	771.0	121.3
ReF ₆	753.7	103.3
OsF ₆	730.7	
IrF ₆	701.7	67.0
PtF ₆	656.4	

Figure 2.9.3(a). Molecular Orbitals in Metal Hexafluorides
(octahedral). (adapted from Orgel⁷⁰)



However, there are two factors which do lead to a decrease in bonding along the Period:

1. The σ orbitals in the hexafluoride are modified[†] by the π type p orbitals of the fluorine ligands thus:-

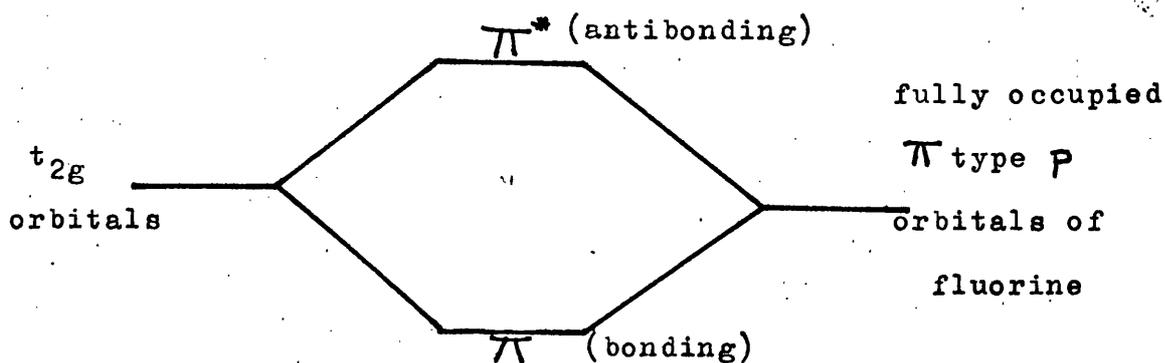


Figure 2.9.3(b) π bonding in MF_6 .

In the case of MoF_6 the t_{2g} orbitals are unoccupied so that only the π bonding molecular orbitals are filled. However, with TcF_6 , the t_{2g} orbitals contain one electron, which must occupy a π^* antibonding orbital. Therefore, the π bond stabilisation energy of TcF_6 is decreased with respect to MoF_6 . Proceeding along the period (to RuF_6 , RhF_6 and PdF_6) further electrons are added to the π^* antibonding orbitals leading to a steady decrease in the π bonding character (and, therefore, in the overall bond strength).

2. The t_{2g} electrons are ineffective in their screening of the nuclear charge. Therefore, along each Period the effective nuclear charge of the metal increases. Consequently the d orbital size and the d σ bonding overlap in the hexafluorides decrease along the period. (ie. a decrease in the σ bond

[†] That fluorine to transition metal π bonding does occur has been demonstrated by Dyer & Ragsdale^{68,69} in a ¹⁹F NMR study of nitrogen base adducts of titanium tetrafluoride.

strength occurs). Although the decreasing size of the d orbitals would tend to cause a decrease in the bond lengths, the hexafluoride bond lengths show no such trend. This is probably due to the opposing bond lengthening effect of the loss of π bonding character.

Each of these factors causes a decrease in bond strengths (in either π or σ bonding) along the 2nd row transition series of hexafluorides and their combination should explain the observed trends. Similar arguments can be used for the 3rd row hexafluorides, the hexachlorides and, with more difficulty, for the pentahalides.

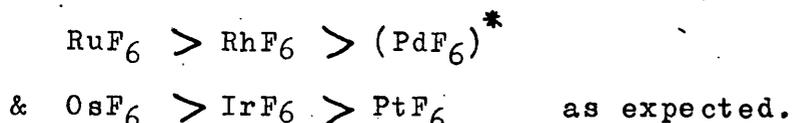
(f) Bond Strengths, Thermal Stability and Chemical Reactivity

Reactivity

Although the energy required to break the first bond is usually the decisive factor in thermal stability and chemical reactivity, the average bond strength gives an indication of this energy and, therefore, of the thermal stability and chemical reactivity.

The steady decrease in bond strength with increasing molecular weight for a particular compound type would, therefore, be expected to lead to a steady decrease in thermal stability and a steady increase in chemical reactivity.

In the case of the hexafluorides, the thermal stabilities of the less stable hexafluorides are in the following order:



The review of Canterford, Colton and O'Donnell¹¹ showed some correlation between the bond strengths (based on

* PdF_6 is unknown.

infra-red frequencies) and the chemical reactivities of the hexafluorides. More specifically the reactions considered (with NO, NOF and Xe) show the oxidising power of the third row hexafluorides to be in the order $\text{PtF}_6 > \text{IrF}_6 > \text{OsF}_6 > \text{ReF}_6 > \text{WF}_6$ as suggested by Bartlett⁷¹. If these reactions are straightforward electron transfer reactions with no unusual kinetic effects then this order of reactivity would be expected to be dependent on the electron affinity of the hexafluoride rather than the bond strength. However, the explanation for the difference in the reactivities of MoF_6 and WF_6 with nitric oxide (see discussion in Section 2.13) considers the important mechanistic step in preventing the reaction of WF_6 to be



This step is dependent on the first bond strength (or the average bond strength - see above). Extrapolation to the other hexafluorides suggests that the reactions of the hexafluorides with nitric oxide should show some dependence on bond strengths and this is reflected in the reactivities (see Table 2.9.3(f) which compares the bond strengths of the hexafluorides with the products of the nitric oxide reaction).

In the case of the pentafluorides thermal breakdown occurs by disproportionation and is not completely dependent on pentafluoride bond strength. In particular, tungsten pentafluoride is thermally very unstable⁶ with respect to disproportionation. Canterford et al¹¹ have put the irregular progression of pentafluoride thermal stabilities down to the three different structural types of the pentafluorides.

With the pentachlorides, there is some correlation between bond strengths and thermal stability. Only the pentachlorides of niobium, tantalum, molybdenum, tungsten and rhenium are known. Niobium and tantalum pentachlorides are thermally stable whereas with molybdenum, tungsten and rhenium pentachlorides thermal breakdown occurs relatively easily.

Table 2.9.3(f). A Comparison of Reactivity and Bond Strength for 3rd Row Hexafluorides

3rd Row Hexafluoride	Reaction Products [‡] of the Hexafluoride with nitric oxide.	Bond Strength (kcal mol ⁻¹ bond ⁻¹)
WF ₆	no reaction	121.3
ReF ₆	NOREF ₆	103.3
OsF ₆	NOOsF ₆	-
IrF ₆	NOIrF ₆ & (NO) ₂ IrF ₆	67.0
PtF ₆	NOPtF ₆ & (NO) ₂ PtF ₆	-

[‡] see references 11 and 71 to 74.

2.9.4. Oxidation of Pentahalides.

From known and estimated enthalpies of formation of the pentahalides and hexahalides, the enthalpies of oxidation of the pentahalides (to the hexahalides) have been calculated and are shown in Table 2.9.4.

The table shows that the three pentafluorides are readily oxidised. The fact that tungsten pentafluoride is the most readily oxidised has been used to explain differences in the oxidising properties of the hexafluorides (Section 2.13).

Table 2.9.4. - Enthalpies of Oxidation of Pentahalides.

Halide type	Oxidation	Enthalpy of oxidation, ΔH_{ox}° (kcal mol ⁻¹)	Source of enthalpies used in determination	Ref.
2nd Row fluorides	$\text{MoF}_5(\text{s}) + \frac{1}{2}\text{F}_2 \rightarrow \text{MoF}_6(\text{g})$	-40.9	this thesis & Hubbard	27
		-43.4	this thesis	
3rd Row fluorides	$\text{WF}_5(\text{s}) + \frac{1}{2}\text{F}_2 \rightarrow \text{WF}_6(\text{g})$	-65.6	Schröder & Sieben	28
		-61.9	this thesis	
3rd Row chlorides	$\text{ReF}_5(\text{s}) + \frac{1}{2}\text{F}_2 \rightarrow \text{ReF}_6(\text{g})$	-28.5(est)	this thesis (ReF ₅ est via bond strengths)	
		-4.2	NBS 270-4	
	$\text{WCl}_5(\text{s}) + \frac{1}{2}\text{Cl}_2 \rightarrow \text{WCl}_6(\text{g})$	+4.6	JANAF Thermochemical Tables	45
		-25.2	NBS 270-4	31
	$\text{WCl}_5(\text{s}) + \frac{1}{2}\text{Cl}_2 \rightarrow \text{WCl}_6(\text{s})$	-19.3	JANAF Thermochemical Tables	45

2.10. Tungsten and Molybdenum Oxyfluorides.

2.10.1 Enthalpies of Formation and Stabilities of Oxytetrafluorides.

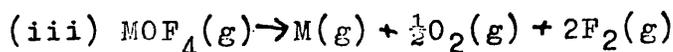
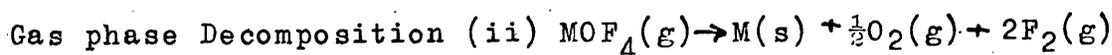
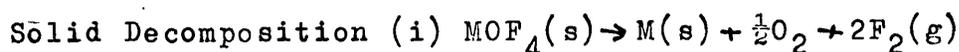
The enthalpies of formation of solid tungsten oxytetrafluoride and solid molybdenum oxytetrafluoride have been measured (Section 2.7) as -358.5 ± 2.2 and -329.8 ± 1.2 kcal mol⁻¹ respectively.

The enthalpies of sublimation of tungsten and molybdenum oxytetrafluoride are 16.5 and 13.1 kcal mol⁻¹ respectively³⁷. Since the vapours are monomeric³⁸⁻⁴¹, the enthalpies of formation of gaseous monomeric tungsten oxytetrafluoride and molybdenum oxytetrafluoride are -342 and -316.7 kcal mol⁻¹ respectively.

The stability of an oxytetrafluoride may be discussed with respect to possible thermal decomposition reactions.

(a) Decomposition to the elements.

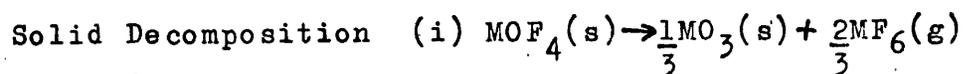
Here the possible decomposition reactions are:-

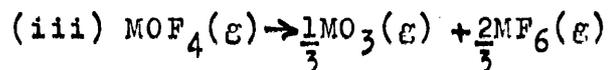
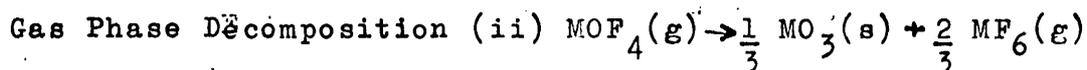


Using the known standard enthalpies of formation (Section 2.7) and known (or estimated) standard entropies,⁴⁵ the free energies, ΔG_{298}° , of these decomposition reactions have been calculated (Table 2.10.1(a)). The large positive free energies indicate that these decompositions will not occur.

(b) Decomposition to oxides and fluorides.

Here the possible decomposition reactions are:-





Again using standard enthalpies of formation (Section 2.7 & 2.5 and JANAF Thermochemical Tables⁴⁵) and known (or estimated) entropies, (Appendix 2 and JANAF Thermochemical Tables⁴⁵) the free energies, ΔG_{298}° , of these decomposition reactions have been calculated (Table 2.10.1(b)). The positive values obtained indicate that these decomposition reactions will not occur at room temperature.

Because the entropy change of the solid decomposition reaction (i) is favourable to decomposition, increasing the temperature will make this reaction less unfavourable. Above a certain undetermined temperature decomposition would be expected to occur. However, both oxytetrafluorides melt and boil without decomposition. The entropy changes of the gaseous decomposition reactions (ii) and (iii) are unfavourable to decomposition. Therefore, increasing ^{the} temperature will make these decomposition reactions more unfavourable.

(c) Decomposition to other oxyfluorides.

Here two possible decompositions are:-



The only thermochemical data available on the other oxyfluorides are the enthalpies of formation of the gaseous dioxydifluorides determined by Zmbov, Uy and Margrave¹⁵ by mass spectrometric methods. Using these and other known enthalpies of formation (Section 2.7 and 2.5) the enthalpies of the decomposition $\text{MOF}_4(\text{g}) \rightarrow \frac{1}{2} \text{MO}_2\text{F}_2(\text{g}) + \frac{1}{2} \text{MF}_6(\text{g})$ have been determined

Table 2.10.1.(a) - Decomposition of the oxytetrafluorides to their elements.

No.	Decomposition Reaction	ΔH_{298}° Enthalpy of decomposition (kcal mol ⁻¹)		ΔS_{298}° Entropy of decomposition (cal mol ⁻¹ deg ⁻¹ c)		ΔG_{298}° Free Energy of decomposition (kcal mol ⁻¹)	
		of WOF ₄	of MoOF ₄	of WOF ₄	of MoOF ₄	of WOF ₄	of MoOF ₄
(i)	$\text{MoF}_4(\text{s}) \rightarrow \text{M}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) + 2\text{F}_2(\text{g})$	+358.5	+329.8	+87.2	—	+322.5	—
(ii)	$\text{MoF}_4(\text{g}) \rightarrow \text{M}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) + 2\text{F}_2(\text{g})$	+342	+316.7	+48.8	+49.25	+327.5	+302.0
(iii)	$\text{MoF}_4(\text{g}) \rightarrow \text{M}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) + 2\text{F}_2(\text{g})$	+545.4	+474	+82.55	+85.87	+520.8	+448.4

Table 2.10.1(b) - Decomposition of the oxytetrafluorides to the oxides and the fluorides.

No.	Decomposition Reaction	ΔH_{298}° Enthalpy of decomposition (kcal mol ⁻¹)		ΔS_{298}° Entropy of decomposition (cal mol ⁻¹ deg ⁻¹ C)		ΔG_{298}° Free Energy of decomposition (kcal mol ⁻¹)	
		of WOF ₄	of MoOF ₄	of WOF ₄	of MoOF ₄	of WOF ₄	of MoOF ₄
(i)	$\frac{1}{3}\text{MoF}_4(\text{s}) \rightarrow \frac{1}{3}\text{MoO}_3(\text{s}) + \frac{2}{3}\text{MF}_6(\text{g})$	+16.8	+20.6	+20.20	—	+10.8	—
(ii)	$\frac{1}{3}\text{MoF}_4(\text{g}) \rightarrow \frac{1}{3}\text{MoO}_3(\text{s}) + \frac{2}{3}\text{MF}_6(\text{g})$	+0.3	+7.5	-18.20	-16.97	+5.7	+12.6
(iii)	$\frac{1}{3}\text{MoF}_4(\text{g}) \rightarrow \frac{1}{3}\text{MoO}_3(\text{g}) + \frac{2}{3}\text{MF}_6(\text{g})$	+44.1	+38.1	-1.45	-0.87	+44.5	+38.4

as $+28.6 \text{ kcal mol}^{-1}$ for tungsten and $-4.7 \text{ kcal mol}^{-1}$ for molybdenum. This suggests that, in the case of molybdenum, the decomposition might occur. However, since the free energies of the decomposition have not been considered (due to lack of data) and since the error in the enthalpy of formation of molybdenum dioxydifluoride is $\pm 10 \text{ kcal mol}^{-1}$ this is not conclusive.

2.10.2. General Stability of Tungsten and Molybdenum oxyfluorides.

Known thermochemical data (Table 2.10.2) have been used to construct a graph (Graph 2.10.2) of enthalpy of formation against number of oxygen atoms, for the series of gaseous species $\text{MO}_n\text{F}_{6-2n}$ ($M=W$ or Mo). The graph is an excellent illustration of the "substitution principle"⁷⁵ which predicts the existence of oxyhalides with enthalpies of formation intermediate between the corresponding binary oxides and halides. The curving nature of the graph gives the stability of the oxyfluorides towards decomposition to the binary oxides and halides. From the graph it appears that, in a consideration of stability towards decomposition, $\text{MoO}_2\text{F}_2(\text{g})$ is more stable than $\text{MoOF}_4(\text{g})$ but $\text{WOF}_4(\text{g})$ is more stable than $\text{WO}_2\text{F}_2(\text{g})$ (see also previous Section).

Table 2.10.2 - Enthalpies of formation of gaseous oxides, fluorides and oxyfluorides of tungsten and molybdenum.

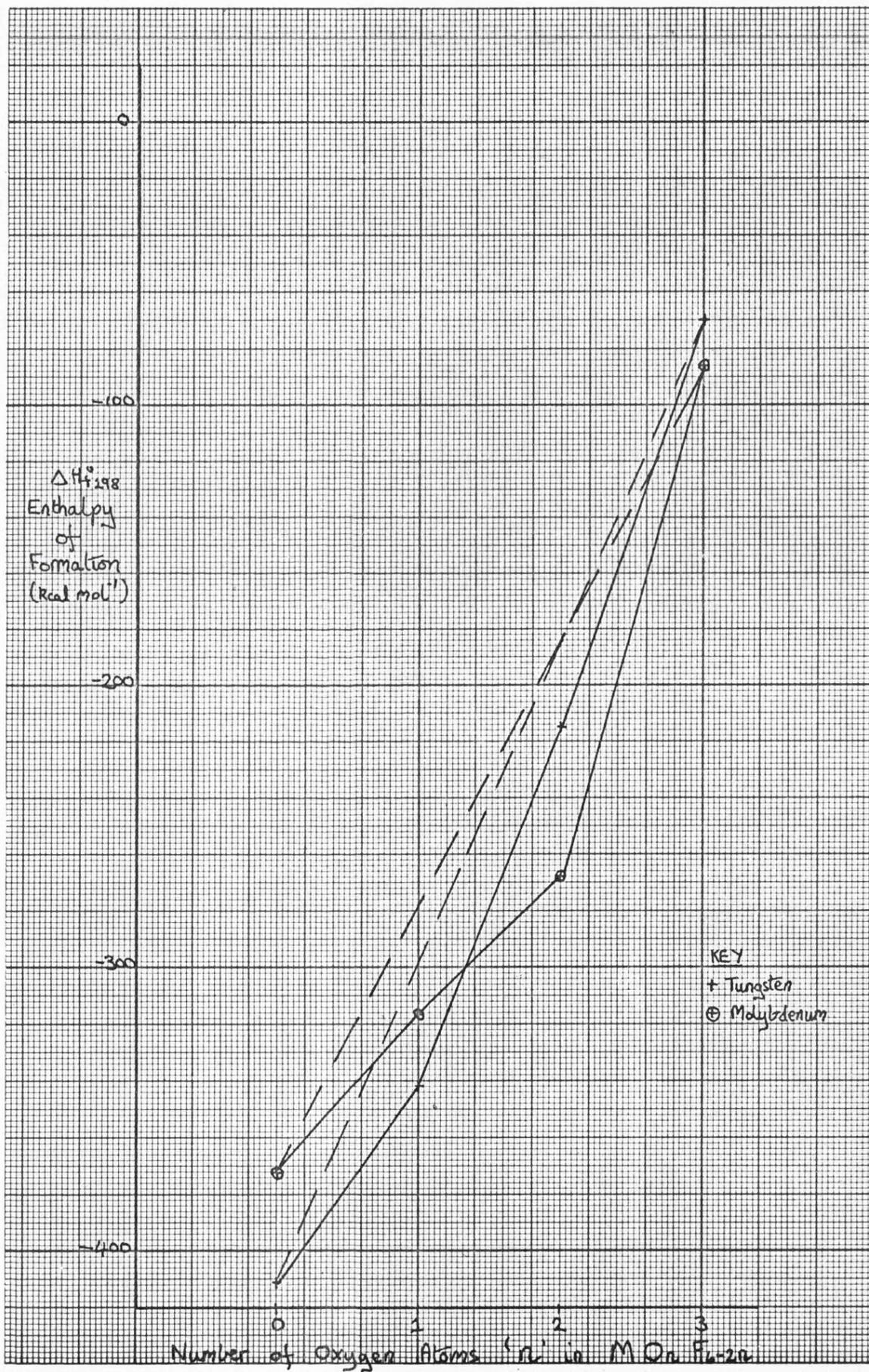
(a) Tungsten Compounds.

Species	Enthalpy of formation, $\Delta H_{f,298}^{\circ}$ (kcal mol ⁻¹)	Source	Ref.
WF ₆ (g)	-411.5	O'Hare and Hubbard	14
WOF ₄ (g)	-342.0	this thesis (Sections 2.7.1 & 2.10.1)	
WO ₂ F ₂ (g)	-215	Zmbov, Uy and Margrave	15
WO ₃ (g)	-70	JANAF Thermochemical Tables	45

(b) Molybdenum Compounds

Species	Enthalpy of formation, $\Delta H_{f,298}^{\circ}$ (kcal mol ⁻¹)	Source	Ref.
MoF ₆ (g)	-372.3	Settle, Feder & Hubbard	27
MoOF ₄ (g)	-316.7	this thesis (Section 2.10.1)	
MoO ₂ F ₂ (g)	-268	Zmbov, Uy and Margrave	15
MoO ₃ (g)	-86.2	JANAF Thermochemical Tables	45

GRAPH 2.10.2. - Enthalpies of Formation of Gaseous Oxyfluorides.



2.11. Electron Affinities of Hexahalides.

2.11.1. Introduction to Electron Affinities.

The electron affinity of an element or compound is a measure of the ease with which that element or compound reacts with an electron (or electron donor). It is defined as the energy given out when one g. atom of the element (or 1 g. mole of the compound) reacts with an equivalent number of electrons (at 0 K).[†]

Although the electron affinities of the elements are fairly well documented, few electron affinities of compounds have been reported. From the reactions of transition metal hexafluorides with oxidisable molecules such as O₂, NO and NO₂, Bartlett⁷¹ has made qualitative estimates of the minimum values of the electron affinities of PtF₆ (156), IrF₆ (135), OsF₆ (108), and ReF₆ (90 kcal mol⁻¹) but so far these have not been confirmed quantitatively.

Footnote †

Electron affinities have been calculated from thermochemical cycles at 298K. The enthalpy of the reaction, $A(g) + e \rightarrow A^-(g)$, at 298K, ΔH_{298} , is related to the electron affinity at 0 K, $-\Delta U_0$, thus: $\Delta H_{298} = \Delta U_0 + \int_0^{298} \Delta C_p dT$

By assuming heat capacities to be zero at 0 K, the heat capacities of A(g) and A⁻(g) to be equal, and the heat capacity of a gaseous electron at 298K to be $\frac{5R}{2}$, the expression becomes $\Delta H_{298} = \Delta U_0 - \frac{5}{2}RT$ or $\Delta U_0 = \Delta H_{298} + 1.5 \text{ kcal mol}^{-1}$.

Where two electrons are involved, i.e. $A(g) + 2e \rightarrow A^{2-}(g)$, the expression becomes $\Delta U_0 = \Delta H_{298} + 3.0 \text{ kcal mol}^{-1}$. In the following work electron affinities are quoted at 298K and 0 K.

Electron affinities of WF_6 , MoF_6 , and WCl_6 have now been calculated from the enthalpies of formation of $\text{KW}^{\text{V}}\text{F}_6$, $\text{KMo}^{\text{V}}\text{F}_6$, $\text{KW}^{\text{V}}\text{Cl}_6$, $\text{K}_2\text{W}^{\text{IV}}\text{Cl}_6$ and the hexahalides.

2.11.2. Electron Affinity of Tungsten Hexafluoride.[†]

In order to calculate the electron affinity of tungsten hexafluoride we have previously determined (Section 2.8.1.) the enthalpy of formation of $\text{KW}^{\text{V}}\text{F}_6(\text{s})$ to be -532.0 ± 2.6 kcal mol⁻¹. The enthalpy of formation of gaseous tungsten hexafluoride has also been determined (Section 2.5.1.) to be -411.8 ± 1.4 kcal mol⁻¹.

$\text{KW}^{\text{V}}\text{F}_6$ has a structure which is slightly distorted tetragonal variant of the CsCl type⁷⁶; the K-W distance, deduced from the lattice constants, is 4.40_4 \AA , from which a lattice energy, U_0 , of 122.5 kcal mol⁻¹ has been calculated (assuming an undistorted CsCl structure) using the Born Mayer equation⁷⁸ (Equation 2.11.2). The lattice enthalpy, $\Delta H_{298} = U_0 + 2RT$, is 123.7 kcal mol⁻¹.

Using the method discussed by Waddington⁷⁸ and the appropriate thermochemical cycle (Figure 2.11.2.), the electron affinity of gaseous tungsten hexafluoride has been calculated to be 117.9 ± 4 kcal mol⁻¹ (at 0 K).

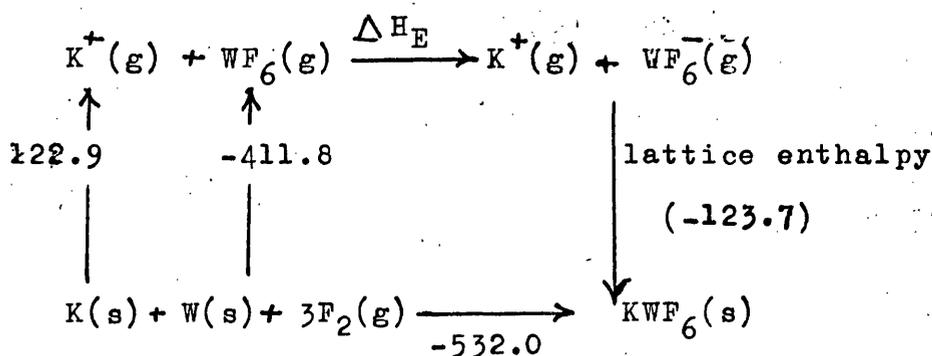
Footnotes

† We have previously reported this work in the literature⁷⁷.

* This assumes that the lattice energy is independent of temperature i.e. $U_0 = U_{298}$. In this and other lattice energy equations London or Van der Waal forces and zero point energy have been neglected.

Bartlett's data suggest a minimum value for the electron affinity of tungsten hexafluoride of 75 - 80 kcal mol⁻¹. This can be reconciled with the present estimate if allowance is made for the probable exothermic nature of the gas reactions considered by Bartlett and the entropy changes in them.

Figure 2.11.2 - Thermochemical cycle (figures in kcal mol⁻¹ at 298 K)



at 298K, electron affinity of $\text{WF}_6(\text{g}) = -\Delta H_E = 119.4 \text{ kcal mol}^{-1}$
 at 0 K, electron affinity of $\text{WF}_6(\text{g})$, $-\Delta U_0 = -(\Delta H_E + 1.5)$
 $= 117.9 \text{ kcal mol}^{-1}$.

Equation 2.11.2 Simple Born Mayer equation

$$\text{Lattice energy, } U_0 = \frac{NMZ_1Z_2e^2(1 - \frac{\rho}{r_0})}{r_0}$$

where N is Avagadro's number

M is the Madelung constant

Z_1 & Z_2 are the valencies of the ions

e is the charge on the electron

r_0 is the distance between nearest unlike ions

ρ is a constant (0.345Å)

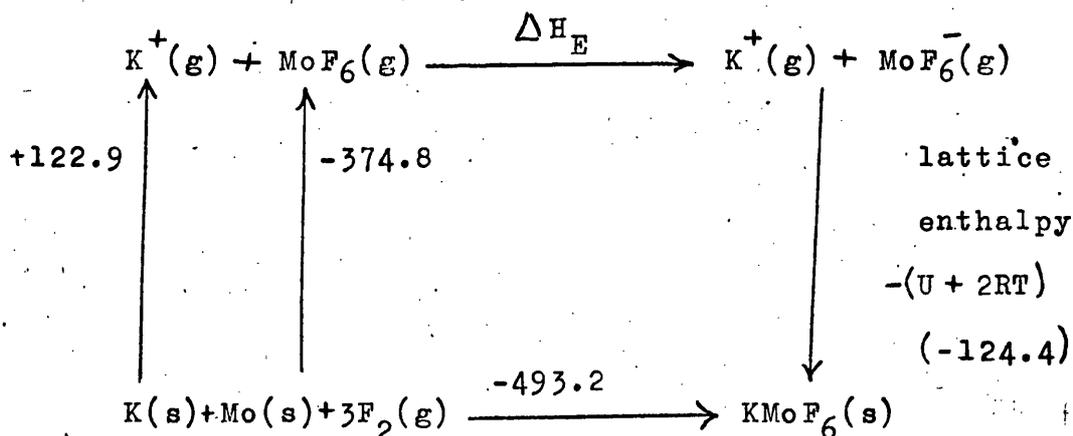
The value of the Madelung constant, M, for a particular structural type has been taken from Table 11 of Waddington's paper.⁷⁸

2.11.3 Electron Affinity of Molybdenum Hexafluoride

The enthalpies of formation of gaseous molybdenum hexafluoride and solid KMoF_6 have previously been determined (Sections 2.5.1 and 2.8.2) to be -374.8 ± 2.5 and -493.2 ± 1.9 kcal mol⁻¹ respectively. Like $\text{KW}\bar{\text{F}}_6$ (and also KReF_6), KMoF_6 has the slightly distorted CsCl type of structure⁷⁶; the K-Mo distance, deduced from the lattice constants, is 4.375^9 \AA from which a lattice enthalpy, $\Delta H_{298} = U_0 + 2RT$, of 124.4 kcal mol⁻¹ has been calculated using the Born Mayer equation (Equation 2.11.2).

Using the same method as for tungsten hexafluoride (and the thermochemical cycle shown in Figure 2.11.3), the electron affinity of gaseous molybdenum hexafluoride has been calculated to be 115.4 ± 4 kcal mol⁻¹ (at 0 K).

Figure 2.11.3 - Thermochemical cycle (figures in kcal mol⁻¹ at 298K).



at 298K, electron affinity of $\text{MoF}_6(\text{g}) = -\Delta H_E = 116.9$ kcal mol⁻¹.

at 0 K, electron affinity of $\text{MoF}_6(\text{g})$, $-\Delta U_0 = -(\Delta H_E + 1.5)$

$$= 115.4 \text{ kcal mol}^{-1}.$$

2.11.4 The First and Second Electron Affinities of Tungsten Hexachloride.

The enthalpy of formation of $\text{KWCl}_6(\text{s})$ from potassium chloride and tungsten pentachloride has been determined by Zaitseva⁷⁹ to be $-11.3 \text{ kcal mol}^{-1}$. Using the enthalpies of formation of potassium chloride and tungsten pentachloride⁴⁵, the standard enthalpy of formation of $\text{KWCl}_6(\text{s})$ has been calculated to be $-238.3 \text{ kcal mol}^{-1}$. The enthalpy of formation of gaseous tungsten hexachloride is $-118.0 \text{ kcal mol}^{-1}$.⁴⁵

The lattice energy, U_0 , of $\text{KWCl}_6(\text{s})$ has been determined, using Kapustinskii's equation^{78,80} (equation 2.11.4) and standard ionic radii, to be $94.67 \text{ kcal mol}^{-1}$. The lattice enthalpy, $\Delta H_{298} = U_0 + 2RT$, of $\text{KWCl}_6(\text{s})$ is $95.85 \text{ kcal mol}^{-1}$.

Using the appropriate thermochemical cycle (Figure 2.11.4 (a)), the first electron affinity of gaseous tungsten hexachloride has been calculated to be $145.8 \text{ kcal mol}^{-1}$ (at OK).

Equation 2.11.4 - Kapustinskii equation^{78,80} for lattice energy.

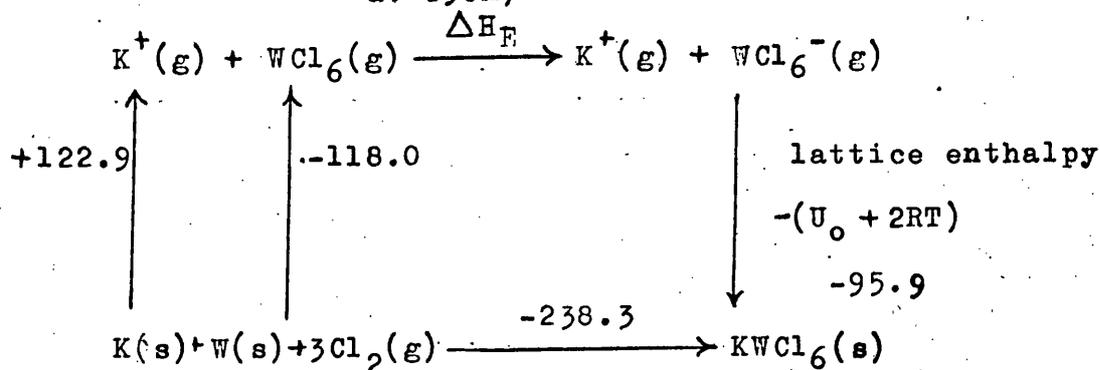
$$\text{Lattice Energy, } U_0 = \frac{287.2 \nu Z_1 Z_2}{r} \left[1 - \frac{0.345}{r} \right] \text{ kcal mol}^{-1}$$

where ν is the number of ions in the chemical molecule

Z_1 & Z_2 are the valencies of the ions
nearest

and r is the distance between unlike ions (and may be replaced by $r_c + r_A$, the sum of the cationic and anionic radii)

Figure 2.11.4(a) - Thermochemical cycle † (figures in kcal mol⁻¹ at 298K)



at 298K, first electron affinity of $\text{WCl}_6(\text{g}) = -\Delta H_{\text{E}} = 147.3$ kcal mol⁻¹.

at 0 K, first electron affinity of $\text{WCl}_6(\text{g})$, $-\Delta U_0 = -(\Delta H_{\text{E}} + 1.5) = 145.8$ kcal mol⁻¹.

The enthalpy of formation of $\text{K}_2\text{WCl}_6(\text{s})$ has previously been determined (Section 2.8.3) to be -329.9 ± 1.8 kcal mol⁻¹.

$\text{K}_2\text{WCl}_6(\text{s})$ has a structure of the cubic K_2PtCl_6 (anti fluorite) type⁸¹, the K - W distance, deduced from the lattice parameters, is 4.27_6 \AA from which a lattice enthalpy has been calculated using the Born Mayer equation⁷⁸ (Equation 2.11.2), as -360.9 kcal mol⁻¹.

Footnote †

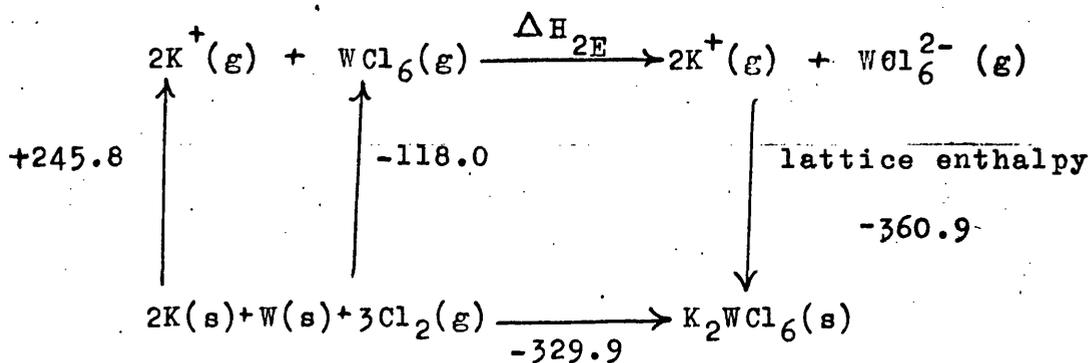
The known enthalpies of formation have been taken from the JANAF Thermochemical Tables (1971)⁴⁵. If the enthalpies of formation (of WCl_5 and WCl_6) are taken from the NBS Tech Note 270/4³¹ the results are:

at 298K, first electron affinity of $\text{WCl}_6(\text{g})$, $-\Delta H_{\text{E}} = 138.7$ kcal mol⁻¹.

at 0 K, first electron affinity of $\text{WCl}_6(\text{g})$, $-\Delta U_0 = 137.2$ kcal mol⁻¹.

Using the appropriate thermochemical cycle (Figure 2.11.4(b)), the sum of the first and second electron affinities of gaseous tungsten hexachloride has been calculated to be $93.8 \text{ kcal mol}^{-1}$, (at 0 K).

Figure 2.11.4(b) - Thermochemical cycle (figures in kcal mol^{-1} at 298K)



at 298K, sum of first and second electron affinities of $\text{WCl}_6(\text{g})$
 $= -\Delta H_{2E} = 96.8 \text{ kcal mol}^{-1}$.

at 0 K, sum of first and second electron affinities of $\text{WCl}_6(\text{g})$,
 $-\Delta U_0 = -(\Delta H_{2E} + 3.0) = 93.8 \text{ kcal mol}^{-1}$.

Then we have

	at 0 K	at 298K
1st electron affinity of gaseous WCl_6	145.8	147.3
2nd electron affinity of gaseous WCl_6	-52.0	-50.5
Sum of 1st and 2nd electron affinities		
of gaseous WCl_6	93.8	96.8
(figures in kcal mol^{-1})		

2.12. Ion Affinities of Pentahalides.

2.12.1. Introduction to Ion Affinities.

The ion affinity of a compound is a measure of the ease with which that compound reacts with the ion concerned. It is defined as the energy evolved when 1g. mol of the compound reacts with an equivalent quantity of the ion.[†]

In the case of an anion, the ion affinity is the heat evolved in the reaction $A + B^- \rightarrow AB^-$. Since this reaction is a Lewis acid/base reaction, the anion affinity of A is a measure of its Lewis acidity.

In this thesis halide ion affinities of pentahalides (particularly tungsten and molybdenum) have been considered. The halide ion affinity of a pentahalide might be useful in such considerations as:

(i) The action of the pentahalide in the non aqueous hydrogen halide solvent. For example, antimony and niobium pentafluorides have been (qualitatively) shown⁸² to act as weak acids in anhydrous hydrogen fluoride thus

$MF_5 + 2HF \rightleftharpoons H_2F^+ + MF_6^-$ with antimony pentafluoride being the more acidic (better F^- acceptor)

(ii) The formation of inorganic salts eg. $KMoF_6$ & $NOMoF_6$

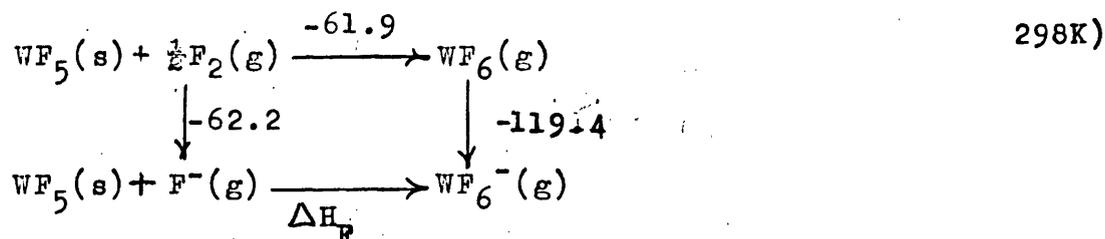
(iii) The formation of less common cations. For example, antimony pentafluoride reacts with propyl, butyl and pentyl fluorides forming SbF_6^- and stable carbonium ions⁸³.

Footnote

† To be in line with electron affinities, ion affinities should be defined at 0 K. However, here the calculations have been limited to 298K. As with electron affinities, a simple conversion to 0 K, involving $\frac{5RT}{2}$, can be made (see footnote to Section 2.11.1).

2.12.2 Fluoride Ion Affinity of Tungsten Pentafluoride.

The enthalpy of oxidation of solid tungsten pentafluoride to the gaseous hexafluoride is $-61.9 \text{ kcal mol}^{-1}$. The electron affinity of gaseous tungsten hexafluoride is $119.4 \text{ kcal mol}^{-1}$. (Section 2.11.2). Using these enthalpies and the enthalpy of formation of $\text{F}^-(\text{g})$ ⁴⁵, in the appropriate thermochemical cycle (Figure 2.12.2), the fluoride ion affinity of solid tungsten pentafluoride has been calculated to be $119.1 \pm 6 \text{ kcal mol}^{-1}$. Figure 2.12.2 - Thermochemical Cycle (figures in kcal mol^{-1} at 298K)



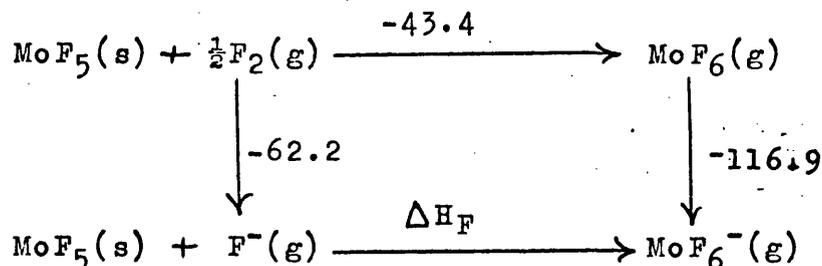
Fluoride Ion affinity of $\text{WF}_5(\text{s}) = \Delta H_F = 119.1 \text{ kcal mol}^{-1}$.

2.12.3. Fluoride Ion Affinity of Molybdenum Pentafluoride.

The enthalpy of oxidation of solid molybdenum pentafluoride to the gaseous hexafluoride is $-43.4 \text{ kcal mol}^{-1}$ (Section 2.9.4).

The electron affinity of gaseous molybdenum hexafluoride is $116.9 \text{ kcal mol}^{-1}$. Using the same method as with tungsten pentafluoride (Section 2.12.2) and the thermochemical cycle shown in Figure 2.12.3, the fluoride ion affinity of solid molybdenum pentafluoride has been calculated to be $98.1 \pm 6 \text{ kcal mol}^{-1}$.

Figure 2.12.3 - Thermochemical Cycle (figures in kcal mol⁻¹ at 298K)

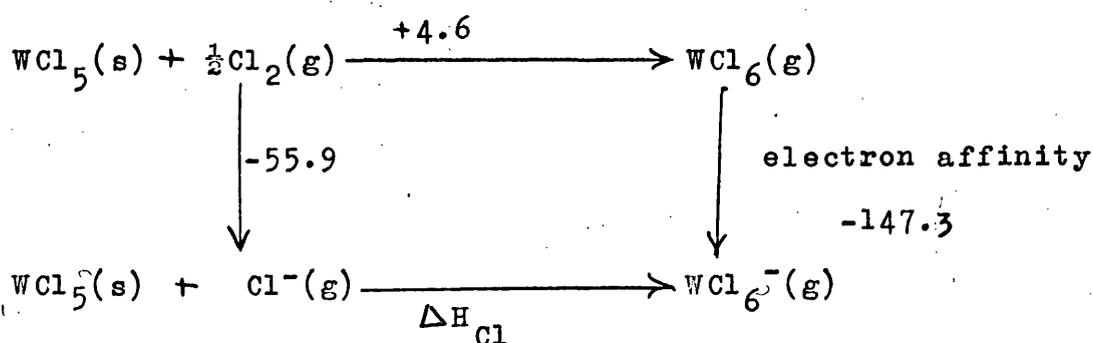


Fluoride Ion affinity of MoF₅(s) = $-\Delta H_{\text{F}} = 98.1 \text{ kcal mol}^{-1}$.

2.12.4. Chloride Ion Affinity of Tungsten Pentachloride.

Using the enthalpies of formation of Cl⁻(g), WCl₅(s) and WCl₆(g)⁴⁵ and the first electron affinity of WCl₆(g) (Section 2.11.4) in the thermochemical cycle (Figure 2.12.4), the chloride ion affinity of solid tungsten pentachloride has been calculated to be 86.8 kcal mol⁻¹.

Figure 2.12.4 - Thermochemical Cycle (figures in kcal mol⁻¹ at 298K)



Chloride Ion Affinity of WCl₅(s) = $-\Delta H_{\text{Cl}} = 86.8 \text{ kcal mol}^{-1}$.

Several groups of workers have shown that tungsten pentachloride acts as a chloride ion acceptor, for example, an examination of the systems RbCl - WCl₅ and CsCl - WCl₅ has shown⁸⁴ the presence of RbWCl₆ and CsWCl₆.

Table 2.12.5. Summary Tables of Electron and Ion Affinities
at 298K.

(a) Electron Affinities.

Species	1st electron affinity (kcal mol ⁻¹)	2nd electron affinity (kcal mol ⁻¹)
MoF ₆ (g)	116.9 ± 4	—
WF ₆ (g)	119.4 ± 4	—
WCl ₆ (g)	147.3	-50.5

(b) Ion Affinities..

Compound species	Ion	Ion Affinity (kcal mol ⁻¹)
MoF ₅ (s)	F ⁻ (g)	98.1 ± 6
WF ₅ (s)	F ⁻ (g)	119.1 ± 6
WCl ₅ (s)	Cl ⁻ (g)	86.8

2.13. Oxidation Reactions of Hexafluorides.

2.13.1. Introduction.

Interest in the oxidation reactions of hexafluorides stems mainly from the discovery of the ionic dioxygenyl hexafluoroplatinate (V) $(O_2^+PtF_6^-)$ ^{85,86}. In order that the oxidation of molecular oxygen (with an ionisation potential $I(O_2) = 281$ kcal mol⁻¹)⁸⁷ by platinum hexafluoride, should occur spontaneously, Bartlett⁷¹ has suggested, using a Born Haber cycle, that the electron affinity of the hexafluoride must be greater than 156 kcal mol⁻¹. After the oxidation of molecular oxygen, attention was focused on the possible oxidation of xenon (with ionisation potential $I(Xe) = 280$ kcal mol⁻¹)⁸⁷ and, as expected, the oxidation of xenon by platinum hexafluoride occurred spontaneously at room temperature⁸⁸. The products of this reaction are $XePtF_6$ (formulated $Xe^+PtF_6^-$) and $Xe(PtF_6)_2$ (formulated $XeF^+Pt_2F_{11}^-$).

2.13.2. A Comparison of the Oxidising Properties of Hexafluorides

(a) Periodic Trends in oxidising reactions of the hexafluorides.

In a comparison of the hexafluorides only platinum, ruthenium and rhodium hexafluorides were found to be capable of oxidising xenon. Nitric oxide (with an ionisation potential $I(NO) = 213$ kcal mol⁻¹) and nitrosyl fluoride have also been used as the reducing agents in a comparison of the oxidising power of the third row hexafluorides. The results, shown in Table 2.13.2, suggest a smooth increase in the oxidising power of the hexafluorides from WF_6 to PtF_6 .

From the reactivity of the hexafluorides with phosphorus trifluoride, arsenic trifluoride and carbon disulphide, Canterford et al ⁹⁰ have suggested that rhenium hexafluoride is a stronger oxidising agent than tungsten hexafluoride.

Table 2.13.2. Oxidation Products of the Third Transition Series Hexafluorides.

3rd Row Hexafluoride	Reaction Products* with		
	NO	NOF	Xe
WF ₆	no reaction	NOWF ₇ or (NO) ₂ WF ₈	no reaction
ReF ₆	NOREF ₆	(NO) ₂ ReF ₈	"
OsF ₆	NOOsF ₆	NOOsF ₇ & NOOsF ₆	"
IrF ₆	(NO) ₂ IrF ₆ & NOIrF ₆	NOIrF ₆	"
PtF ₆	(NO) ₂ PtF ₆ & NOPtF ₆	(NO) ₂ PtF ₆ & NOPtF ₆	Xe(PtF ₆) _x

Footnote *

from references 11, 72-74, 88 and 89.

(b) Oxidising properties and electron affinity predictions
(see also Section 2.11)

From the results in Table 2.13.2 and other similar oxidation reactions, Bartlett⁷¹ made qualitative estimates of the minimum values[†] of the electron affinities of PtF₆ (156), IrF₆ (135), OsF₆ (108) and ReF₆ (90 kcal mol⁻¹). As noted earlier (Section 2.11.2) the trend of Bartlett's data suggests a minimum value for the electron affinity of WF₆ of 75 - 80 kcal mol⁻¹.

(c) Oxidation mechanisms of hexafluorides (see also Section 2.13.3)

Hexafluorides are reduced in two possible ways (ie $MF_6 + e \rightarrow MF_6^-$ and $MF_6 \rightarrow MF_5 + F$) and individual oxidations must be considered in terms of both oxidation types and possible reaction mechanisms. For example, from the actual value of the electron affinity of tungsten hexafluoride (117.9 kcal mol⁻¹ - Section 2.11.2) it can be shown that the reaction,

$WF_6 + NO \longrightarrow NO^+ WF_6^-$ has a favourable enthalpy of reaction. However, the mechanism for the non reaction of nitric oxide with tungsten hexafluoride is considered (in Section 2.13.3) to involve two steps. (Step 1 $WF_6 + NO \not\rightarrow WF_5 + NOF$, and Step 2 $WF_5 + NOF \rightarrow NO^+ WF_6^-$) with step 1 being unfavourable (ie it is

Footnote †

These values ignore entropy changes in the oxidation reactions. The minimum value of each electron affinity is that value which would lead to a zero enthalpy for the most difficult oxidation which occurs.

the lack of reduction of WF_6 to WF_5 rather than a low electron affinity of WF_6 which prevents the reaction). It can be seen, therefore, that although the reaction of a hexafluoride with nitric oxide can give a minimum value for the electron affinity of the hexafluoride, the lack of reaction cannot necessarily be used in a consideration of this electron affinity.

(d) Reduction of hexafluorides to pentafluorides.

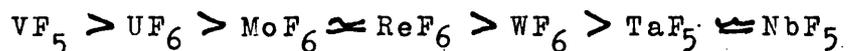
For the third transition^{row} hexafluorides, the only available thermodynamic data on the reduction to the pentafluorides (this thesis Section 2.9.4) are the enthalpies of reduction of WF_6 (+61.9 kcal mol⁻¹) and ReF_6 (+28.5 kcal mol⁻¹). These data adequately explain the differing reactivities of tungsten and rhenium hexafluorides towards nitric oxide using the above two step mechanism.

2.13.3. A Comparison of the Oxidising Properties of Tungsten and Molybdenum Hexafluorides.

Early literature^{91,92} suggested that tungsten and molybdenum hexafluoride are very reactive and almost identical in chemical as well as physical properties. However, more recent literature has shown molybdenum hexafluoride to be the more reactive.

Several workers have recently made comparisons of the oxidising properties of tungsten and molybdenum hexafluoride by chemical methods. Geichman et al^{73,89} have studied the oxidation reactions of both hexafluorides with nitric oxide

and nitrosyl chloride. The results, shown in Table 2.13.3(a) suggest that molybdenum hexafluoride is the stronger oxidising agent. O'Donnell and co-workers^{7,90,93-96} have made several studies of the oxidising reactions of hexafluorides and pentafluorides from which they have deduced the order of oxidising strengths



From a study of band positions in the charge transfer spectra[†] of the fluorides with organic donors, Hammond⁹⁷⁻⁹⁹ has suggested that the molecular electron affinity of molybdenum hexafluoride is greater than that of tungsten hexafluoride.

However, V_{\max} values of ^{the} charge transfer spectra[†] of McLean, Sharp and Winfield^{100,101} (with WF_6 and MoF_6 and Group IV compounds) show no simple dependence on the ionisation potential of the donor or the electron affinity of the fluoride.

Footnote †

A charge transfer band or spectrum is produced when the absorption of radiation causes an electronic transition between molecular orbitals largely located in different parts of the molecule or complex.

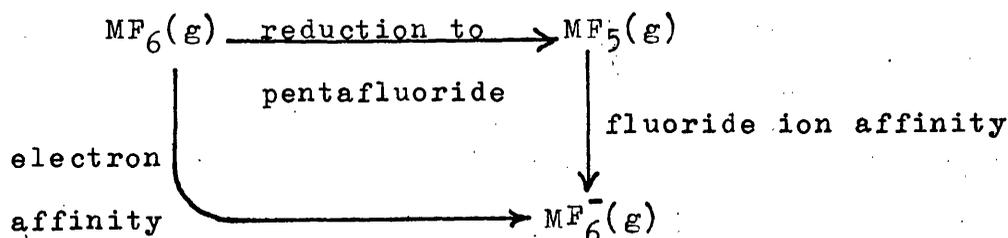
Table 2.13.3(a) Oxidising reactions of tungsten and molybdenum hexafluoride with nitric oxide and nitrosyl chloride.

Reagent	Product		Ref.
	with MoF ₆	with WF ₆	
NO	NO ⁺ MoF ₆ ⁻	no reaction	73
NOCl	NO ⁺ MoF ₆ ⁻	no reaction	89

Quantitative measurements of the oxidising power of tungsten and molybdenum hexafluoride have now been made. The electron affinities of tungsten and molybdenum hexafluoride are 119.4 and 116.9 kcal mol⁻¹ (at 298K) respectively (see Section 2.11). The enthalpy of reduction of the gaseous hexafluoride to the solid pentafluoride is 61.9 kcal mol⁻¹ for tungsten and 43.4 kcal mol⁻¹ for molybdenum. (see Section 2.9.4.)

The difference in the two sets of figures is accounted for by the difference in the fluoride ion affinity of the pentafluoride as shown in the following thermochemical cycle (Figure 2.13.3).

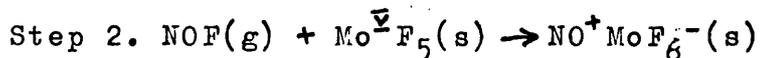
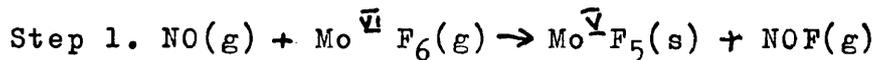
Figure 2.13.3. - Thermochemical cycle showing the significance of the fluoride ion affinity.



Both the sets of figures are measures of the oxidising power of the hexafluorides and individual oxidation reactions must be considered in the light of both and possible reaction mechanisms.

The results of these chemical reactions which suggest that molybdenum hexafluoride is a stronger oxidising agent than tungsten hexafluoride must be explained in terms of the difference in the enthalpy of the reduction of the hexafluoride to the pentafluoride. Take, for example, the different behaviour of the hexafluorides with nitric oxide (ie MoF₆ is reduced by

nitric oxide but WF_6 is not). The basic reaction under consideration is $NO + MF_6 \rightarrow NO^+ + MF_6^-$. However, Geichman⁷³ has suggested, on the basis of gas phase infra red evidence and the reaction of molybdenum pentafluoride with nitrosyl fluoride, that the oxidation of nitric oxide by molybdenum hexafluoride takes place in two steps thus:-



This has now been taken as the general mechanism for the oxidation of nitric oxide by an hexafluoride. Although the overall reaction is dependent on the electron affinity of the hexafluoride, Step 1 of the mechanism is dependent on the reduction of the hexafluoride to the pentafluoride and Step 2 of the mechanism is dependent on the fluoride ion affinity of the pentafluoride.

$NO^+MoF_6^-(s)$ has a cubic structure⁷³. From the unit cell constant ($a_0 = 5.080\text{\AA}$) the mean $NO-Mo$ distance has been calculated as 4.399\AA . The lattice enthalpy, $U + 2RT$, of $NO^+MoF_6^-(s)$ has been calculated, using the Born Mayer equation (equation 2.11.2) to be $123.8\text{kcal mol}^{-1}$. The lattice enthalpy of the unprepared $NO^+WF_6^-(s)$ has also been taken as $123.8\text{kcal mol}^{-1}$ (cf. the lattice enthalpies of $KMoF_6$ and KWF_6 which are 124.4 and $123.7\text{kcal mol}^{-1}$ respectively - see Section 2.11). Using known standard enthalpies of formation (Table 2.13.3(b)) and the calculated lattice enthalpies, the enthalpies of Step 1 and Step 2 of the mechanism have been calculated for the reaction of nitric oxide with molybdenum hexafluoride and for the possible reaction of nitric oxide with tungsten hexafluoride. The results (Table 2.13.3(c) and Graph 2.13.3) suggest

a high energy barrier to the reaction between $WF_6(g)$ and $NO(g)$ but not to the reaction between $MoF_6(g)$ and $NO(g)$. Therefore, the thermodynamic evidence, based on the mechanism of Geichman, is compatible with the present experimental evidence.

Although the differing oxidising properties of tungsten and molybdenum hexafluorides are, therefore, compatible with the differing ease of reduction to the pentafluorides, an explanation is not simple. It involves differences in bond strengths[†] in both the pentafluorides and the hexafluorides resulting from the higher^{quantum number outer} orbitals and the ineffective screening by the 4f electrons in the tungsten compounds.

Footnote †

σ and π bonding overlap may be involved in both hexafluoride and pentafluoride bonding.

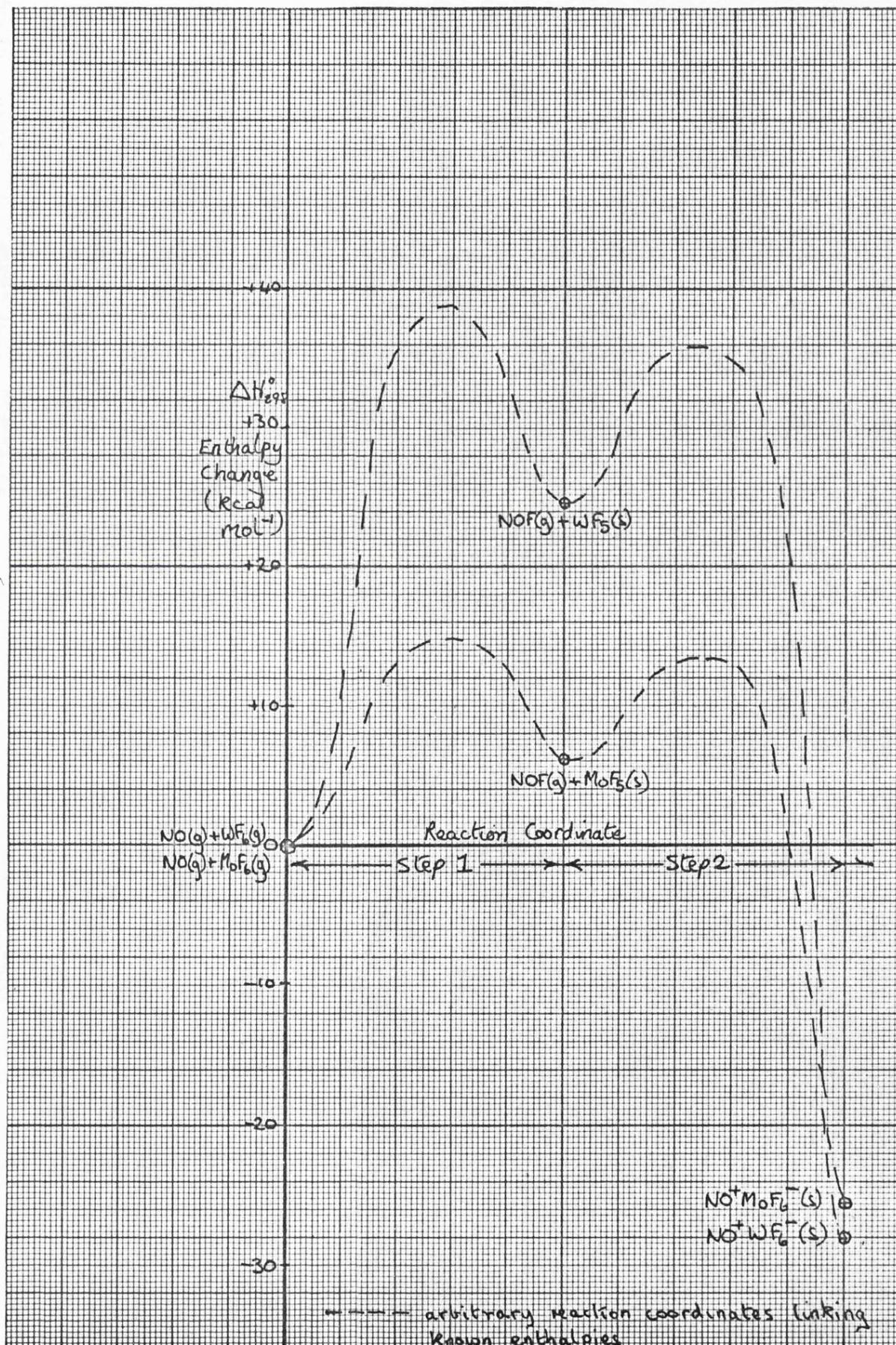
TABLE 2.13.3(b) Known Standard Enthalpies of Formation.

Species	Enthalpy of formation, $\Delta H_{f,298}^{\circ}$ (kcal mol ⁻¹)	Source
NO(g)	+21.58	} JANAF Thermochemical Tables(1971) ⁴⁵
NO ⁺ (g)	+236.66	
NOF(g)	-15.7	
MoF ₅ (s)	-331.4 ± 1.3	This thesis - Section 2.6.2
WF ₅ (s)	-349.9 ± 3.5	This thesis - Section 2.6.1
MoF ₆ (g)	-374.8 ± 2.5	This thesis - Section 2.5.1(b)
WF ₆ (g)	-411.8 ₅ ± 1.4	This thesis - Section 2.5.1(a)
MoF ₆ ⁻ (g)	-491.7	This thesis - from electron affinity of MoF ₆ - Section 2.11.3
WF ₆ ⁻ (g)	-531.2	This thesis - from the electron affinity of WF ₆ - Section 2.11.2

TABLE 2.13.3 (c) - Stepwise Enthalpies of Reaction for the Reaction of Nitric Oxide with Hexafluorides.

Reacting Hexafluoride	Step	Equation of the mechanistic step	Enthalpy of the step, ΔH_{298}° (kcal mol ⁻¹)
MoF ₆	1	$\text{NO}(g) + \text{MoF}_6(g) \rightarrow \text{NOF}(g) + \text{MoF}_5(s)$	+ 6.1
	2	$\text{NOF}(g) + \text{MoF}_5(s) \rightarrow \text{NO}^+ \text{MoF}_6^-(s)$	-31.7
	overall reaction	$\text{NO}(g) + \text{MoF}_6(g) \rightarrow \text{NO}^+ \text{MoF}_6^-(s)$	-25.6
WF ₆	1	$\text{NO}(g) + \text{WF}_6(g) \rightarrow \text{NOF}(g) + \text{WF}_5(s)$	+24.6
	2	$\text{NOF}(g) + \text{WF}_5(s) \rightarrow \text{NO}^+ \text{WF}_6^-(s)$	-52.7
	overall reaction	$\text{NO}(g) + \text{WF}_6(g) \rightarrow \text{NO}^+ \text{WF}_6^-(s)$	-28.1

GRAPH 2.13.3. - Enthalpy Change During the Reaction of Nitric Oxide with MoF_6 and WF_6 .



2.13.4. A Comparison of the Oxidising Properties of Tungsten Hexafluoride and Tungsten Hexachloride.

Several oxidising reactions of tungsten hexafluoride and tungsten hexachloride have been investigated.

Tungsten hexafluoride has been reduced by phosphorus trifluoride⁷ and alkali iodides (in liquid sulphur dioxide)⁷⁶. It has been shown that neither nitric oxide,⁷³ nor iodine¹⁰² reduce tungsten hexafluoride. Tungsten hexachloride has been reduced by potassium chloride⁸¹, potassium iodide⁸¹, stannous chloride¹⁰³ and a number of organic donor molecules (for example, 2,2'-bipyridyl and 1,10-phenanthroline¹⁰⁴). Although no systematic comparison of the oxidising strengths of the hexafluoride and hexachloride has been made the hexachloride does appear to undergo more reductions.

From a study of the positions of charge transfer bands between the halides and organic donors, Hammond⁹⁹ has suggested that the molecular electron affinity of tungsten hexachloride is greater than that of the hexafluoride.

The quantitative measurements of the oxidising power of tungsten hexafluoride and tungsten hexachloride, which have now been made give the first electron affinities as 119.4 and 147.3 kcal mol⁻¹ (at 298K) respectively (Section 2.11) and the enthalpies of reduction of the gaseous hexahalide to the solid pentahalide as 61.9 and -4.6 kcal mol⁻¹ respectively (Section 2.9.4).

As stated in the previous section, both these sets of

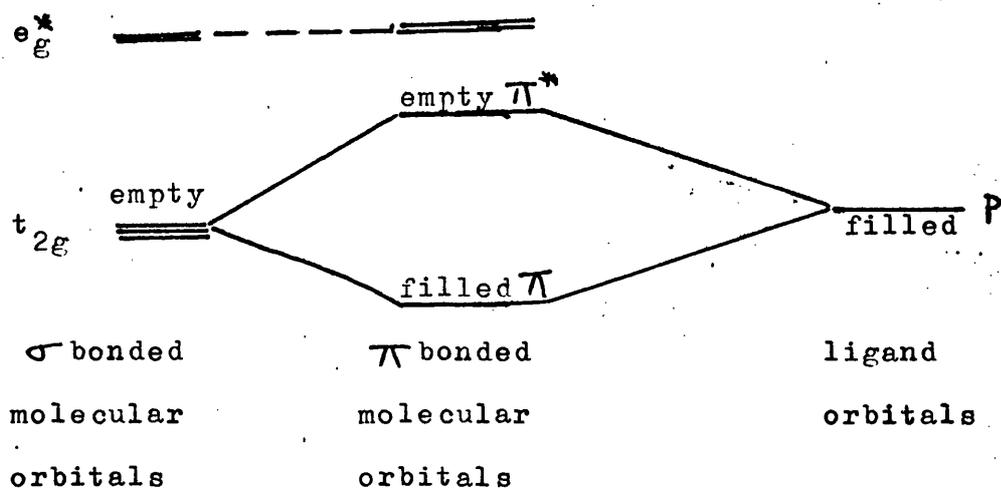
figures are measures of the oxidising power of the hexahalide. Individual oxidations must be considered in terms of both sets of figures and possible reaction mechanisms. The figures suggest that tungsten hexachloride is the stronger oxidising agent for both types of oxidation. However, the difference in the electron affinities of the hexahalides is small compared with the difference in their ease of reduction to the pentahalides. Therefore, the oxidation reactions involving the reduction of the hexahalide to the pentahalide should show larger differences in reactivity between the hexafluoride and the hexachloride.

That tungsten hexachloride has a higher electron affinity than tungsten hexafluoride is explained as follows. The electron affinity of a hexahalide is influenced by its electronic structure, which involves a basic σ -bonded structure (see Section 2.9.3.) on to which is superimposed a certain amount of π -bonding. In transition metal fluorides the π -bonding is an interaction between the filled p_{π} -orbitals of fluorine and the metal d_{π} orbitals. However, it has been suggested^{9,105} that in transition metal chlorides the π -bonding is an interaction between the metal d_{π} orbitals and the empty d_{π} orbitals of chlorine. The π molecular orbitals for the hexahalides of a d^0 transition metal (eg W^{VI}) are shown in figure 2.13.4. It can be seen that for the addition of an extra electron to the hexafluoride π -structure a π^* -antibonding orbital must be used whereas in the addition of an extra electron to the hexachloride π -structure a π -bonding orbital may be used.

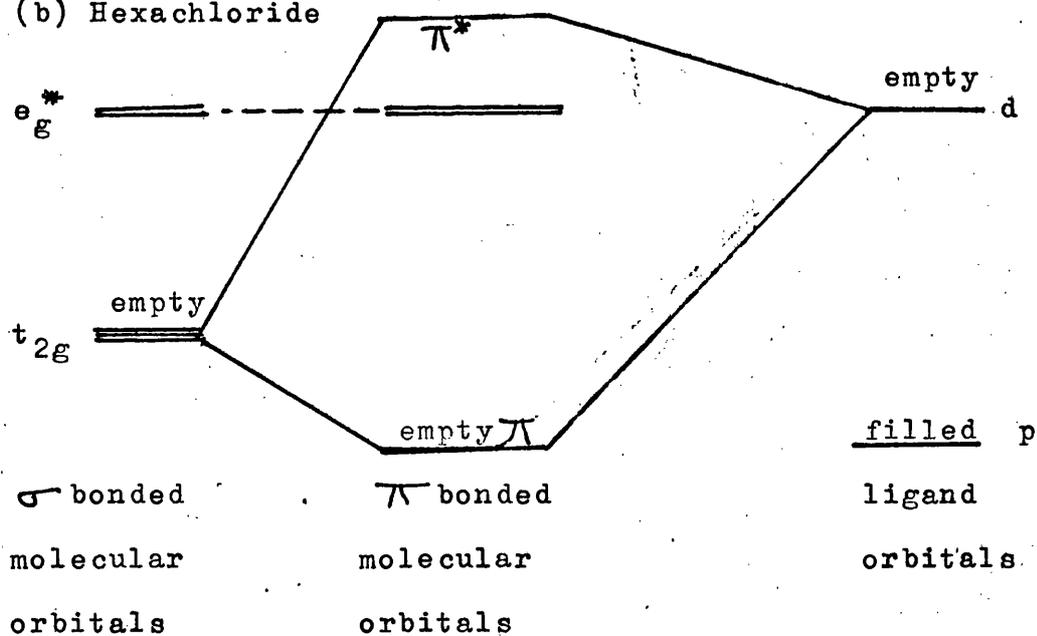
Therefore, the hexachloride should have a greater tendency to accept electrons (i.e. a higher electron affinity).

Figure 2.13.4. π Bonding Structure in d^0 Transition Metal Hexahalides.

(a) Hexafluoride.



(b) Hexachloride



That the reduction of tungsten hexachloride to the pentahalide is more favourable than the similar reduction of tungsten hexafluoride is dependent on the usual factors which lead to stabilisation of high oxidation state fluorides i.e. the high electronegativity of fluorine, its small size and the low dissociation energy of the fluorine molecule.

2.14. A Comparison of the Fluoride Ion Affinities of Tungsten and Molybdenum Pentafluorides.

The fluoride ion affinity of a pentafluoride is the energy evolved in the reaction $\text{MF}_5(\text{s}) + \text{F}^-(\text{g}) \rightarrow \text{MF}_6^-(\text{g})$. Since this can be considered as the reaction of an electron donor species (the fluoride ion) with the pentafluoride to form an addition compound ($\text{MF}_6^-(\text{g})$), the fluoride ion affinity is a measure of the ease with which the pentafluoride will form addition compounds with electron donors (i.e. its Lewis acidity).

Very little of the chemistry of tungsten and molybdenum pentafluorides has been investigated. Sharp et al.^{106,107} have shown that molybdenum pentafluoride forms adducts with acetonitrile, pyridine, ammonia, dimethyl ether, dimethyl sulphide, and chloroacetonitrile. Geichman et al.⁷³ have shown that molybdenum pentafluoride adds a fluoride ion from nitrosyl fluoride to form $\text{NO}^+\text{MoF}_6^-$. However, since no similar reactions have been investigated for tungsten pentafluoride, it has not been possible to compare the addition reactions of tungsten and molybdenum pentafluorides.

The fluoride ion affinities of solid tungsten and molybdenum pentafluorides are 119.1 and 98.1 kcal mol⁻¹ respectively (Section 2.12) indicating that tungsten pentafluoride is the better fluoride ion acceptor. Therefore, tungsten pentafluoride should be more likely to form adducts with electron donors and it may even be useful in the production of stable carbonium ions (cf. antimony pentafluoride⁸³).

An explanation of the differences in the fluoride ion affinities of tungsten and molybdenum pentafluorides is not simple. It involves differences in bond strengths in both the pentafluorides and the hexafluorometallate anions resulting from the higher quantum number outer orbitals and the ineffective screening by the 4f electrons in the tungsten compounds.

CHAPTER 3. THE TUNGSTEN FLUORINE INCANDESCENT LAMP.

3.1. Early Incandescent Lamp Development.

The first commercial incandescent lamp, consisting of a carbon filament mounted in an evacuated glass bulb, was patented by Edison¹⁰⁸ in 1880. The high vapour pressure of carbon restricted the working filament temperature of the lamp, in order to give a reasonable filament life and prevent bulb blackening. Subsequent developments were aimed at producing a more suitable filament material. Mixed oxides,¹⁰⁹ the metals osmium and tantalum and sintered tungsten powder were used before the advent of the drawn tungsten filament in 1910¹¹⁰. Incandescent lamps are still based on tungsten filaments.

Gas-filled bulbs were first successfully produced by Langmuir¹¹¹ in 1913. The use of a pressure of an inert gas, such as argon or nitrogen, in the bulb had the effect of reducing the effective evaporation of tungsten from the filament by collision of the gaseous tungsten molecules with the atoms or molecules of the gas-filling. Langmuir¹¹¹ made a detailed study of the heat losses in the gas filling and found that the filament was surrounded by a quasi stationary layer of gas from which heat was lost only by radiation and conduction. This heat loss was found to be dependent on the filament length and diameter and was minimised by the introduction of the coiled filament, which, by causing the Langmuir layers to overlap, acted like a short cylindrical filament. The coiled-coil was introduced later¹¹².

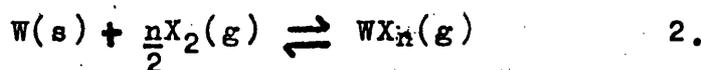
Further developments involved the use of higher atomic or molecular weight inert gases and 'getters' for the removal of trace impurities.

3.2 Development and Theory of Tungsten Halogen Incandescent Lamps.

The first attempt at the addition of a halogen to an incandescent lamp in order to increase filament life and prevent bulb blackening was made in 1882 when chlorine was added to a carbon filament lamp¹¹³.

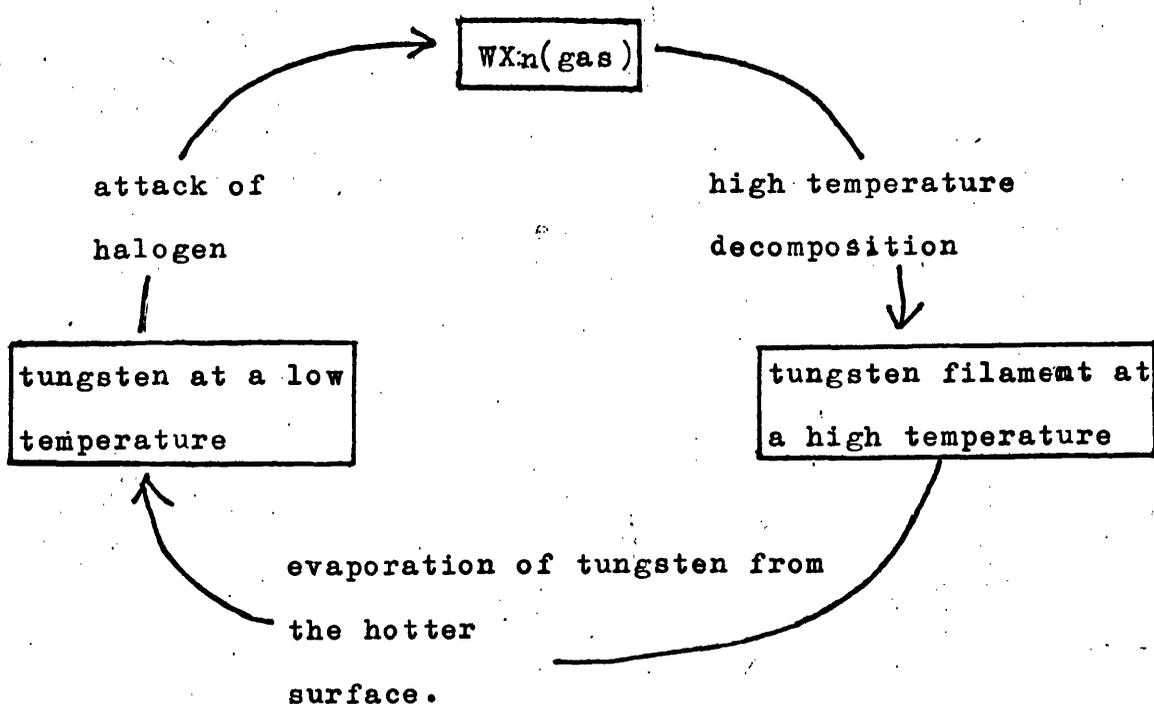
In 1915 Langmuir¹¹⁴ took two tungsten wires, under a low chlorine pressure, to different temperatures and showed that, at suitable temperatures, the hotter wire became thicker and the cooler wire became thinner. This demonstrated the possibility of transporting tungsten to the hotter parts of the wire, where the evaporation is greatest.

This 'positive' transporting property of the halogen, now adapted to the tungsten halogen incandescent lamp for the redeposition of tungsten on the hot filament, is based on the equilibria:



The equilibria are temperature dependent, such that at low temperatures the production of $WX_n(\text{gas})$ is favourable, whilst at high temperatures the decomposition of $WX_n(\text{gas})$ (and, therefore, the deposition of tungsten) is favourable. The action of the halogen in a running lamp can be shown in a 'halogen cycle' as shown in Figure 3.2.1.

Figure 3.2.1 — The Halogen Cycle.



For each halogen the temperature at which the decomposition of $WX_n(\text{gas})$ becomes favourable, called the 'inversion temperature', is determined from thermodynamic information as the temperature at which the Gibbs free energy, ΔG_T° , of the most favourable decomposition of the most stable halide species (WX_n) is zero.

The inaccurate theoretical work of Brewer¹² on the tungsten halides indicated that the 'inversion temperatures' for the iodide, bromide, and chloride are 950, 1600 and 2200K respectively. With this information it was thought that the only halogen which would be useful would be iodine since the other halides would attack the cooler parts of the filament legs.

After a method was developed for sealing tungsten filaments into small quartz envelopes, the tungsten iodine lamp was developed (patented in 1949¹¹⁵ and first commercial details published in 1959¹¹⁶).

In this tungsten iodine incandescent lamp it was envisaged that the whole of the running filament would be maintained above the 'inversion temperature' of the iodine cycle so that the iodine would not attack the cooler filament legs. The filament life in this lamp was increased in the following way:

1. The iodine prevents the deposition of tungsten on the bulb wall and redeposits the evaporating tungsten on the filament.
2. The envelope size can therefore be reduced (using quartz as the envelope material).
3. With a strong small envelope, a high pressure (eg. three atmospheres) of inert gas can be used to inhibit the evaporation of tungsten from the filament and, therefore, extend the filament life.

The colour of iodine and the difficulty of dosing proved to be disadvantages of the tungsten iodine lamp and so attention was turned to the bromine cycle. It was found that, providing the maximum bromine partial pressure was 1 torr (in 3.5 atmospheres of argon), the colder filament legs were not noticeably attacked by the bromine¹¹⁷. Therefore, with a fine control on the bromine dose a tungsten bromine lamp could be produced.

A more satisfactory solution to the attack of the cold filament legs by bromine was obtained by modifying the tungsten bromine cycle with hydrogen¹¹⁸. Hydrogen bromide does not react with tungsten in the range of conditions in a lamp^{12,117}.

Commercial tungsten bromine lamps are now produced with bromine introduced in the more convenient form of alkyl bromides¹¹⁸.

A further development has been the introduction of bromine in the form of bromophosphonitride¹¹⁷. The phosphorus produced in this lamp acts as a 'getter' for oxygen and water vapour.

Because of their reactivities, neither chlorine nor fluorine has been used in a commercial tungsten halogen lamp, although some patents have been granted. For example, Schröder has patented a (tungsten fluorine) lamp in which fluorine is introduced as tungsten hexafluoride¹¹⁹.

3.3 Recent Thermochemical Advances of Importance to the Tungsten Halogen Incandescent Lamp.

3.3.1 The Thermochemical Advances.

The original work on tungsten halogen incandescent lamps was based on inaccurate theoretical work of Brewer¹². Recently further thermochemical estimations have been carried out. The most recent, those of Neumann and Knatz¹²⁰ which are based on the 1965-68 JANAF Thermochemical Tables¹²¹, suggest that no gaseous tungsten iodide is stable above room temperature, a gaseous bromide(WBr_4) is stable to $\sim 1500K$, a gaseous chloride(WCl_2) is stable to $\sim 2400K$ and a gaseous fluoride(WF_2) is stable to $\sim 3900K$.

Thermodynamic calculations which have now been carried out (Appendix 1) indicate that the 'inversion temperature' for the equilibrium $W(s) + 6F(g) \rightleftharpoons WF_6(gas)$ is 3360K

3.3.2 The Effect of these Advances.

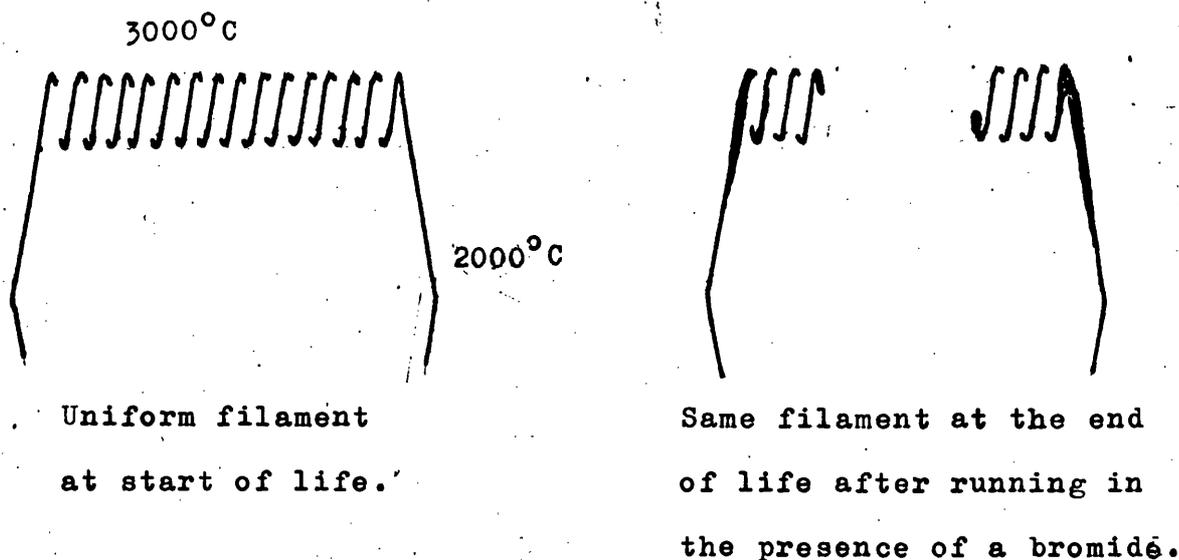
These estimates of Neumann and Knatz support the suggestion of Rabenau¹⁰⁹ that in the tungsten iodine lamp oxygen impurity is necessary and that this lamp is based on the species WO_2I_2 . They¹²² also (rightly) suggest that the bromine, chlorine and fluorine cycles are possible without the presence of oxygen but that if oxygen is present the important equilibria will involve the oxyhalides.

Tungsten bromine lamps are now being produced¹¹⁷ contain bromine in the form of bromophosphonitrile. In these lamps, phosphorus acts as an 'oxygen getter' so that a pure tungsten bromine cycle (rather than a tungsten oxy-bromine cycle) must be in operation.

3.4 The Special Significance of the Fluorine Cycle.

In the halogen lamps produced at present (containing iodine or bromine) the halogen is used to remove tungsten from the bulb wall (or prevent its deposition) and to redeposit it on the filament. Since the whole, or great majority, of the filament is above the 'inversion temperature' this redeposition is indiscriminate. In fact, near the hot zones of the filament the tungsten halides might decompose in the gaseous state ($WX_n(g) \rightarrow W(g) + nX(g)$) without redepositing the tungsten on the filament. Then, in a lamp of this type, taking evaporation into consideration, there is a gradual redistribution of tungsten on the filament as shown in Figure 3.4.1.

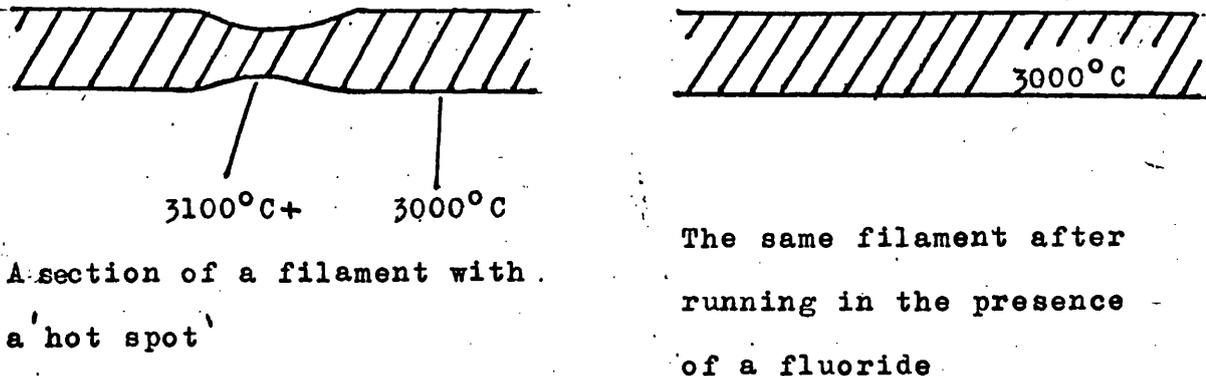
FIGURE 3.4.1. - Redistribution of Tungsten Through Life in a Tungsten Bromine Lamp



The tungsten fluorine cycle has an 'inversion temperature' of the order of 3100°C (Appendix 1) so that gaseous tungsten fluorides will only deposit tungsten at points on

the filament exceeding this temperature. Therefore, the addition of fluorine or a suitable fluoride[‡] to a tungsten filament lamp should lead to a more selective deposition of tungsten only on the filament 'hot spots' - where evaporation of tungsten is greatest and filament failure occurs (see Figure 3.4.2). This should extend the filament life, provided that the initial pressure of fluorine is low so that the attack of fluorine on the cooler parts of the filament ($< 3100^{\circ}\text{C}$) is not detrimental to lamp life.

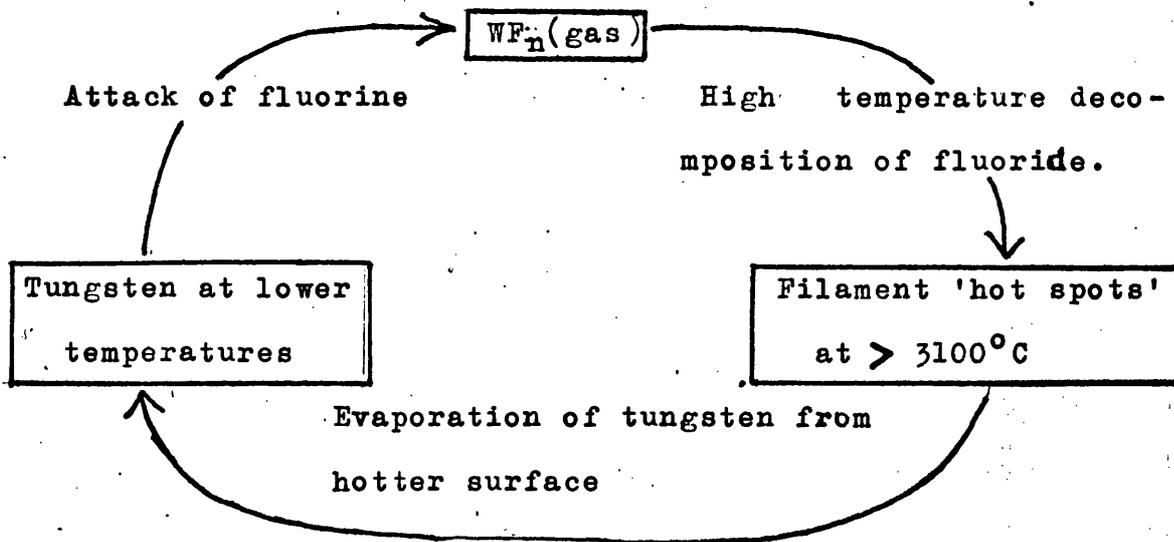
FIGURE 3.4.2 - The Sealing of 'Hot Spots' in the Presence of a Fluoride.



The tungsten fluorine cycle should work as shown in Figure 3.4.3

[‡] A suitable fluoride is one which will decompose at, or below, the running temperature of the filament to give fluorine atoms or fluorine molecules.

FIGURE 3.4.3. The Fluorine Cycle.



3.5 Previous Work on the Tungsten Fluorine Cycle.

6(a), 109, 123, 124.

Schröder and co-workers have shown that running an artificially etched tungsten wire, with the thin part of the wire at $\sim 3100^\circ\text{C}$ and the thick part of the wire at $\sim 2800^\circ\text{C}$, in the presence of a small pressure of WF_6 produces a uniform wire. Diagrams from three of these references 6(a), 109, 124 suggest that the final temperature of the wire was $\sim 3100^\circ\text{C}$ (although this is not stated). This would imply that fluorine (or the fluoride) preferentially attacks tungsten at the lower temperature but it does not prove any redeposition of the tungsten onto the hotter wire. From different diagrams, 123, 124 in two of the references it is not clear whether the uniform wire was produced by selective thinning of the thicker part of the wire, or by thickening of the thinner part of the wire, or by both.

By running a standard filament in the presence of NF_3 , 109 Rabenau has produced a filament of uniform temperature.

However, since this final uniform temperature was equal to the maximum original temperature (ie. the filament was thinned) no regenerative properties of the tungsten fluorine cycle were shown.

Taking a tungsten filament lamp which had grown black during several hours operation at $\sim 3000^{\circ}\text{C}$ in the presence of 500 torr argon, Schröder^{6(a),123,124} showed that the introduction of 2 torr WF_6 and 15 minutes running at 3100°C led to the removal of the black tungsten deposit from the bulb wall. This again proves that fluorine or the fluoride attacks tungsten at the lower temperatures to form a volatile product. However, although this (like the other experiments) indicates that a tungsten fluorine cycle is in operation, no proof of the redeposition of tungsten above the 'inversion temperature' has been published.

3.6 The Present Work.

The work now documented on the tungsten fluorine incandescent lamp is split into two parts:

(1) A simple investigation into the effects of fluorides in quartz envelope, tungsten filament incandescent lamps.

(2) An investigation of the tungsten fluorine regenerative cycle (and a comparison with the tungsten bromine cycle) using a radiochemical tracer technique.

3.7 An Investigation into the Effects of Fluorides in Quartz Envelope Tungsten Filament Lamps Using Infra-Red Spectroscopy.

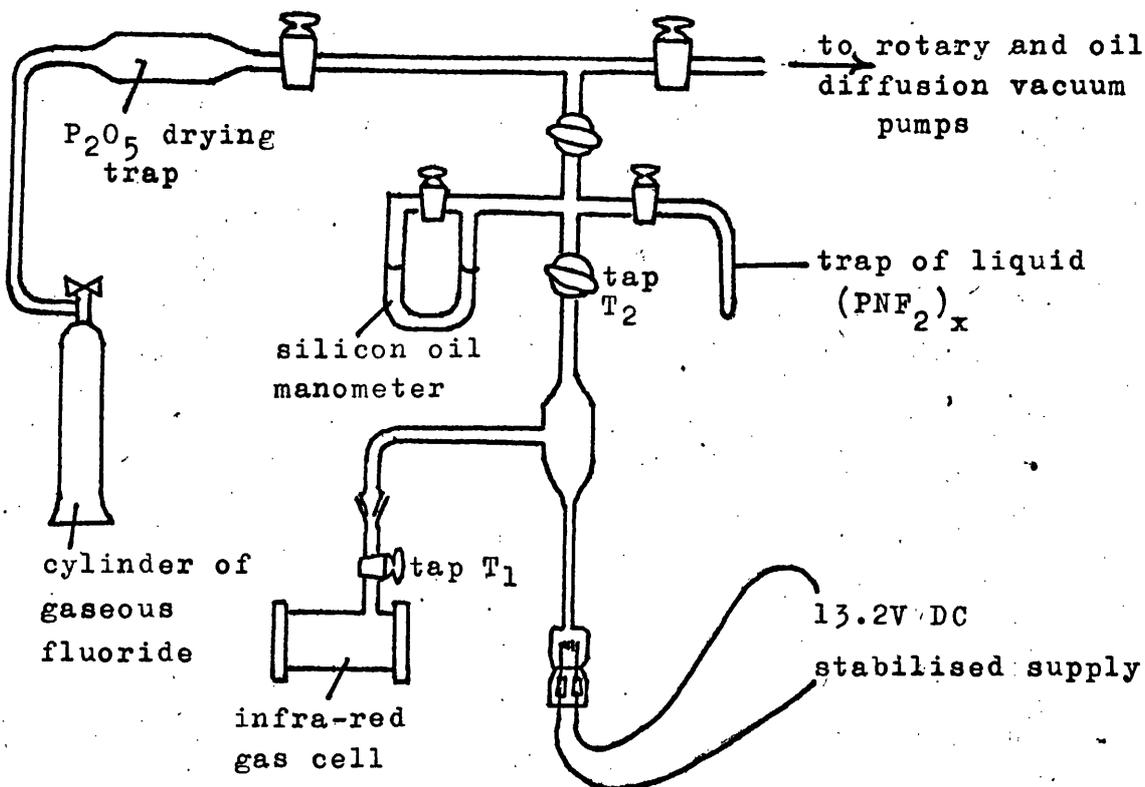
3.7.1 Introduction.

The major chemical reactions of gaseous fluorides in operating quartz envelope tungsten filament incandescent lamps have been investigated by infra-red spectroscopy. The gas-phase infra-red spectrum of a fluoride was recorded. A quartz envelope incandescent lamp containing the fluoride was run. The infra-red spectrum of the products was recorded and compared with the first spectrum.

3.7.2 Experimental Procedure.

The apparatus (Figure 3.7.2) consisted of a standard vacuum system attached to which was a standard 12V, 55W tungsten halogen lamp and an infra-red gas cell of optical length 91.5cm (with sodium chloride windows).

FIGURE 3.7.2 - Apparatus for Infra-Red Studies.



The spectrum of an unreacted gaseous fluoride was obtained by directly filling the gas cell with a known pressure of the fluoride, removing the gas cell from the vacuum line and recording the infra-red spectrum (800-2000 cm^{-1}) on a Unicam SP200 spectrometer.

The spectrum of the gaseous products of operating a fluoride containing lamp was obtained as follows. With a vacuum in the gas cell and a high pressure of the fluoride in the lamp (taps T1 and T2 closed) the lamp was run at 13.2V for about 1 hour or until filament failure occurred. Tap T1 was opened and the gaseous products were distilled into the gas cell (to equal pressures). With tap T1 closed, the gas cell was removed and the spectrum was recorded.

3.7.3. Experimental Results.

The results (Table 3.7.3) show that operating a quartz envelope, tungsten filament incandescent lamp containing a gaseous covalent fluoride produces a compound with a strong infra-red absorption at $\sim 1030\text{cm}^{-1}$. This is indicative of silicon tetrafluoride^{128,129} which is presumably formed by the reaction of the fluoride, fluorine molecules or fluorine atoms with the silica envelope. The results suggest that a substantial proportion of the fluoride is converted to silicon tetrafluoride during the first hour of lamp operation.

TABLE 3.7.3 Effects of Fluorides in Quartz Envelope
Tungsten Filament Lamps.

(a) Infra-Red Spectra of Fluorides Not Run in the Lamp.

Fluoride	Pressure in Gas Cell	Major Absorption Peaks of the Fluoride (cm^{-1}).	Reference for Comparison
$(\text{PNF}_2)_x$	1 torr	1425 (strong with shoulder at 1490) 990 (strong and sharp with shoulders at 970 & 955)	125
NF_3	7 torr	1030 (medium and sharp) & 910 (strong & broad with shoulder at 900)	126
CF_4	15 torr	1280 (very strong & broad) & 1240 (medium & sharp)	127
SiF_4	24 torr	1200 (medium weak), 1180 (med- ium weak), 1030 (very strong)	128, 129

TABLE 3.7.3 (b) Infra-Red Spectra of the Gaseous Products of Operating Fluoride Containing Lamps.

Fluoride	Original Pressure of Fluoride in Lamp (torr)	Pressure of Products in Gas Cell * (torr)	Length of run of Fluoride containing Lamp (h)	Major Absorption Peaks of gaseous Lamp Products (cm ⁻¹).	Inferred Products.
PNF ₂ x	1	0.11	½	1030 (medium & sharp), 990 (very weak), 980 (weak) & 1420 (very weak).	SiF ₄ & (PNF ₂)x
NF ₃	25	3.2	½	1030 (strong & sharp) & 910 (medium with shoulder at 900)	NF ₃ & SiF ₄
CF ₄	20	2.3	½ (lamp failure - re occurred)	1275 (medium strong & sharp) & 1030 (strong & sharp)	CF ₄ & SiF ₄
SiF ₄ **	69	7.8	½ (lamp failure occurred)	1200 (weak), 1190 (weak) 1030 (strong & sharp)	SiF ₄

* The pressure in the gas cell was calculated from the pressure in the lamp & the volume of the lamp system (13.4cm³) & the gas cell (106.5cm³).

** A spectrum of 7.8 torr of SiF₄ which had not been run in the lamp was found to be identical to this spectrum

3.8. A Radiochemical Examination of the Tungsten Fluorine Regenerative Cycle.

3.8.1. Introduction.

Radiochemical tracer experiments in twin filament incandescent lamps have been used to investigate the tungsten fluorine regenerative cycle and, for comparison, the tungsten bromine cycle.

When operating, the experimental twin filament tungsten halogen lamps have consisted of one hot (running) filament and one cold (non running) filament.

Around the cold filament the reaction $W(s) + nX(g) \rightarrow WX_n(g)$ (or $W(s) + \frac{nX_2(g)}{2} \rightarrow WX_n(g)$) is favourable provided that the temperature of the cold filament is less than the 'inversion temperature' for the reaction. However, at positions on the hot filament where the temperature exceeds the 'inversion temperature' the reaction $WX_n(g) \rightarrow W(s) + nX(g)$ is favourable and tungsten is deposited on that filament. Therefore, if the tungsten halogen cycle is operational a certain amount of transfer from the cold filament to the hot filament should occur and the distribution of the deposited tungsten should be dependent on the 'inversion temperature'.

A radiochemical tracer technique has been used to determine if (and, if so, how much) transfer of tungsten occurs from the cold (non running) tungsten filament (labelled with ^{185}W) to the hot (running) tungsten filament (unlabelled) in the presence of a halide. The occurrence of transfer proves the operation of the particular tungsten halogen cycle and the amount and distribution of the transfer gives an indication of the 'inversion temperature' of the halogen cycle.

The experiments have been carried out on lamps dosed with various fluorides (to investigate the tungsten fluorine cycle) and, for comparison, on lamps dosed with bromine in the form of bromophosphonitrile.

In order that the distribution of any transferred tungsten could be compared with the variation in temperature along the operating filament, the temperatures at points along a typical filament have been determined.

3.8.2 Experimental Procedure.

(a) Radiochemical Tracer Experiments.

Filaments of standard 12V 55W tungsten halogen auto lamps were irradiated (at Harwell) for 30 hours with a neutron flux of 7×10^{12} neutrons $\text{cm}^{-2} \text{sec}^{-1}$. At unload the activity on 10g of the filaments was 50mCi of β emitting ^{185}W and 3.2 Ci of γ emitting ^{187}W . The filaments were retained at Harwell until the activity due to ^{187}W was negligible.

Twin filament 12V 55W tungsten halogen type auto lamps were constructed with one irradiated and one non-

irradiated filament in a fused quartz envelope (Figure 3.8.2(a)). Each lamp was dosed with a known pressure or mass of a halide and a known pressure of argon on the vacuum system shown in Figure 3.8.2(b). The procedure involved condensing gases from the system A into the lamp and calculation of the resultant lamp pressures. The pressures in the vacuum system were measured on the Pirani gauge (for the low pressures of the fluorides) and the Bourdon gauge (for the higher pressures of argon). Pirani gauge pressures were corrected for the differing thermal conductivities of the gases used.¹³⁰

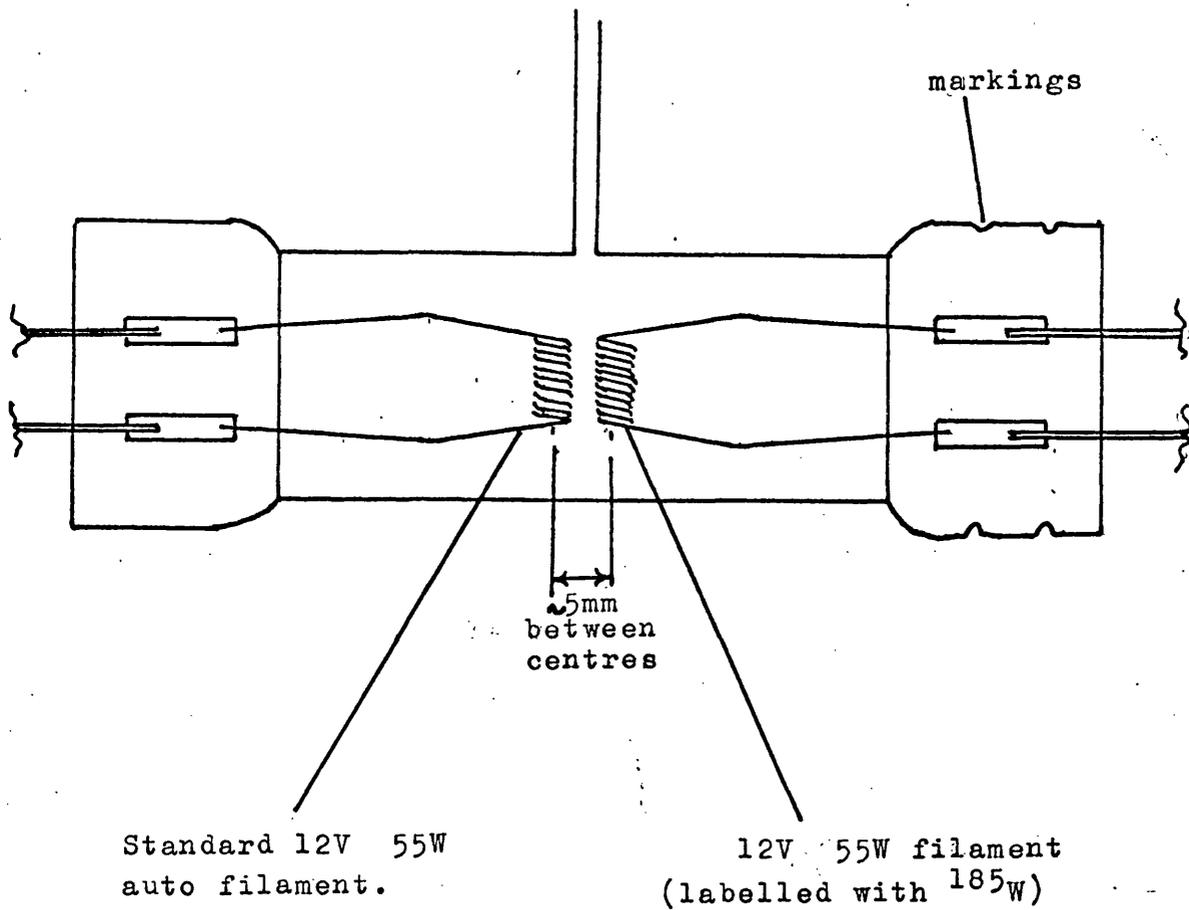
The non-irradiated filament of the dosed twin filament lamp was run at a known voltage until just before the filament would be expected to fail (determined from previous life test experiments). The lamp was broken open, the operated filament removed, and the total radioactive count on this filament was recorded (using a thin window Geiger Muller tube, Mullard MX123, and a Panax type D657 counter) in Table 3.8.2/1. The filament was then sectioned as shown in Figures 3.8.2(c) or (d) and the radioactive count and mass of each section was recorded. The results are expressed in Tables 3.8.2/2 and 3.8.2/3 and Graphs 3.8.2/1 to 3.

(b) Temperature Determinations.

Temperatures along the filament of a 12V 55W tungsten halogen type incandescent lamp dosed only with argon (3 atmos.) have been measured.

The 12V 55W lamp was placed vertically, pinch down, in a draught free enclosure and a measured stabilised

FIGURE 3.8.2(a) - The Experimental Lamps.*



* not to scale.

FIGURE 3.8.2(b) - Apparatus for dosing the lamps.

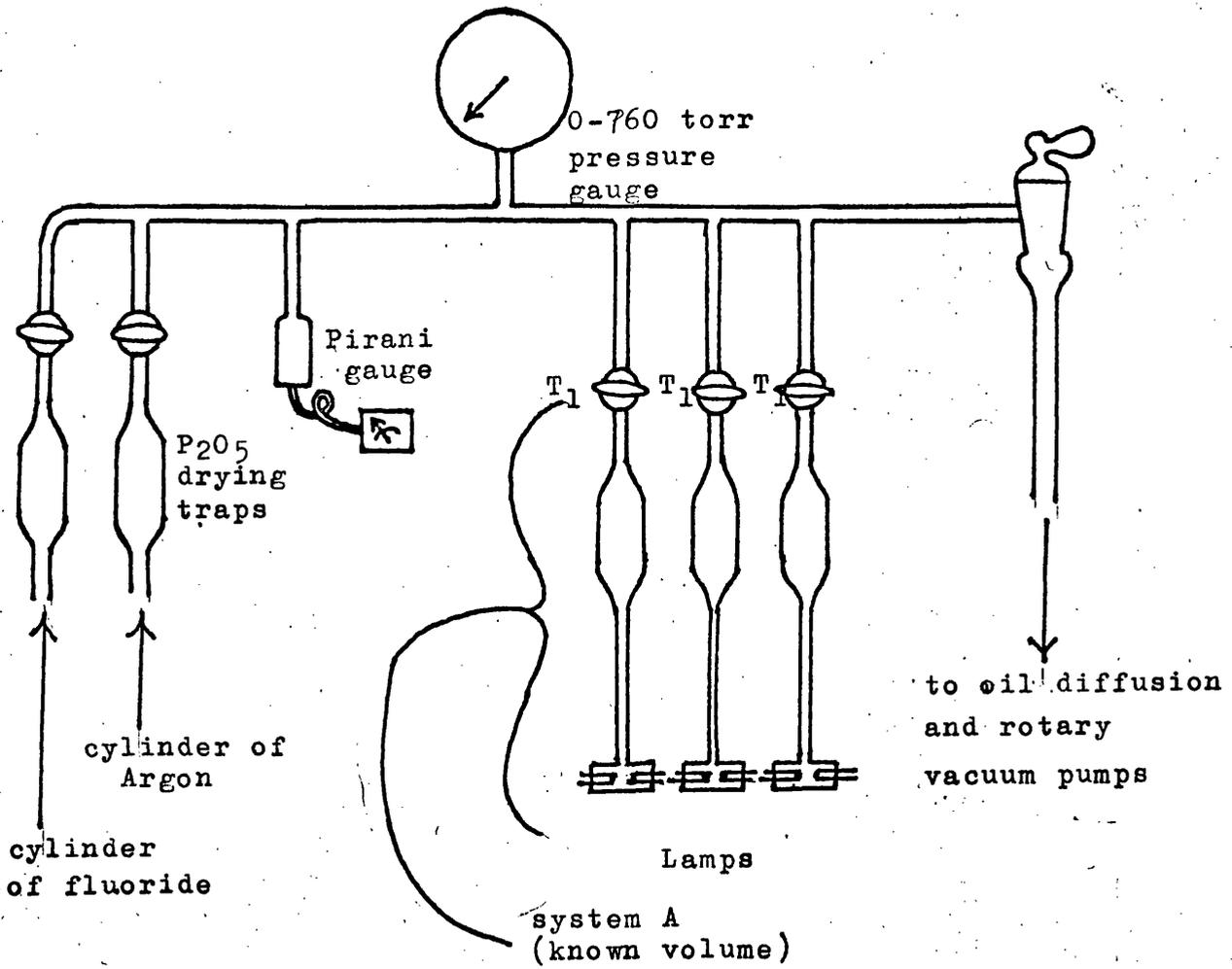
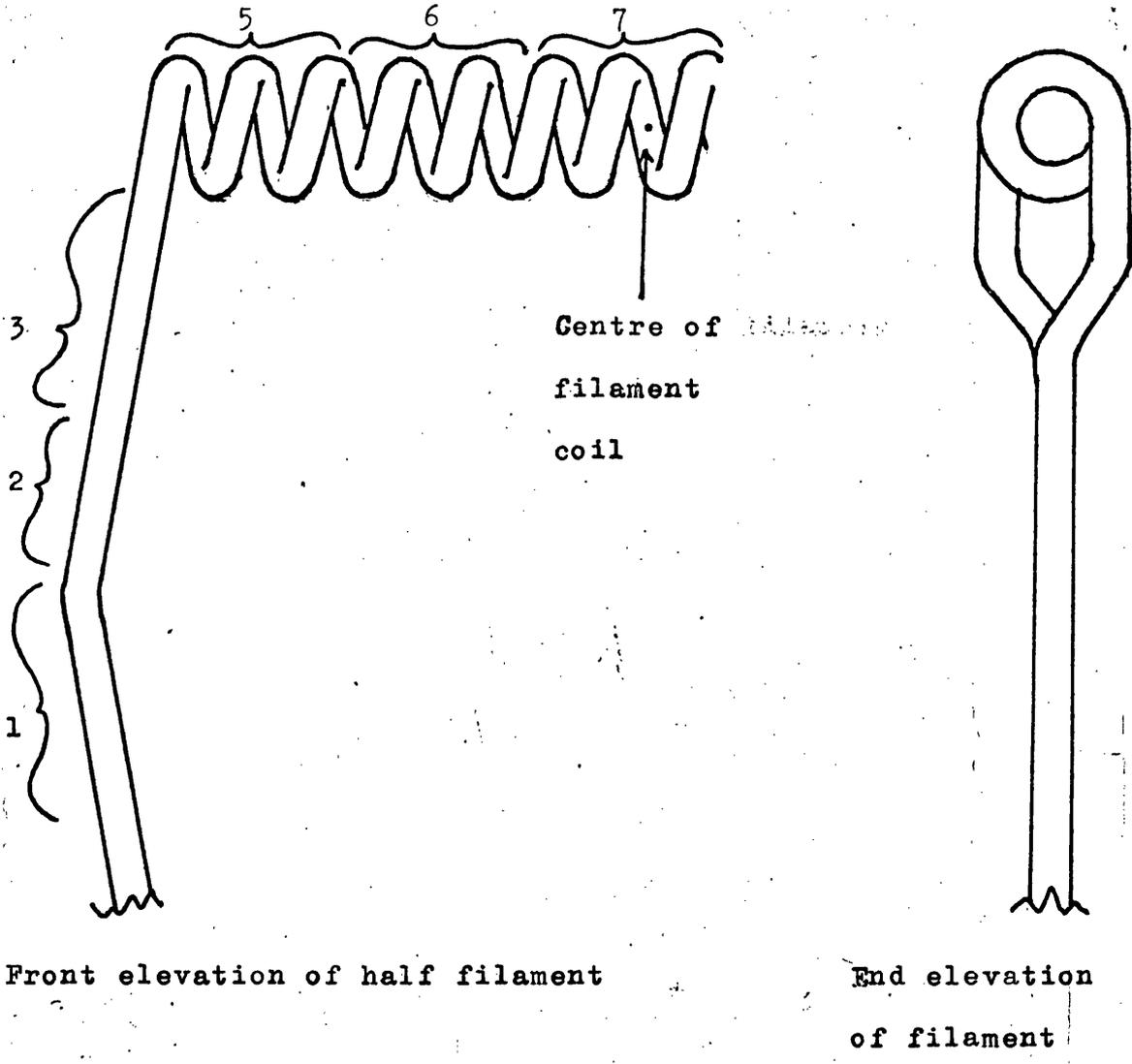


TABLE 3.8.2/1 - TRANSFER OF 185W ON TO THE HOT (RUNNING) FILAMENTS

LAMP NO.	NUMBER OF LAMPS	LAMP CONTENTS						LENGTH OF RUN(h)	RUNNING VOLTAGE (V)	AVERAGE AMOUNT OF TRANSFER ON TO HOT FILAMENTS AFTER RUNNING (COUNTS MIN-1 ABOVE THE BACKGROUND)	AMOUNT OF TRANSFER ON TO INDIVIDUAL HOT FILAMENTS (COUNTS MIN-1 ABOVE THE BACKGROUND)
		SIF (torr)	PNF ₁ (torr)	PNF ₂ (torr)	PNF ₃ (torr)	PNBr ₂ (μs) (atmos)	Ar N ₂ (torr)				
D1-3	3	-	-	-	-	3	-	50	13.2	none	-
2A1-6	6	-	-	-	-	3	-	100	13.2	938	231, 498, 806, 3271, 249, 575.
3A2	1	-	-	-	-	3	-	50	13.2	24757	-
2B1-6	6	1	-	-	-	3	-	100	13.2	1525	14, 3962, 1113, 3669, 84, 299
E1-4	4	3.5	-	-	-	3	-	42	13.2	none	-
F1-2	2	7	-	-	-	3	-	21	13.2	none	-
G1-2	2	7	-	-	-	3	20	1	18.8	none	-
J1-4	4	35	-	-	-	3	-	0.3	13.2	none	-
K1-4	4	-	4	-	-	3	-	0.2	13.2	none	-
L1-2	2	-	1/2	-	-	3	20	1	18.8	none	-
M1	1	-	1/2	-	-	3	-	100	13.2	none	-
M2-3	2	-	1/2	-	-	3	-	50	13.2	none	-
NE4/1-4	4	-	-	6	-	3	-	1.2	18.8	410	528, 816, 57, 241
NE4/5-6	2	-	-	6	-	3	-	1.1	19.0	1556	1217, 1495
NE4A/1-2	2	-	-	6	-	3	-	16	13.2	297	470, 124
NE4E1	1	-	-	6	-	3	-	20	13.2	238	-
NE4/C1	1	-	-	6	-	3	-	16	13.2	69	-
NE4/D1	1	-	-	6	-	3	-	1.5	13.2	256	-

FIGURE 3.8.2(c). Filament Sections
(used in Table 3.8.2/2)



Front elevation of half filament

End elevation of filament

FIGURE 3.8.2(d). Filament Sections
(used in Table 3.8.2/3)

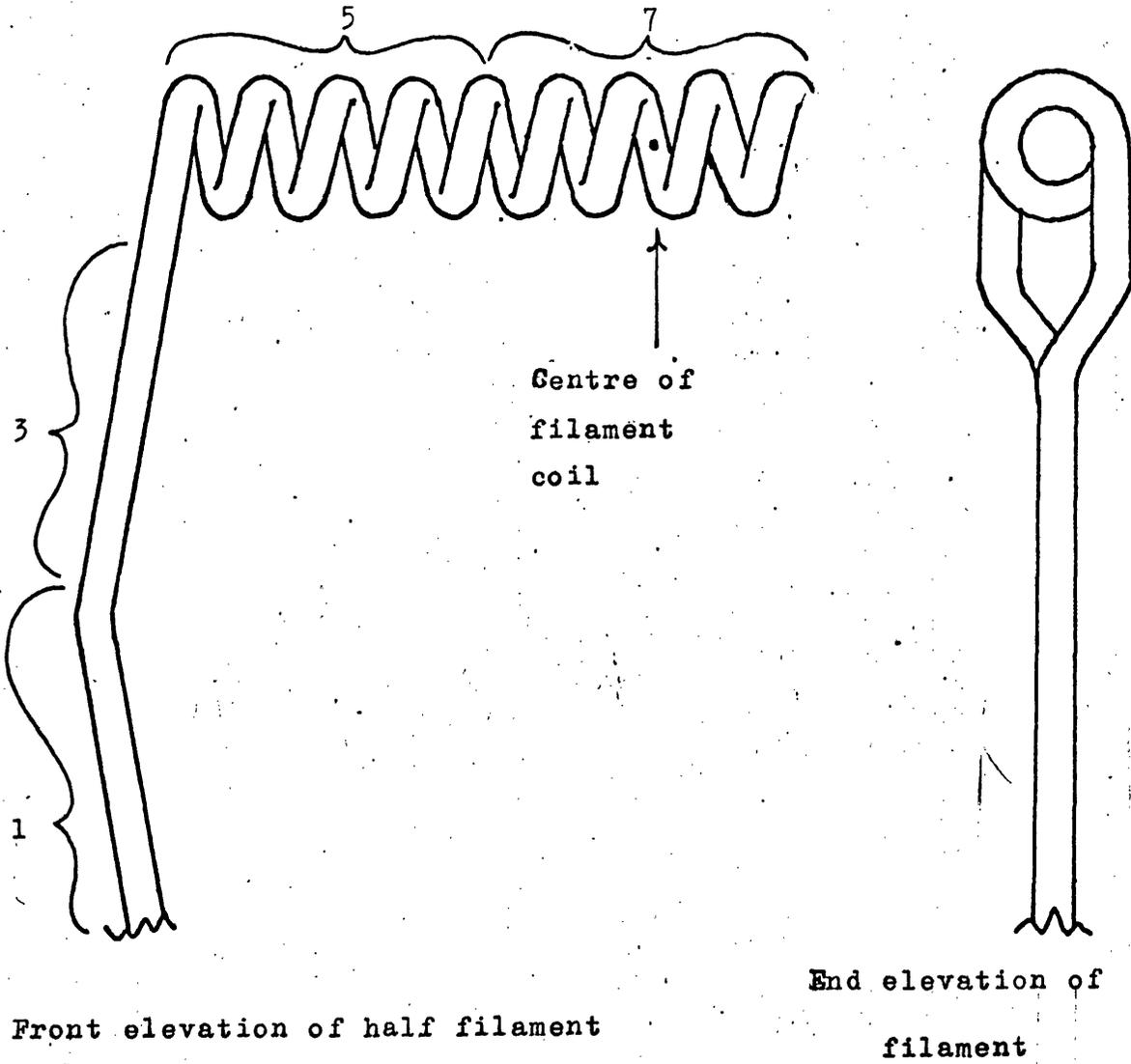


TABLE 3.8.2/2 - Distribution of W Transfer on to the
Hot (running) Filaments in Lamps Containing
P_NBr₂ and Argon.

(a) Lamp 2A4 (containing 25 μ g P_NBr₂ and 3 atmos. Ar).

Section of filament	Section* No.	Ave. Count min ⁻¹ above background	Ave. Section Mass (mg)	Count min ⁻¹ mg ⁻¹
bottom of filament legs	1	739	2.41	336
middle of filament legs	2	807	2.07	389
top of filament legs	3	646	2.45	263
end turns of coil	5	216	5.03	42.9
next turns of coil	6	127	4.87	26.0
centre turns of coil	7	110	4.48	24.6

*The Section Nos. refer to Figure 3.8.2(c).

TABLE 3.8.2/2 (continued).

(b) Lamp 3A2 (containing 50 μ g PNB r_2 and 3 atmos. Ar).

Section of filament	Section No. [*]	Ave. Count min ⁻¹ above background	Ave. Section Mass (mg)	Count min ⁻¹ mg ⁻¹
bottom of filament legs	1	2694	0.95	2737
middle of filament legs	2	4051	1.03	3930
top of filament legs	3	8951	2.54	3402
end turns of coil	5	8543	11.74	727
next turns of coil	6	2361	7.57	312
centre turns of coil	7	1375	5.70	242

(c) Lamps containing a fluoride as well as PNB r_2

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The distribution of ¹⁸⁵W transferred on to the hot (running) filament was noted for lamps 2B2 & 2B4 containing 1 torr SiF₄, 25 μ g PNB r_2 and 3 atmos. Ar. There was no significant difference in the distribution of the transferred ¹⁸⁵W between the lamps containing SiF₄ and those without SiF₄ (i.e. lamps 2A4 and 3A2).

* The Section Nos. refer to Figure 3.8.2(c).

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TABLE 3.8.2/3 - Distribution of W Transferred on to the
Hot (running) Filaments in Lamps containing
NF₃ and Argon.

(a) Lamp 2NF4/A1 (containing 6 torr NF₃ and 3 atmos. Argon)

Section of filament	Section No. *	Counts min ⁻¹ above background	Section Mass(mg)	Counts min ⁻¹ mg ⁻¹
bottom of filament legs	1	74.7	3.1	24.1
top of filament legs	3	36.9	2.47	14.9
end turns of coil	5	257.1	14.4	17.9
centre turns of coil	7	44	2.15	20.5

(b) Lamp 2NF4/B1 (containing 6 torr NF₃ and 3 atmos. argon)

Section of filament	Section No. *	Counts min ⁻¹ above background	Section Mass(mg)	Counts min ⁻¹ mg ⁻¹
bottom of filament legs	1	48.5	3.57	13.6
top of filament legs	3	6.7	2.57	2.6
end turns of coil	5	139.4	17.17	8.7
centre turns of coil	7	81.4	8.6	9.35

* Section Nos refer to Figure 3.8.2(d)

TABLE 3.8.2/3 (continued)

(c) Lamp 2NF4/D1 (containing 6 torr NF₃ and 3 atmos. Argon)

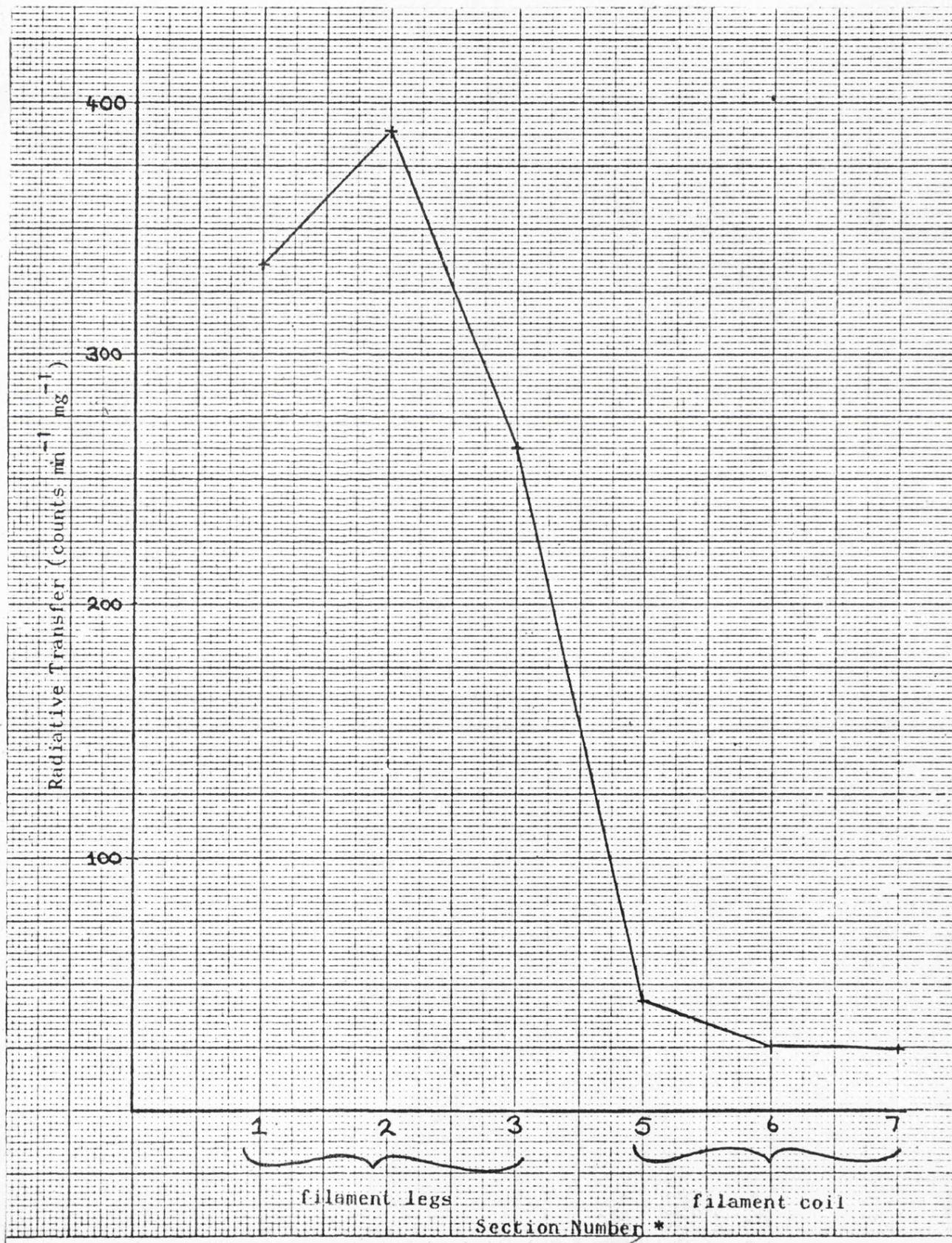
Section of filament	Section No.*	Counts min ⁻¹ above background	Section Mass(mg)	Counts min ⁻¹ mg ⁻¹
bottom of filament legs	1	19.6	3.15	6.2
top of filament legs	3	8.6	2.85	3.0
end turns of coil	5	167	17.75	9.4
centre turns of coil	7	52.8	6.75	7.8

* Section Nos. refer to Figure 3.8.2(d).

GRAPH 3.8.2/1. Radiative Transfer on to Filament 2A4.

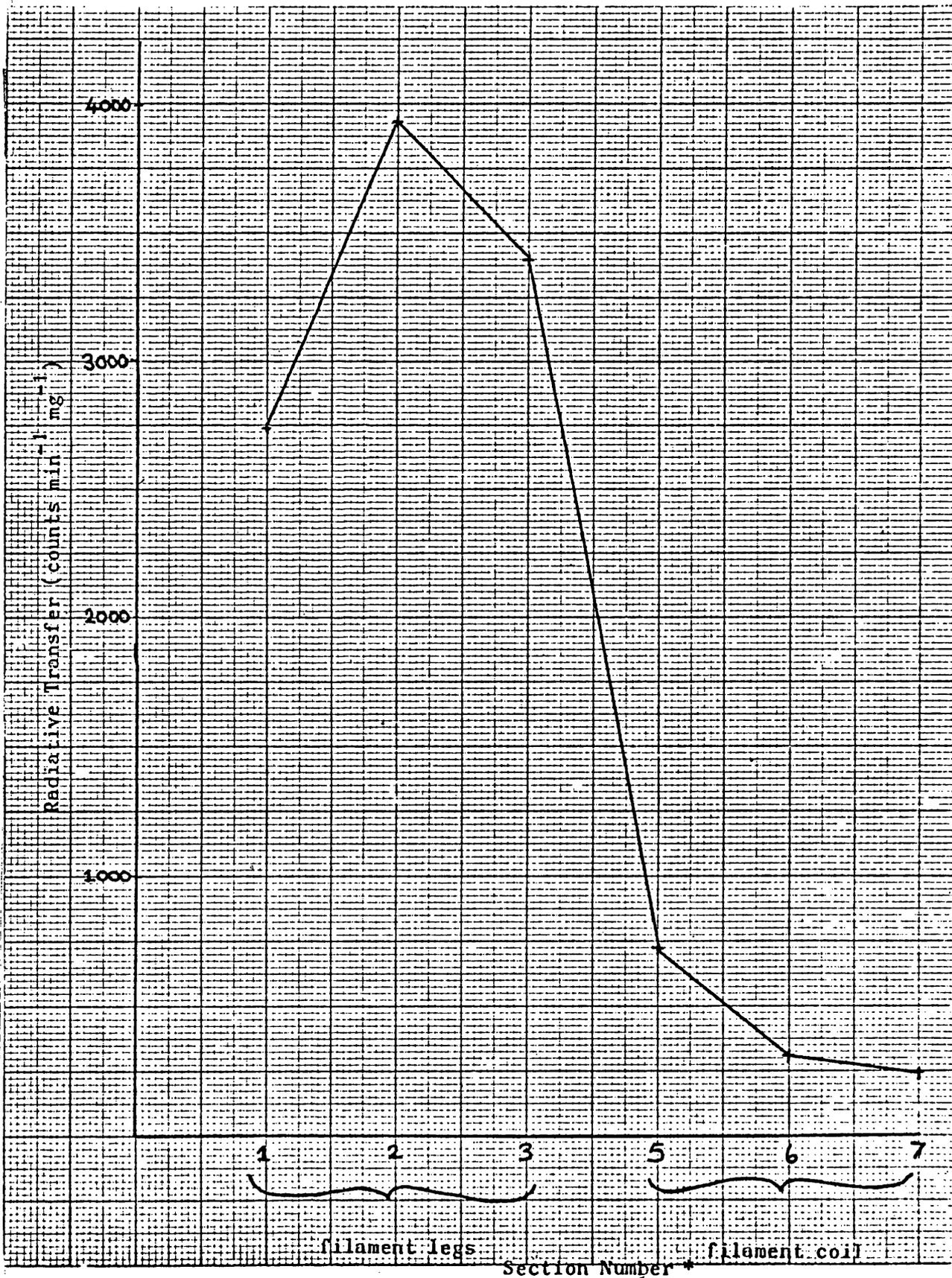
(lamp contained 25 μ g PNB r_2 and 3 atmos. Ar)

* refers to Figure 3.8.2(c)



GRAPH 3.8.2/2. Radiative transfer on to Filament 3A2
 (lamp contained 50 μ g PNB r_2 and 3 atmos Ar)

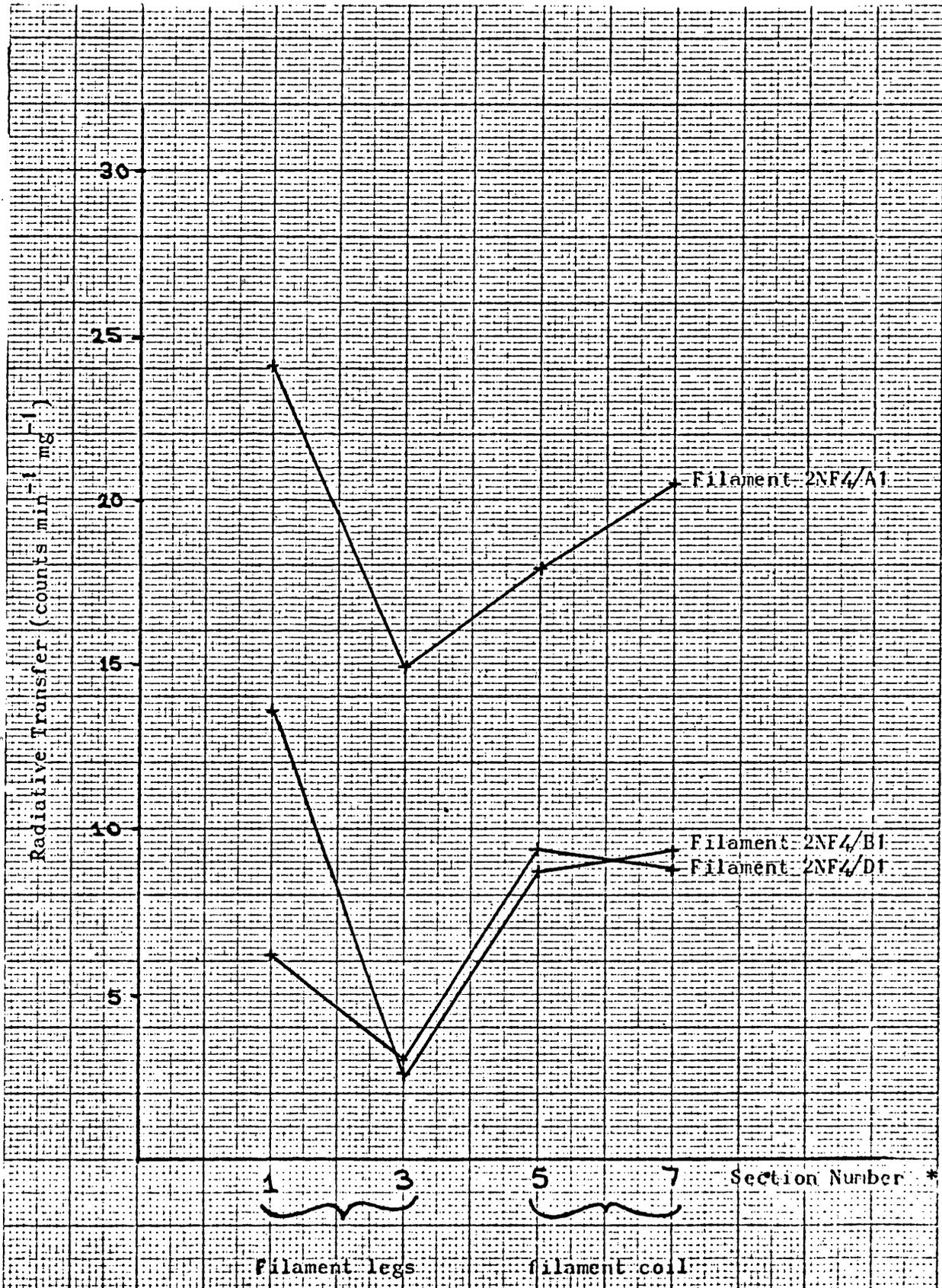
* refers to Figure 3.8.2(c)



GRAPH 3.8.2/3. Radiative Transfer on to Filaments of the 2NF4 Type.

(lamps contained 6 torr NF_3 and 3 atmos Ar)

* refers to Figure 3.8.2(d)



voltage applied to the filament. The apparent (brightness) temperature of any part of the filament was measured by comparing the brightness of that part with the brightness of the filament of a direct reading disappearing filament optical pyrometer (Pyro-Werk No3161 with specified lens G). Several readings of the filament temperature were taken in order to minimise visual errors. The apparent temperature was measured at various points both on the filament legs and on the inside and outside of the filament coil. The apparent (brightness) temperatures were converted to true temperatures, according to de Vos¹³¹, using the formula

$$\frac{C_2}{\lambda} \left(\frac{1}{T} - \frac{1}{T_p} \right) = \log_e \epsilon(\lambda T)$$

where λ is the wavelength of the pyrometer filter (6500Å)

C_2 is the constant in the Planck equation for the distribution of energy in the spectrum.

$\epsilon(\lambda T)$ is the emissivity of the part being measured*

T is the true temperature.

T_p is the temperature measured on the pyrometer.

The results for an applied voltage of 13.2V are shown on Table 3.8.2/4 and Graph 3.8.2/4.

Further measurements of the temperature of the centre

Footnote *

The figures for the emissivity of the different parts of the filament at different temperatures were obtained from reference 131 (filament legs and outside of coil) and reference 132 (inside the filament coil).

TABLE 3.8.2/4 Temperature of a Filament at 13.2V.

Position No [*]	Apparent(brightness) Temperature (K)	Emissivity at 6500Å	True temperature (K)
1	3058	0.8	3155
2	2920	0.4243	3292
3	3011	0.8	3105
4	2920	0.4243	3292
5	3018	0.8	3113
6	2920	0.4243	3292
7	3020	0.8	3115
8	2888	0.4249	3251
9	3013	0.8	3107
10	2848	0.4257	3200
11	2956	0.8	3047
12	2745	0.4276	3068
13	2888	0.8	2975
14	2586	0.4308	2868
15	2322	0.4358	2544
16	2197	0.4381	2393
17	2095	0.4401	2271

* The position Nos. refer to Figure 3.8.2(e).

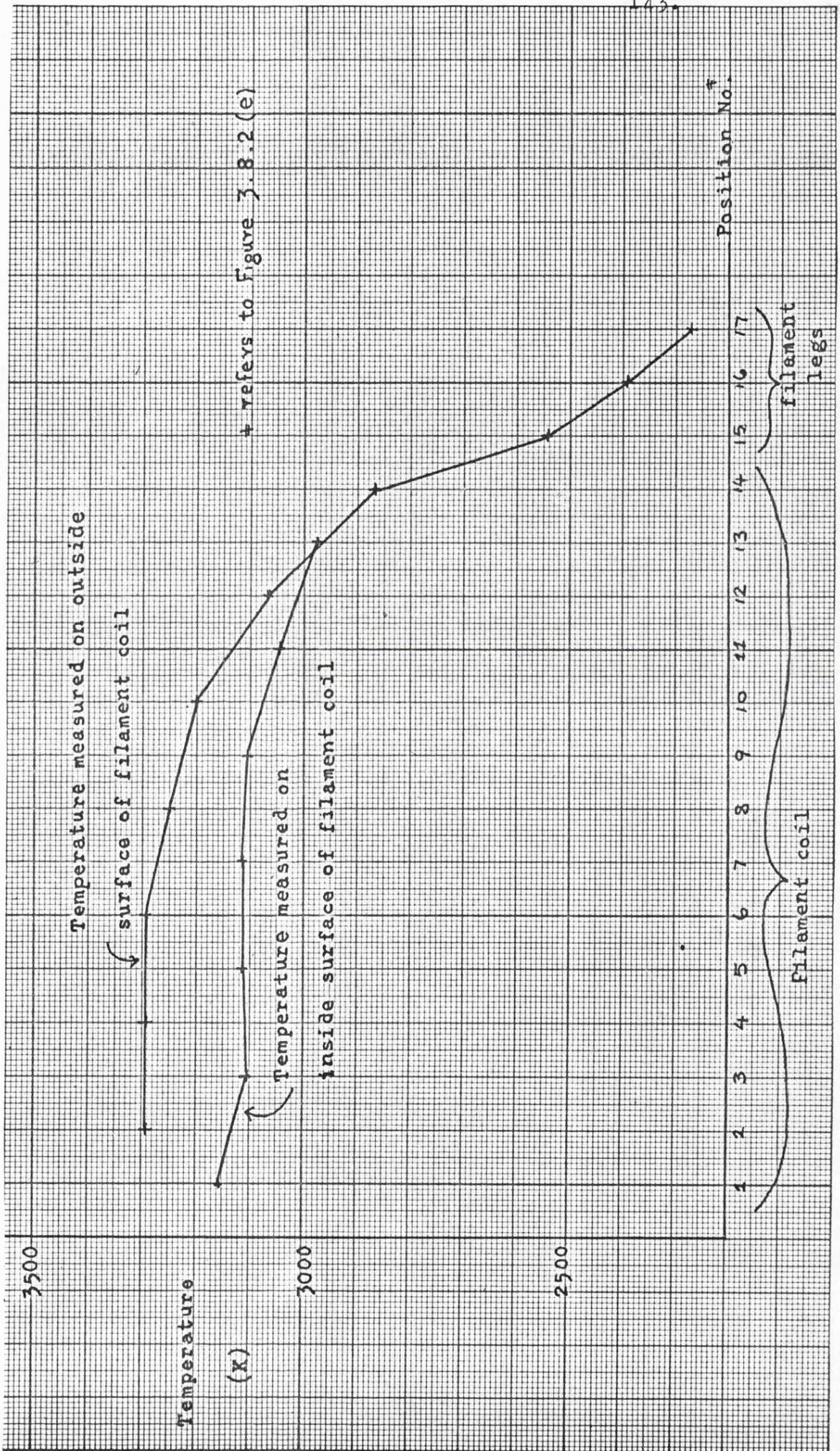
TABLE 3.8.2/5. Variation in the Temperature of the Centre of the Filament Coil with Voltage.

Voltage	Apparent (brightness) Temperature (K)		Emissivity		True temperature (K) [†]	
	Outside	Inside	Outside	Inside	Outside	Inside
	coil	coil	coil	coil	coil	coil
13	2904	3031	0.424 ₆	0.8	3272	3127
13.2	2922	3058	0.424 ₃	0.8	3295	3155
14	2984	3111	0.423 ₁	0.8	3375	3211
16	3106	3249	0.420 ₈	0.8	3535	3359
17	3138	3280	0.420 ₂	0.8	3578	3392
18	3280	3365	0.417 ₅	0.8	3768*	3483

† The true temperature measured on the outside surface of the coil is expected to be more accurate than that measured on the inside surface of the coil because the emissivity of the outside surface has been measured more accurately.

* This figure must be in error since it exceeds the melting point of tungsten.

GRAPH 3.8.2/4, Temperature of Points on a Running 12V 55W Filament At 13.2V.



GRAPH 3.8.2/5. 'True Temperature' of 12V 55W Filament
Coil against Applied Voltage.

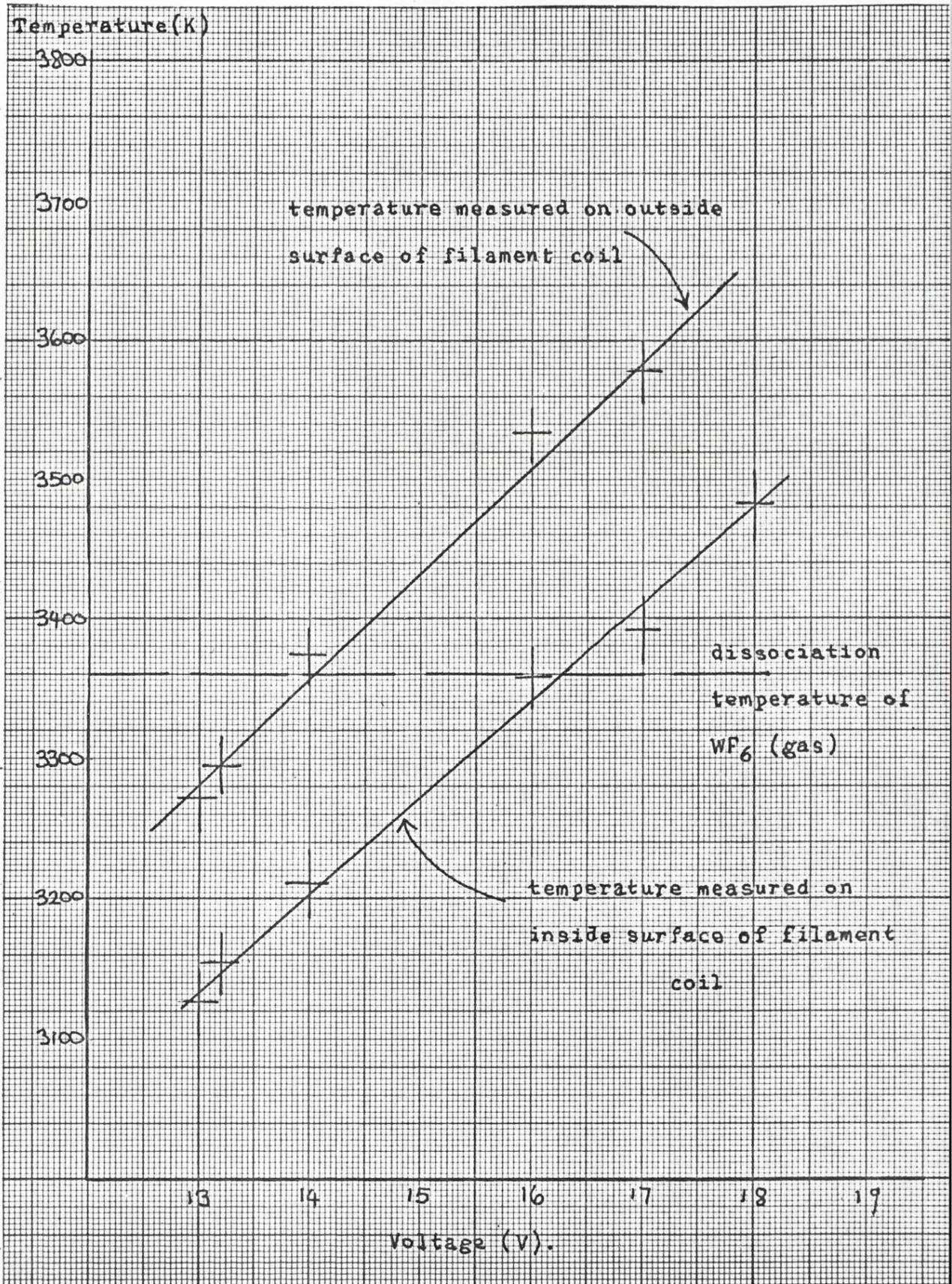
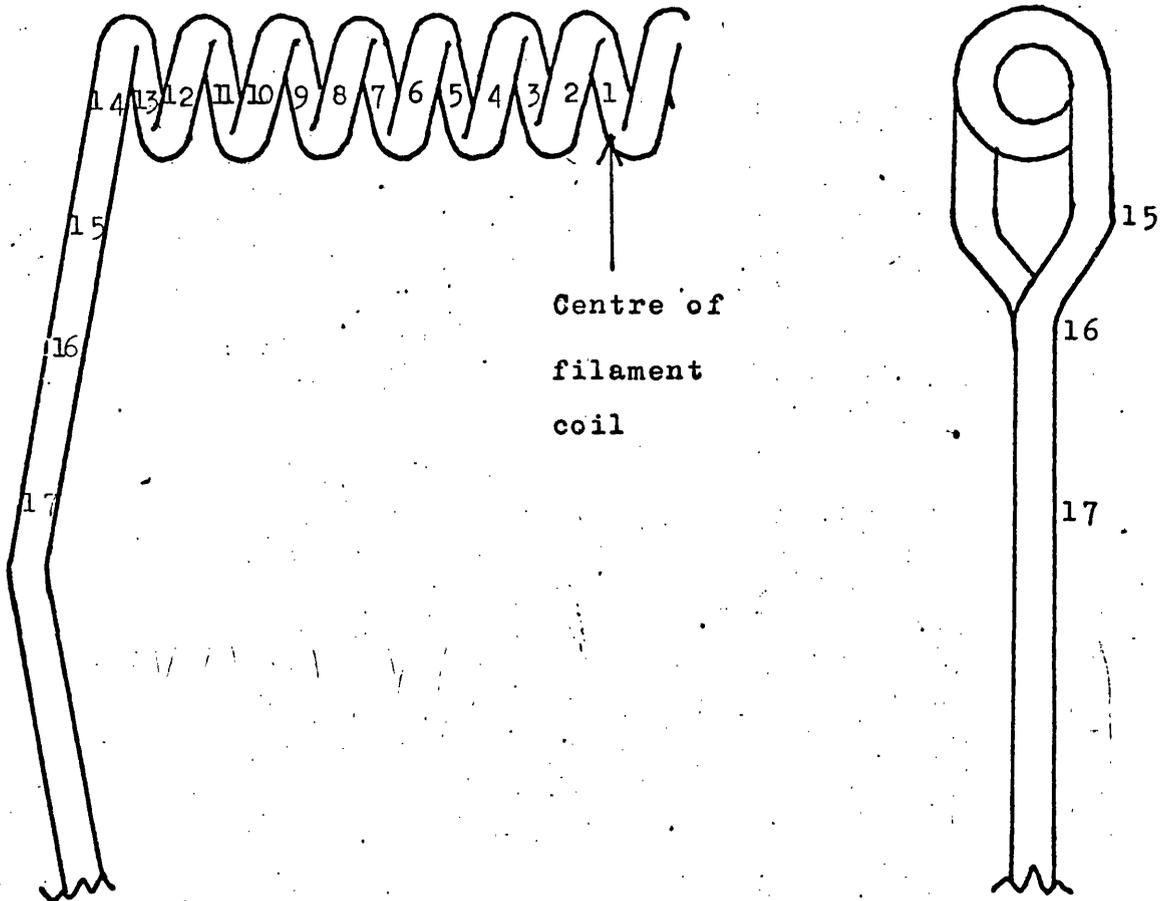


FIGURE 3.8.2(e). Points on Filament - used in the
Temperature Measurements (Table 3.8.2/4)



Front elevation of half filament

End elevation
of filament

section of the filament were made at a range of voltages (Table 3.8.2/5 and Graph 3.8.2/5).

3.8.3. Discussion of Experimental Results.

In a twin filament lamp, transfer of tungsten from the cold to the hot filament has been found to occur when either nitrogen trifluoride or bromophosphonitrile was introduced into the lamp.

It has been suggested earlier (section 3.8.1), that where transfer of tungsten occurs a tungsten halogen regenerative cycle is in operation. Therefore, it follows that with nitrogen trifluoride introduced into the lamp a tungsten fluorine regenerative cycle is set up, whereas, with either silicon tetrafluoride or fluorophosphonitrile introduced into the lamp it is not.

This can be explained thermodynamically by considering the decomposition of the introduced fluoride thus $AF_n \rightleftharpoons A + nF$. At low temperatures the decomposition of the introduced fluoride is thermodynamically unfavourable i.e. for the forward reaction as shown the Gibbs free energy, ΔG_T^0 , is positive and the equilibrium constant, K , is less than unity. At high temperatures the decomposition becomes favourable (ΔG_T^0 becomes negative and K becomes greater than unity). The temperature at which the decomposition becomes favourable ($\Delta G_T^0 = 0$ and $K = 1$) is shown, for the different introduced fluorides and for tungsten hexafluoride, in Table 3.8.3/1

Since the highest temperatures obtained in 12V 55W tungsten halogen type auto lamps (when run at 13.2V) is of

TABLE 3.8.3/1

Fluoride	Temperature(K) at which the Gibbs Free Energy of Fluoride Decomposition (ΔG_T^0) is Zero.	Source	Reference
WF_6 NF_3 SiF_4 PF_3	3360 2150 4450 3950	Appendix 1 B.J. McBride, S. Hermel, J.G. Ehler & S. Gordon.	133

the order of 3200-3600K (on the 'hot spots') it can be seen that SiF_4 and PF_3 will not be decomposed in a lamp, whereas NF_3 will be almost completely decomposed and the special case of WF_6 will decompose only on the 'hot spots'. The setting up of a regenerative fluorine cycle requires the decomposition of the introduced fluoride in order to provide free fluorine atoms for the regenerative equilibrium $\text{W(s)} + n\text{F(g)} \rightleftharpoons \text{WF}_n(\text{g})$. Therefore, of the fluorides considered only NF_3 (and WF_6) will lead to the setting up of the fluorine regenerative cycle.

During the life of a fused quartz envelope lamp containing a covalent fluoride (NF_3 , PNF_2 , CF_4 and SiF_4 were considered) SiF_4 is formed (Section 3.7) by the action of fluorine or the fluoride on the fused quartz envelope. When this occurs the fluorine is 'trapped' i.e. cannot form free fluorine atoms at the filament temperature and, therefore, cannot participate in the regenerative cycle. After 1-2 hours of normal running in a 12V. 55W auto lamp the majority of the fluorine is present as SiF_4 , so that after this time the tungsten fluorine regenerative cycle will cease to function in this lamp. This agrees with the experimental evidence (Table 3.8.3/2) which showed that as much transfer of radioactive ¹⁸⁵W occurred in a NF_3 dosed lamp run (at 13.2V) for 1 hour as in a similarly dosed lamp run (at 13.2V) for 16 or 20 hours. However, this (latter) evidence is not conclusive since re-evaporation of the transferred tungsten could have occurred.

The results (Table 3.8.2/1) show that several times more transfer of ¹⁸⁵W has occurred in the normally run 'bromine' lamps than has occurred in the similarly run 'fluorine' lamps. This is in keeping with the aim of fluoride doses (ie for the redeposition (or transfer) of tungsten only on to the 'hot spots') It was expected on thermodynamic grounds since at any temperature, throughout the considered temperature range, the 'bromine' reaction

$WBr_n(g) \rightarrow W(s) + nBr(g)$ is more favourable than the 'fluorine' reaction $WF_n(g) \rightarrow W(s) + nF(g)$ (ie. the Gibbs free energy at any considered temperature, ΔG_T° , is more negative (or less positive) in the case of the 'bromine' reaction).

Further experimental evidence on the 'fluorine lamp' has shown that a greater amount of transfer has occurred when the temperature of the running filament has been increased (Table 3.8.3/2) This is also compatible with thermodynamic data which suggest that the fluoride decomposition reaction $WF_n(g) \rightarrow W(s) + nF(g)$ becomes more favourable as the temperature increases (ie. ΔG_T° for the reaction becomes more negative with increasing temperature).

The results giving the distribution of transferred tungsten show that in the case of the 'fluorine lamp' the transferred tungsten has been deposited along the whole filament (Table 3.8.2/3 and Graph 3.8.2/3) whereas in the case of the 'bromine lamp' the majority of the transfer has been on to the filament legs (Table 3.8.2/2 and Graphs 3.8.2/1 and 3.8.2/2).

TABLE 3.8.3/2. Variation in amount of Transfer of ^{185}W in 'Fluorine Lamps' with Temperature
or with Length of Run.

LAMP NUMBER	NUMBER OF LAMPS	CONTENTS OF LAMP		LENGTH OF RUN(h)	VOLTAGE (V)	TEMP. ON OUTSIDE SURFACE OF FILAMENT COIL (K)	AVE. AMOUNT OF TRANSFER OF ^{185}W (COUNTS MIN-1 ABOVE BACKGROUND)
		NF_3 (torr)	Ar (a.tmos)				
NF4/D1	1	6	3	1½	13.2	3295	256
NF4/A1,2 & C1	3	6	3	16	13.2	3295	122
NF4/B1	1	6	3	20	13.2	3295	238
NF4/1-4	4	6	3	1.2	18.8	~3700	410
NF4/5-6	2	6	3	1.1	19.0	~3700	1356

The measured distribution of the transferred tungsten on the hot running filament is determined by

- (1) The deposition of transferring tungsten which occurs only above the 'inversion temperature'. Above this temperature the rate of deposition should be dependent on the temperature increase above the 'inversion temperature'.
- (2) The re-evaporation of transferred tungsten. The evaporation of tungsten from a particular point on the filament is dependent on the temperature of that point.
- (3) The movement of the transferred tungsten along the temperature gradient of the filament. The rate of this movement is dependent on the temperature gradient.

With the 'fluorine lamp' (inversion temperature $\sim 3100^{\circ}\text{C}$) transfer appears to have occurred on to sections of the filament where the temperature was only $\sim 2000^{\circ}\text{C}$. This suggests either that the 'inversion temperature' in the 'fluorine lamp' is lower than 3100°C or that a substantial amount of movement of the transferred tungsten along the hot (running) filament has occurred after the original deposition.

With the 'bromine lamp' (inversion temperature $\sim 1600^{\circ}\text{C}$) a combination of the three factors might easily lead to a distribution of ¹⁸⁵W of the type obtained.

3.8.4. Conclusions.

These radiochemical experiments have shown that transfer of tungsten from a cold (non-running) filament to a hot (running) filament does occur in the presence of a suitable

fluoride. This occurrence of transfer has proved that a 'fluorine regenerative cycle' is in operation in a tungsten fluoride lamp and that, in principle, a healing cycle is possible, which could minimise the rate of formation of 'hot spots' and increase filament life.

The distribution of transferred tungsten with a fluoride dose is far more even than is obtained with a bromide dose. However, the amount of transfer with a bromide dose is far greater than is obtained with a fluoride dose.

3.9 Development of a Commercial Tungsten Fluorine Incandescent Lamp.

Although it has been proved that a healing cycle with fluorine is possible, there are many problems to solve before the production of a commercial fluorine lamp. The two principle problems are:

(1) Early Lamp Failure.

It has been shown by life test experiments that the use of a relatively large fluorine dose in a lamp leads to early failure. This is due to the attack of fluorine on the tungsten filament, the majority of which is below the 'inversion temperature' of the fluorine reaction. This attack might be compensated for by using a mixed bromide/fluoride dose. The 'bromine cycle' might then cause tungsten to be redeposited on parts of the filament which are attacked by fluorine.

(2) The 'trapping' of fluorine as silicon tetrafluoride.

It has been shown that, in a fused quartz envelope

tungsten fluorine lamp, the fluorine attacks the quartz envelope and is quickly 'trapped' as silicon tetrafluoride. When this occurs the fluorine can no longer take part in the fluorine regenerative cycle. In a commercial tungsten fluorine lamp the attack of fluorine on the fused quartz envelope must be prevented. This can be done in two possible ways: the internal fused quartz surface can be protected with a layer of a fluorine resistant material; or a different envelope material can be used. In this latter case it would be necessary either for the envelope material to be completely fluorine resistant or for any fluoride produced to be non-volatile so that a layer of fluoride produced on the envelope surface protects that surface from further fluorine attack.

In a patent¹¹⁹, Schröder has suggested the use of calcium fluoride or magnesium fluoride as protective coatings for the internal surface of the quartz envelope. However, these coatings do not appear to have been developed in a commercial lamp.

The tungsten fluorine incandescent lamp is now being developed by the Research Department, THORN LIGHTING LIMITED, Leicester.

CHAPTER 4. HALIDE FLUORIDES OF TUNGSTEN(VI).

4.1 Introduction to Hexavalent Transition Metal Mixed Halides.

Before the identification of a hexavalent transition metal mixed-halide, lower oxidation state transition metal mixed halides were well characterised. Examples of these lower oxidation state mixed halides are titanium chloride trifluoride (TiClF_3),¹³⁴ vanadium chloride trifluoride (VClF_3),¹³⁵ niobium tetrachloride fluoride (NbCl_4F),¹³⁶ tantalum tetrachloride fluoride (TaCl_4F)¹³⁷ and osmium iodide tetrafluoride (OsIF_4)¹³⁸.

The hexavalent transition metal mixed halide, tungsten chloride pentafluoride (WClF_5), was prepared by the exchange reaction between tungsten hexafluoride and titanium tetrachloride.¹³⁹

Since that time the complete range of tungsten(VI) chloride fluorides $\text{WCl}_n\text{F}_{6-n}$, have been prepared or identified^{7,140,141} and rhenium chloride pentafluoride has been prepared¹⁴².

Although the mixed chloride fluorides of molybdenum(V), MoCl_2F_3 ¹⁴³ and MoCl_4F ¹⁴⁴, have been prepared, no mixed chloride fluoride of molybdenum(VI) has been reported. The decisive factor must be the oxidising strength of the hexafluoride since the halogen exchange reactions of molybdenum hexafluoride are more numerous than those of tungsten hexafluoride but reduction of Mo(VI) always occurs⁷. For example, boron trichloride reacts with tungsten hexafluoride to form $\text{W}^{(\text{VI})}\text{Cl}_3\text{F}_3$ whereas the reaction of boron trichloride with molybdenum hexafluoride produces $\text{Mo}_2\text{Cl}_3\text{F}_6$.

Hexavalent transition metal bromide fluorides have proved more difficult to prepare than the chloride fluorides. Thermally unstable hexavalent ^(VI) Mo Br₄F₂ (cis and Trans) and other molybdenum(VI) bromide fluorides have been reported¹⁰⁶ in low yields in the preparation of the pentavalent solid ^(V) Mo BrF₄ from the reaction between molybdenum hexafluoride and molybdenum hexacarbonyl in the presence of bromine. There have been no other reports of hexavalent transition metal bromide fluorides.

Although it is difficult to prepare the hexavalent transition metal bromide fluorides, some of the corresponding Group VI non metal bromide fluorides are fairly easy to prepare. Tellurium bromide pentafluoride has been prepared by the action of fluorine on tellurium tetrabromide at 25°C¹⁴⁵. Sulphur bromide pentafluoride has been prepared by the bromination of disulphur decafluoride at 150°C¹⁴⁶ and by the action of bromine and bromine pentafluoride on sulphur tetrafluoride at 100°C¹⁴⁷.

4.2 Stability of Hexavalent Transition Metal Mixed Halides.

The hexavalent transition metal mixed halides are thermally unstable: tungsten chloride pentafluoride decomposes slowly at room temperature (24hr) but is stable for several weeks at -10°C¹⁴⁰, and rhenium chloride pentafluoride decomposes rapidly at room temperature and slowly even at -30°C.¹⁴²

4.3. Methods of Preparation of Hexavalent Transition Metal Mixed Halides.

Hexavalent chloride fluorides can be prepared by fluorination of an appropriate chloride or chlorination of an appropriate fluoride. All the known $MClF_5$ compounds except $SeClF_5$ have been prepared by the slow fluorination of a chloride: $SbClF_5$ from sulphur dichloride at $-10^\circ C$ ¹⁴⁸, $TeClF_5$ from $TeCl_4$ ¹⁴⁵, $WClF_5$ from WCl_6 ¹⁴⁰ and $ReClF_5$ from $ReCl_5$ ¹⁴². Selenium chloride pentafluoride has been prepared by chlorination of the salt $CsSeF_5$ with $ClSO_3F$ ¹⁴⁹. Tungsten chloride fluorides have been prepared from the hexafluoride by halogen exchange with titanium tetrachloride^{139,140}, boron trichloride⁷ or trimethyl chlorosilane (in the presence of anhydrous hydrogen chloride^{60,141}).

Tungsten chloride fluorides have now been prepared by the chlorination of tungsten pentafluoride (this thesis Section 4.5).

Some attempts have been made to prepare the bromide fluorides of tungsten (VI), (Section 4.6). Tungsten bromide pentafluoride has possibly been produced in the bromination of tungsten pentafluoride and in the bromofluorination of tungsten hexacarbonyl.

4.4. Identification of Hexavalent Transition Metal Mixed Halides by N.M.R. Spectroscopy.

In this work on mixed halides of the hexavalent transition metals, the technique of ^{19}F nuclear magnetic resonance spectroscopy (N.M.R.) has proved useful for the

identification of reaction products without the need for separation, The book of Emsley, Feeney and Sutcliffe¹⁵⁰ has been used in the identification of chemical shifts and coupling constants.

Experimental details of the N.M.R. Spectroscopy are given in Section 5.3,9.

4.5. Preparation of Tungsten(VI) Chloride Fluorides by the Chlorination of Tungsten Pentafluoride.

Tungsten pentafluoride was prepared as described in Section 5.2.3.

The previously dried apparatus (Figure 4.5.1) was assembled, evacuated and flamed out. After breaking the break seal (A), an excess of dry chlorine was distilled on to the tungsten pentafluoride in trap B (at -196°C).

Arcton (CFCl_3) from trap C was added to act as a solvent. The reaction mixture in trap B was held at -40°C for 7 hours and then at -78°C overnight. During this time a slow colour change occurred from yellow through deep red to brown. Chlorine was distilled from the reaction mixture at -96°C .

Some of the volatile products were distilled from trap B (at -50°C) into N.M.R. tube D (at -196°C). The N.M.R. tube was sealed off at X. The ^{19}F N.M.R. spectrum (at -30°C) of this more volatile fraction (a pale yellow solution) showed signals which were attributable to tungsten hexafluoride, tungsten chloride pentafluoride and arcton.

Trap B, containing the less volatile products, was sealed at Y. The liquid from this fraction was decanted into N.M.R. tube E.

N.M.R. tube E which was sealed off at Z. At -30°C this less volatile fraction was an orange solution (containing some orange/yellow solid) which gave a ^{19}F N.M.R. spectrum (Figure 4.5.2) showing signals attributable to tungsten hexafluoride, tungsten chloride pentafluoride and arcton and a very weak signal attributable to trans tungsten dichloride tetrafluoride.

FIGURE 4.5.1. - Apparatus for the Reaction Between Chlorine and Tungsten Pentafluoride.

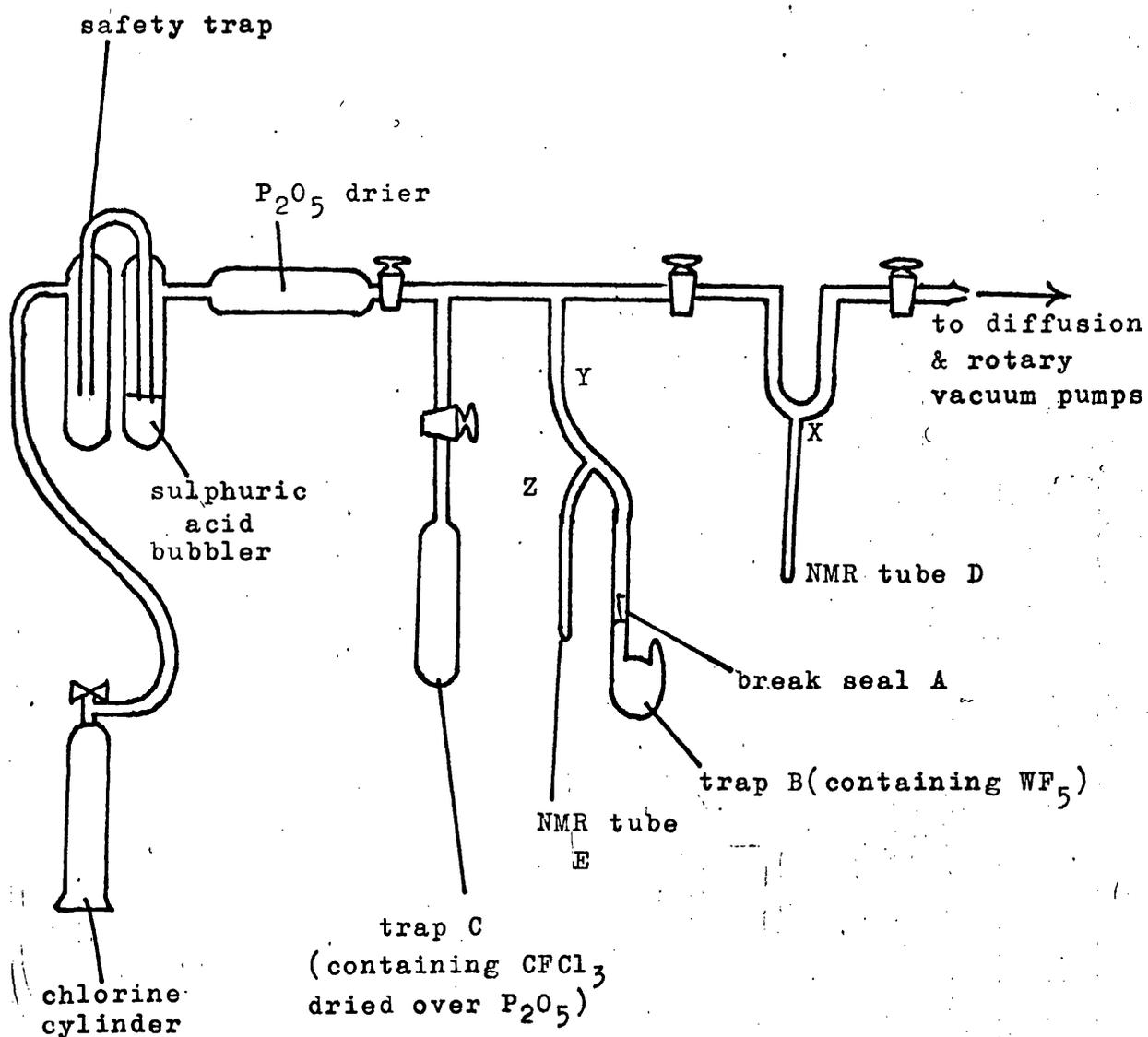
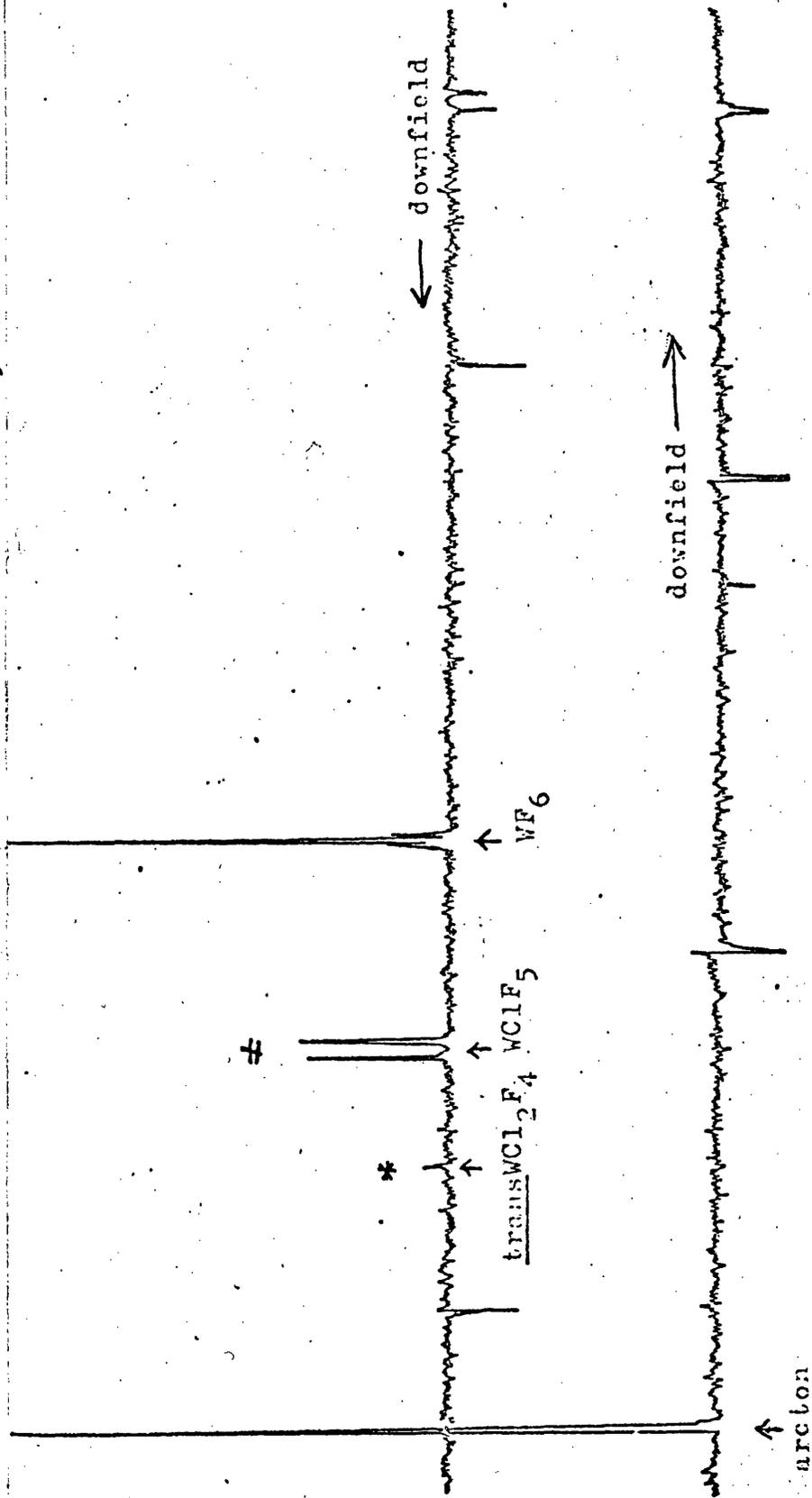


FIGURE 4.5.2. ^{19}F Spectrum of the Less Volatile Products of the Reaction between WF_5 & Cl_2 in Arcton



a doublet, with coupling constant 73cps, at 15.7ppm downfield from WF₆ attributable to WClF₅.

* a singlet at 24.4ppm downfield from WF₆ attributable to trans WCl₂F₄.

4.6. Attempted Preparations of Tungsten(VI) Bromide Fluorides.

4.6.1. By the Reaction between Bromine and Tungsten Pentafluoride.

Tungsten pentafluoride was prepared as described in Section 5.2.3. In this reaction it was used in a fairly impure form (contaminated with tungsten tetrafluoride).

Bromine was purified by several distillations and dried by standing over phosphorus pentoxide for one day.

The previously dried apparatus (Figure 4.6.1(a)) was assembled, evacuated and flamed out. After breaking break seal A, a small quantity of bromine was distilled on to the tungsten pentafluoride in trap B (at -196°C). Arcton was distilled into trap B to act as a solvent. The reaction mixture was held at -40°C for 12hr.

Some of the most volatile fraction was distilled from trap B (at -78°C) to the N.M.R. tube C (at -196°C). The N.M.R. tube was sealed off at X. The ^{19}F N.M.R. spectrum (at -20°C) of this volatile fraction (a pale yellow solution) showed signals which were attributable only to tungsten hexafluoride and arcton.

Trap B was sealed off at Y, the liquid decanted into N.M.R. tube D, and this N.M.R. tube sealed off at Z. At -20°C this less volatile fraction was a red/brown solution containing a brown/black solid. The ^{19}F N.M.R. spectrum of this fraction was recorded at -20°C (Figure 4.6.1(b)) and showed signals due to tungsten hexafluoride and arcton and a very weak doublet which might be attributable to the equatorial fluorine atoms in tungsten bromide pentafluoride.

This doublet occurred at ~ 18 ppm downfield from tungsten hexafluoride and had a coupling constant of ~ 67 cps.

FIGURE 4.6.1(a). Apparatus for the Reaction between Bromine and Tungsten Pentafluoride.

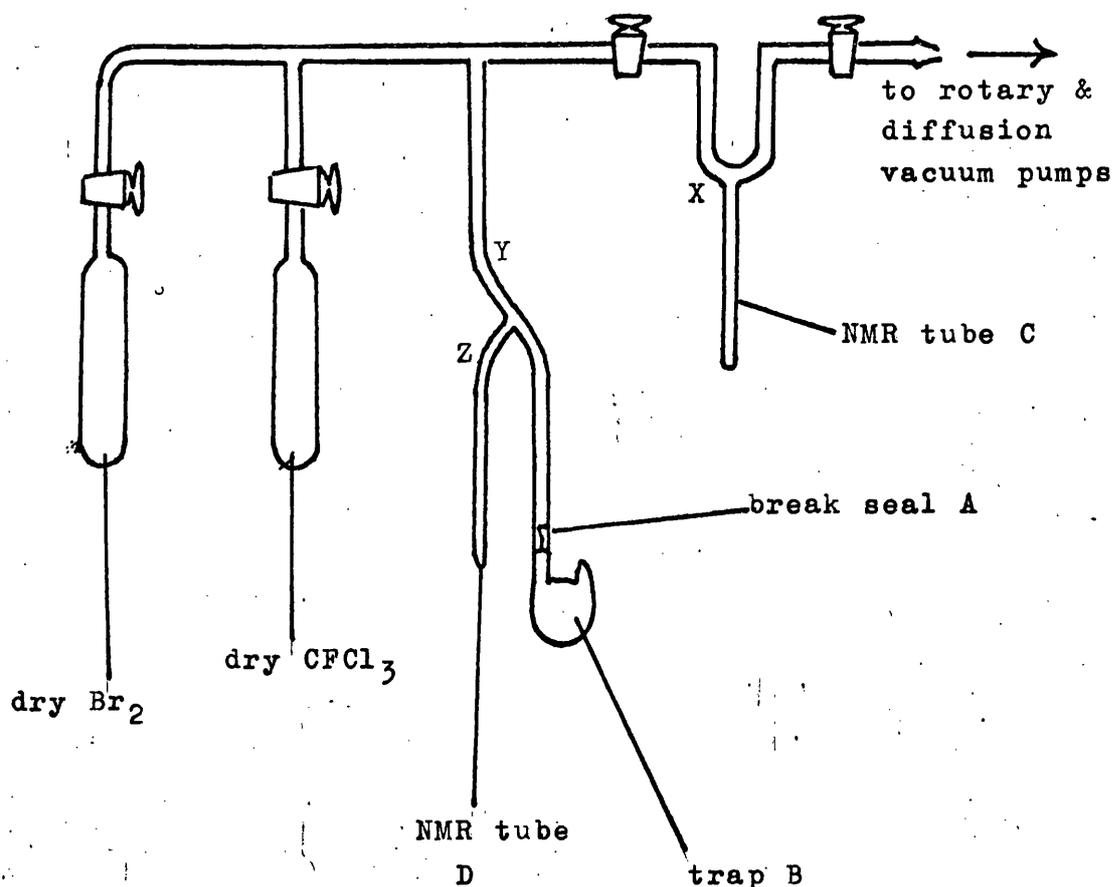
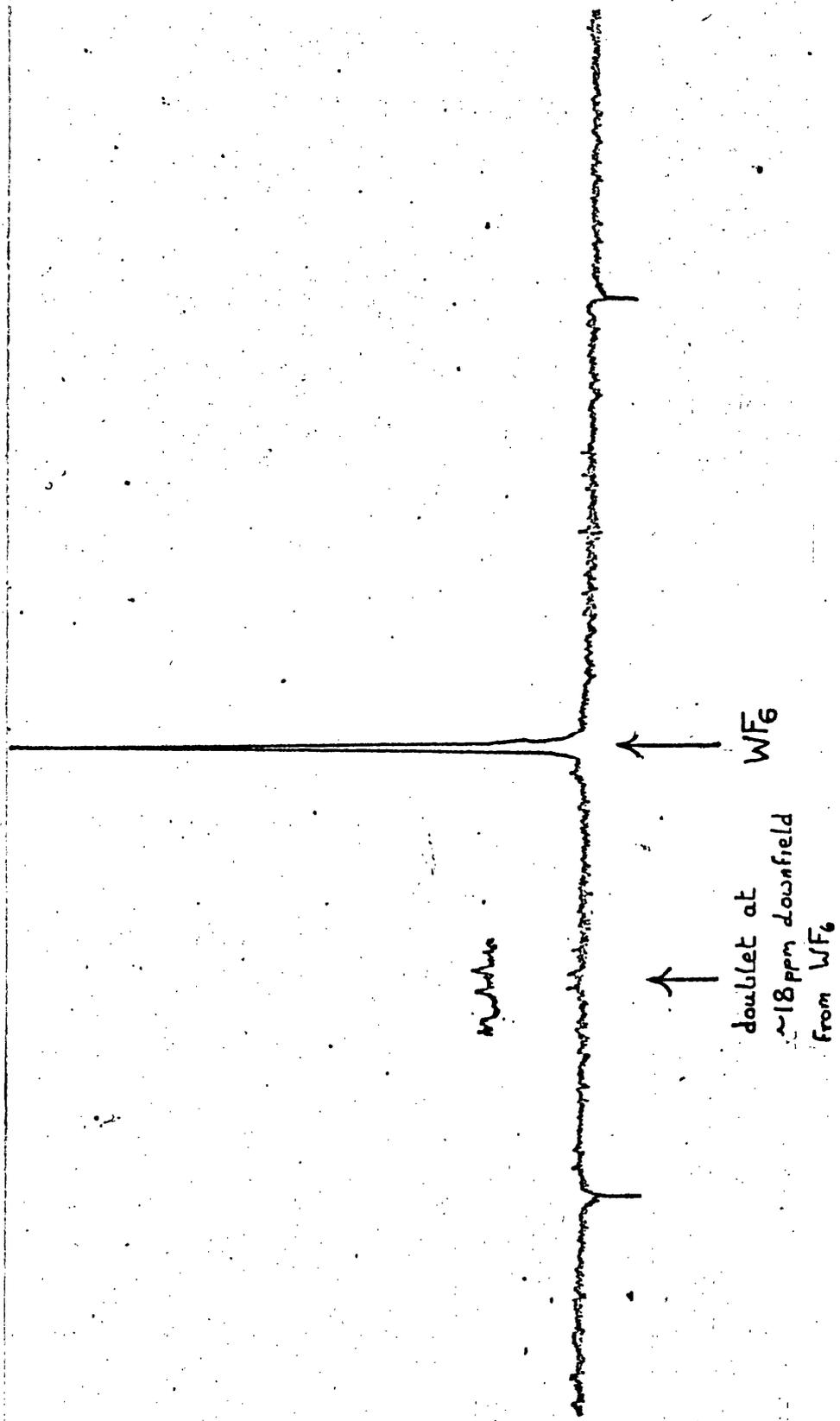


FIGURE 4.6.1(b). ^{19}F N.M.R. Spectrum of the Less Volatile Products of the Reaction between WF_5 and Br_2 .



4.6.2. By the Bromofluorination of Tungsten Hexacarbonyl.

Bromine was purified by several distillations, dried by standing over phosphorus pentoxide, and distilled into trap A. Tungsten hexacarbonyl (3g) was purified by sublimation before being introduced into the nickel reactor.

The previously dried apparatus (Figure 4.6.2(a)) was assembled on the standard fluorine generating system (Section 5.1.3). Dry nitrogen was passed overnight (through tap T₁). With tap T₁ closed and taps T₂ and T₃ open, fluorine (diluted with nitrogen) was passed through the apparatus at a rate of 7g/hr (the fluorine generator was set at 10A) for two hours. The fluorine passing through the bromine caused a mixture of the bromofluorides (including bromine and fluorine) to be passed over the tungsten hexacarbonyl. The tungsten hexacarbonyl was heated at regular intervals with a gas torch. Non volatile products were collected in trap B (at room temperature) and volatile products were collected in trap C (at -183°C)

With tap T₁ open, nitrogen was passed through the apparatus for several hours to expel fluorine from the system. The apparatus was connected to a vacuum system (at J) and evacuated back to tap T₃. Traps B and C were sealed off at X, Y and Z.

The volatile products in trap C were fractionally vacuum distilled through traps at -30°C, +78°C and -196°C (Figure 4.6.2(b)). Specimens from each trap were poured into the N.M.R. tubes and the ¹⁹F N.M.R. spectra were recorded.

The ^{19}F N.M.R. spectrum of the specimen from the -130°C trap (D) only showed a signal attributable to BrF_3 . The ^{19}F N.M.R. spectrum (at -15°C) of the specimen from the -196°C trap (F) showed signals attributable to WF_6 and BrF_5 (a doublet 28ppm upfield from WF_6 and a quintet 112ppm downfield from WF_6) - see Figure 4.6.2(c). However, the ^{19}F N.M.R. spectrum (at 0°C) of the specimen from the -78°C trap (E) (see Figure 4.6.2(d)) showed signals due to BrF_5 (as above) and BrF_3 (a broad signal 168ppm upfield from the BrF_5 doublet) and an unidentified doublet (6ppm downfield from the BrF_5 doublet or 22ppm upfield from WF_6) which might be attributable to the four equivalent fluorine atoms in WF_5Br . This doublet, with a coupling constant, ($J_{\text{F-F}}$), of 86cps showed further splitting which could be due to ^{183}W - ^{19}F coupling.

FIGURE 4.6.2(a) - Apparatus for the Bromofluorination of Tungsten Hexacarbonyl.

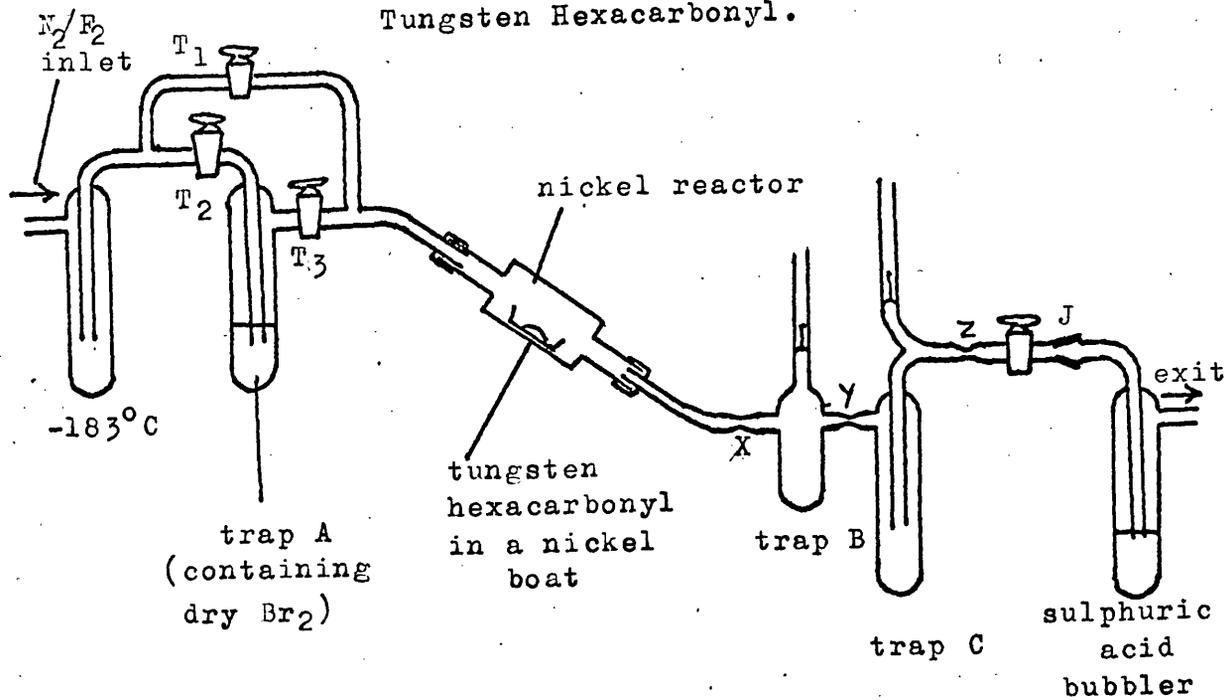


FIGURE 4.6.2(b) - Vacuum Distillation Apparatus.

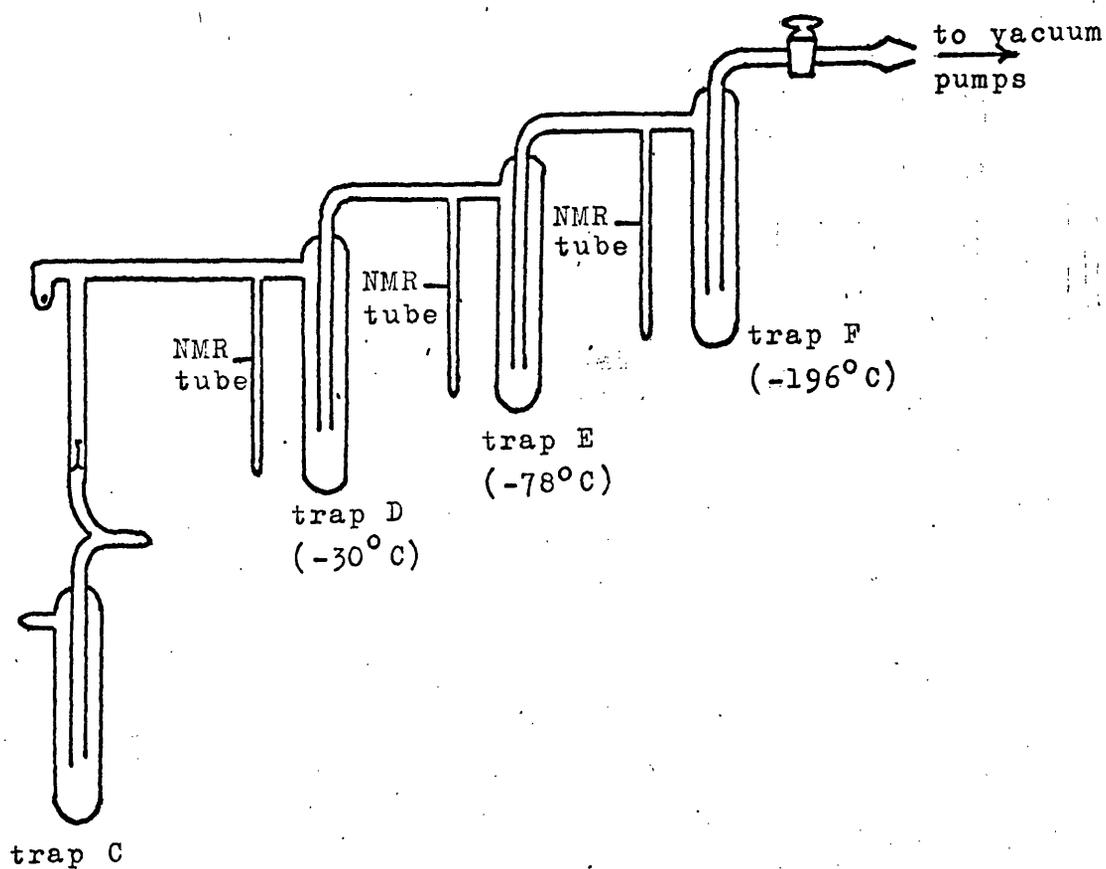


FIGURE 4.6.2(c) - ^{19}F N.M.R. Spectrum from Trap F.

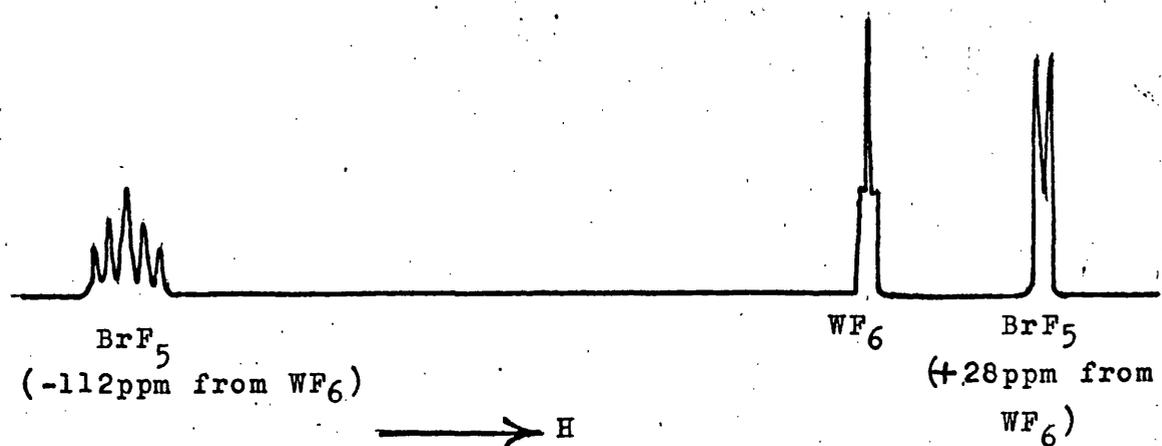
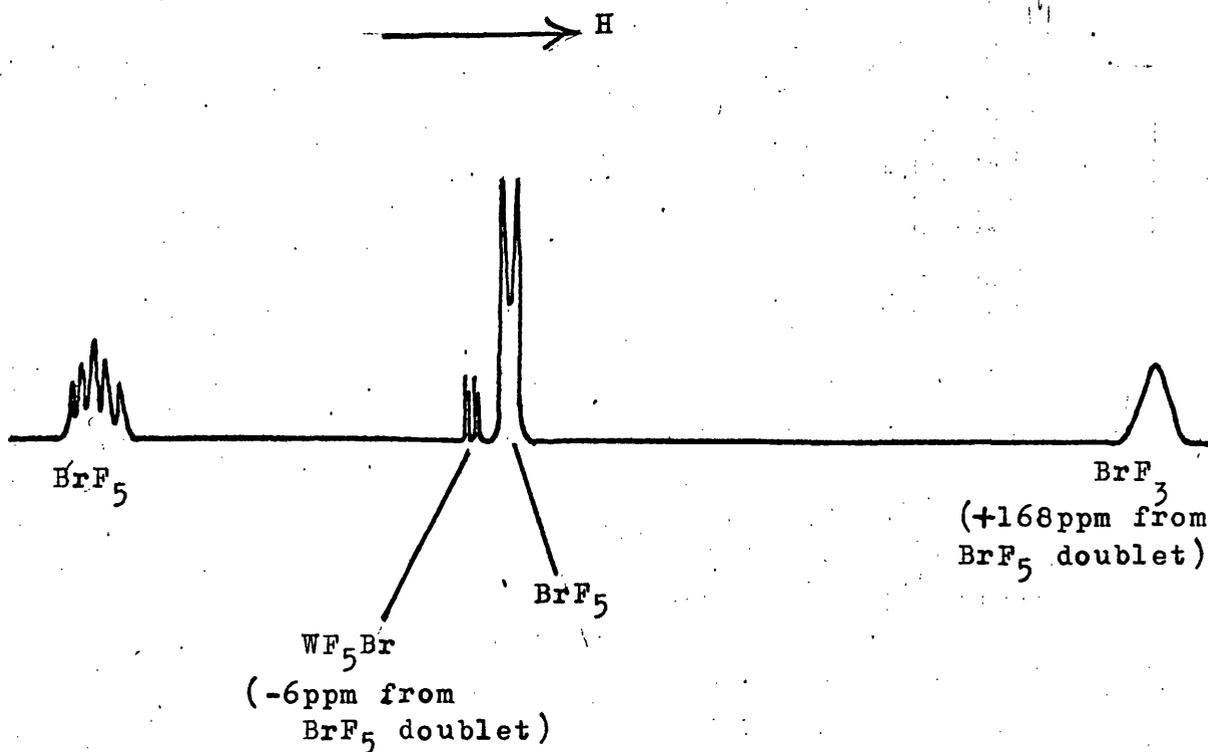


FIGURE 4.6.2(d) - ^{19}F N.M.R. Spectrum from Trap E.



4.6.3. Unsuccessful Attempted Preparations of Bromide Fluorides of Tungsten(VI).

Several other possible methods of preparation of tungsten(VI) bromide fluorides were attempted but all proved to be completely unsuccessful. The reaction between tungsten hexafluoride and boron tribromide (both in the absence and in the presence of free bromine) produced only solid tungsten bromides even in the presence of excess tungsten hexafluoride. The reaction between tungsten hexafluoride, tungsten hexacarbonyl and bromine was also not successful in the production of tungsten(VI) bromide fluorides.

4.7. A Discussion on the Formation of Tungsten(VI) Bromide Pentafluoride.

4.7.1. The Conflicting Evidence.

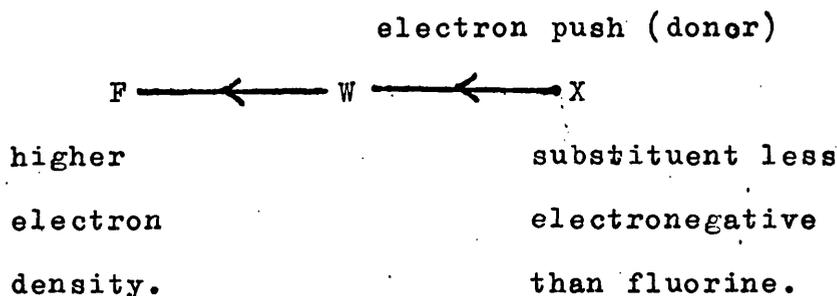
The experiments (Section 4.6) have shown two possible methods of preparation of tungsten bromide pentafluoride. In both cases ^{19}F N.M.R. evidence was used to suggest the presence of WF_5Br in the product. However, the ^{19}F N.M.R. evidence from the reactions is conflicting. The products of the reaction between bromine and tungsten pentafluoride show a very weak ^{19}F N.M.R. doublet at 18ppm downfield from tungsten hexafluoride, whereas, the products of the bromo-fluorination of tungsten hexacarbonyl show a ^{19}F N.M.R. doublet at 22ppm upfield from tungsten hexafluoride. Each doublet was originally assigned to the four equivalent fluorine atoms in WF_5Br . Clearly both doublets cannot be assigned to these atoms.

4.7.2. Possible Prediction of Chemical Shifts in Tungsten(VI) bromide pentafluoride.

^{19}F N.M.R. chemical shifts are, like all N.M.R. chemical shifts, dependent on the shielding of the nucleus by the surrounding electrons i.e. on the electron density around the nucleus.

In a simple treatment of a mono substituted tungsten(VI) fluoride the chemical shift is dependent on the electronegativity of the substituted group (X). Decreasing the electronegativity of this group causes an increase in the electron density around the fluorine atoms (an increase in shielding) and, therefore, an upfield chemical shift (Figure 4.7.2).

FIGURE 4.7.2. - Shielding Mechanisms



This upfield chemical shift is observed in the compound MeOWF_5 whose ^{19}F chemical shifts are 47 and 76ppm upfield with respect to tungsten hexafluoride¹⁵¹.

Using this argument the chemical shifts in WF_5Br would be upfield with respect to WF_6 since bromine is less electronegative than fluorine. However, the ^{19}F N.M.R. spectrum of WF_5Cl ,^{140,141} which contains a doublet at 16ppm downfield from WF_6 due to the four equivalent fluorine atoms and a quintet at 39ppm upfield from WF_6 due to the remaining

fluorine atom, cannot be explained in terms of the electro-negativity of chlorine. In fact the factors contributing to ^{19}F chemical shifts are complex, so that a prediction of the chemical shifts in tungsten bromide pentafluoride is not possible.

4.7.3. Assignment of the Conflicting N.M.R. Data.

It is now suggested that the ^{19}F N.M.R. doublet observed at 22ppm upfield from tungsten hexafluoride should be assigned to the four equivalent fluorine atoms in WF_5Br . The reasons for this are:

- (1) This signal is a well characterised doublet showing further coupling (^{183}W - ^{19}F coupling) whereas the signal at 18 ppm downfield from WF_6 is very weak (hardly more than noise) and no fine structure can be observed.
- (2) The reaction between bromine and tungsten pentafluoride was carried out in the presence of arcton (CFCl_3) and it is possible that an exchange reaction might have led to the formation of WF_5Cl . This would explain a weak doublet at ~ 18 ppm downfield from WF_6 (WF_5Cl produces a doublet at 16 ± 5 ppm downfield from WF_6 ¹⁴¹).

The suggestions imply that the bromofluorination of tungsten hexacarbonyl (Section 4.6.2) produces some tungsten bromide pentafluoride, whereas the reaction between bromine and tungsten pentafluoride (Section 4.6.1) does not.

4.8 Conclusions and Suggestions for Future Work.

The evidence suggests that tungsten bromide pentafluoride is produced, together with tungsten hexafluoride and some non volatile tungsten bromides, in the bromofluorination of tungsten hexacarbonyl. Therefore, this preliminary preparative work shows the possibility of production of the series of tungsten(VI) bromide fluorides. Further work is necessary. A further study of the bromofluorination of tungsten hexacarbonyl might prove fruitful.

A comparison of the reactions of tungsten pentafluoride with chlorine (giving WF_6 , WF_5Cl and WF_4Cl_2) and with bromine (giving WF_6 with no other definite product) suggests that the bromide fluorides of tungsten(VI) are even less stable than the corresponding chloride fluorides. Therefore, special care must be taken in future preparative work to ensure that any tungsten bromide fluorides are not inadvertently decomposed.

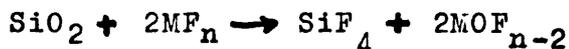
CHAPTER 5. EXPERIMENTAL METHODS.

5.1 Reaction Procedures

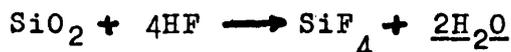
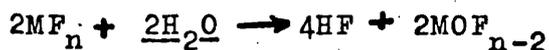
5.1.1 Introduction.

The halides which have been considered in this work are extremely moisture sensitive and have required special care in preparation and handling.

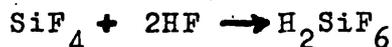
Fluorides (the most reactive halides) attack glass by reactions of the type



In the presence of traces of moisture, the hydrolysis leads to a chain decomposition reaction thus



which has chain terminating steps thus



However, it has been possible to use pyrex[†] glass apparatus for handling the fluorides at temperatures below 200°C provided that the glass was adequately dried.

5.1.2 General Handling Technique.

The halides have been handled in vacuum, dry gas flow and dry box systems.

(a) Vacuum systems

Glass vacuum systems have been widely used. The vacuum,

Footnote †

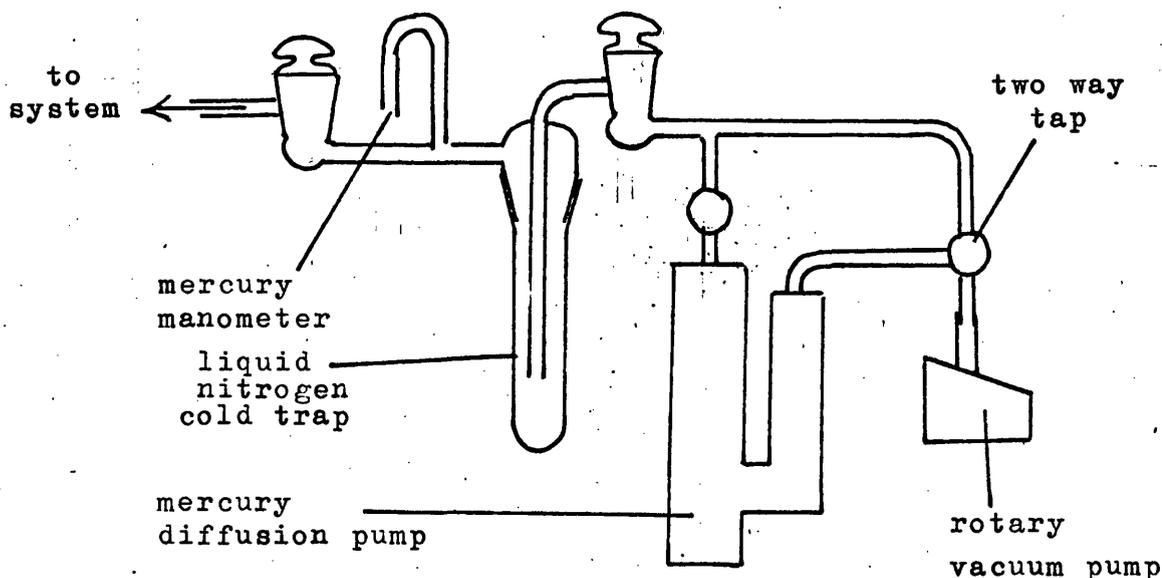
'Pyrex' is a tradename. A typical composition of pyrex glass is 75.5% SiO₂, 17% B₂O₃, 2% Al₂O₃, 4% Na₂O & 1.5% K₂O

with pressures down to 10^{-3} torr, was obtained by the use of a 'Genevac' rotary pump and a mercury diffusion pump.

Where possible on the glass vacuum system, joining was achieved by glass blowing. 'Quickfit' type taps and joints were used but were kept to a minimum, particularly in the vicinity of the reaction. The 'Quickfit' taps and joints were greased with Edwardshigh vacuum grease or Apiezon L grease except in the vicinity of the reaction where Kel F 90* grease was used.

Before use, all glass vacuum systems were dried by flaming under high vacuum. The design of a reaction system was varied to suit the particular preparation but the pumping arrangement was not altered (Figure 5.1.2(a)).

FIGURE 5.1.2(a). Vacuum Pumping Arrangement for Vacuum Reaction Systems.



Footnote. *

Tradename. A polymeric grease $(Cl(CF_2-CFCl)_x Cl_2)$ which is unreactive.

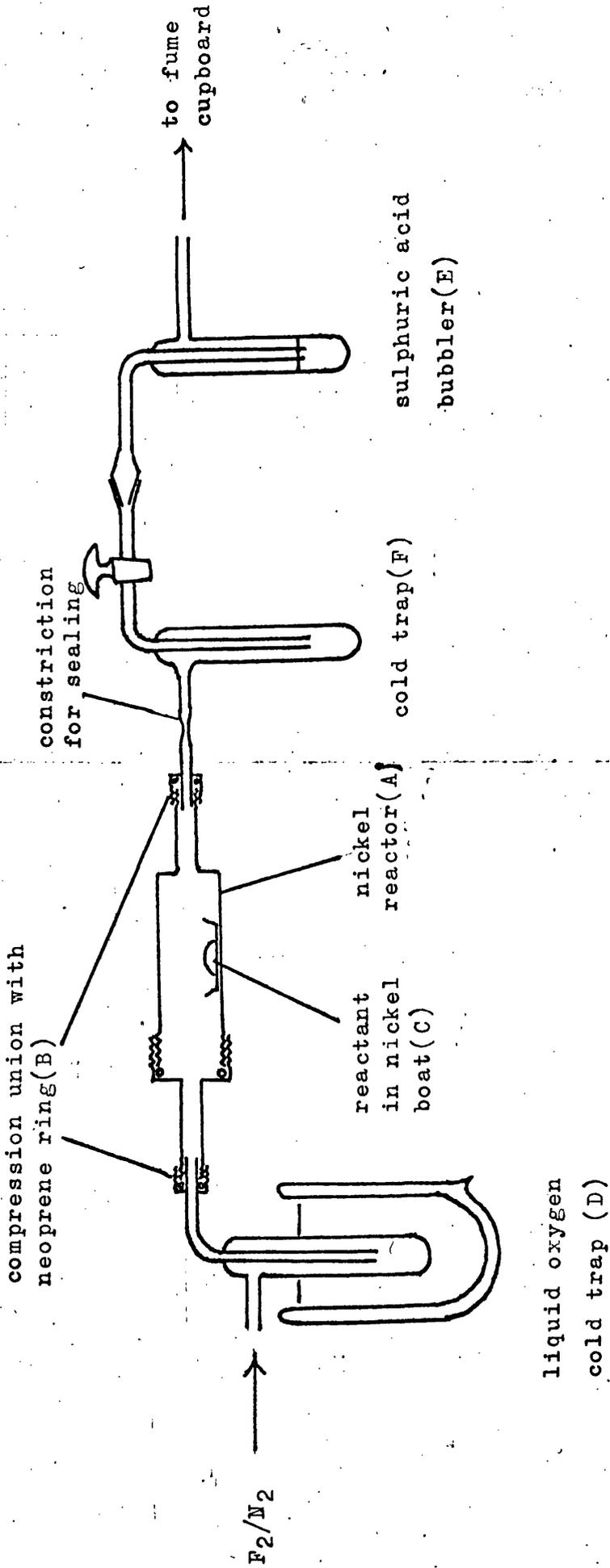
(b) Gas Flow Systems.

The major gas flow system which has been used is the fluorine/nitrogen gas flow system particularly for the fluorination of metals.

A mixture of pure dry fluorine (see Section 5.1.3) and nitrogen was passed over the usually heated metal. A typical reaction apparatus is shown in Figure 5.1.2(b). Since the reaction temperature often exceeded 200°C (either by external heating or because the reaction was exothermic) it was necessary to use a nickel reactor (A). The remainder of the apparatus was usually 'pyrex' glass. Air tight seals were obtained between the reactor and the glass by means of compression unions and neoprene rings (B). For ease of installation, a nickel boat (C) was used to contain the reactant metal. It was usual to further dry the gas mixture before reaction by passing through a liquid oxygen cold trap (D) (at -183°C). Liquid nitrogen (B.Pt. -196°C) cannot be used because it would condense out liquid fluorine (B.Pt. -187°C). The sulphuric acid bubbler (E) at the end of the flow apparatus prevented moisture entering the apparatus.

The products of fluorination were condensed in cold traps (F), the nature of which was dependent on the particular fluorination.

FIGURE 5.1.2(b). A Fluorine/Nitrogen Gas Flow System.



(c) Dry Box Systems.

Involatile halides were handled in an automatically recirculating dry, oxygen free, Lintott Mark 11 glove box, using standard dry box procedure. The moisture and oxygen were continuously removed from the glove box by molecular sieve (type Lindé No. 5) and heated (250°C) manganous oxide respectively. The regeneration of both agents could be carried out regularly in situ. The entry/exit chamber was connected to a vacuum pump and the recirculating gas supply so that moisture could be excluded when introducing apparatus into the dry box. In addition all apparatus was dried before introduction into the dry box and operations in the dry box were carried out as quickly as possible.

5.1.3 Use of the Fluorine Generating Cell.

Reactions involving fluorine gas were carried out using a standard medium temperature fluorine generator (Figure 5.1.3(a)) supplied by Imperial Chemical Industries Ltd, Mond Division. The standard operating and servicing instructions were followed.

The fluorine produced was freed from hydrogen fluoride by passage through a copper trap containing anhydrous sodium fluoride. The last traces of hydrogen fluoride were removed in a liquid oxygen trap incorporated in the reaction apparatus.

The permanent system (Figure 5.1.3(b)) was constructed of copper. The leads of $\frac{1}{4}$ " copper tubing were connected to the glass reaction apparatus using compression unions and neoprene rings.

The whole apparatus was enclosed in a fume cupboard.

FIGURE 5.1.3(a) Fluorine Generating Electrolytic Cell.
(diagrammatic)

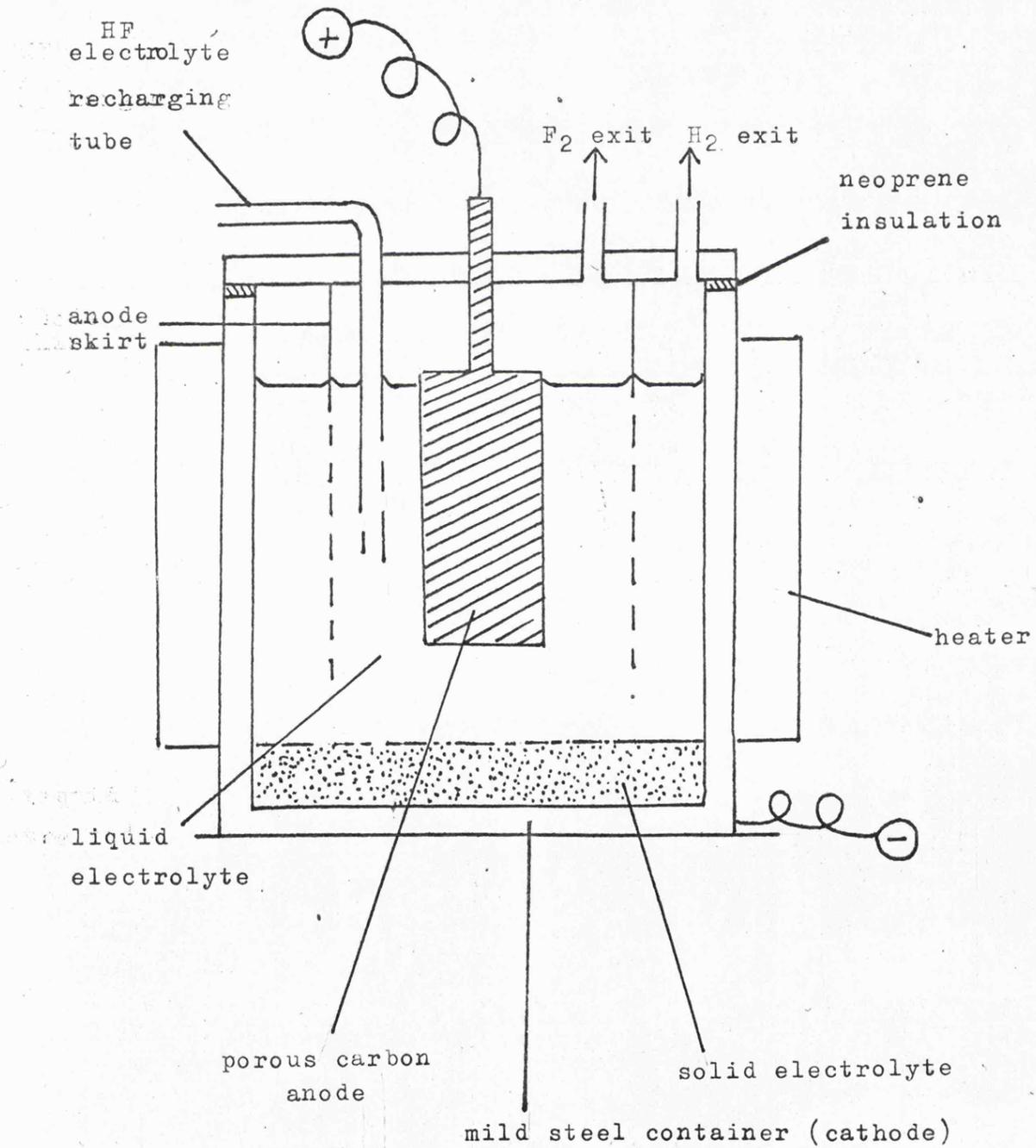
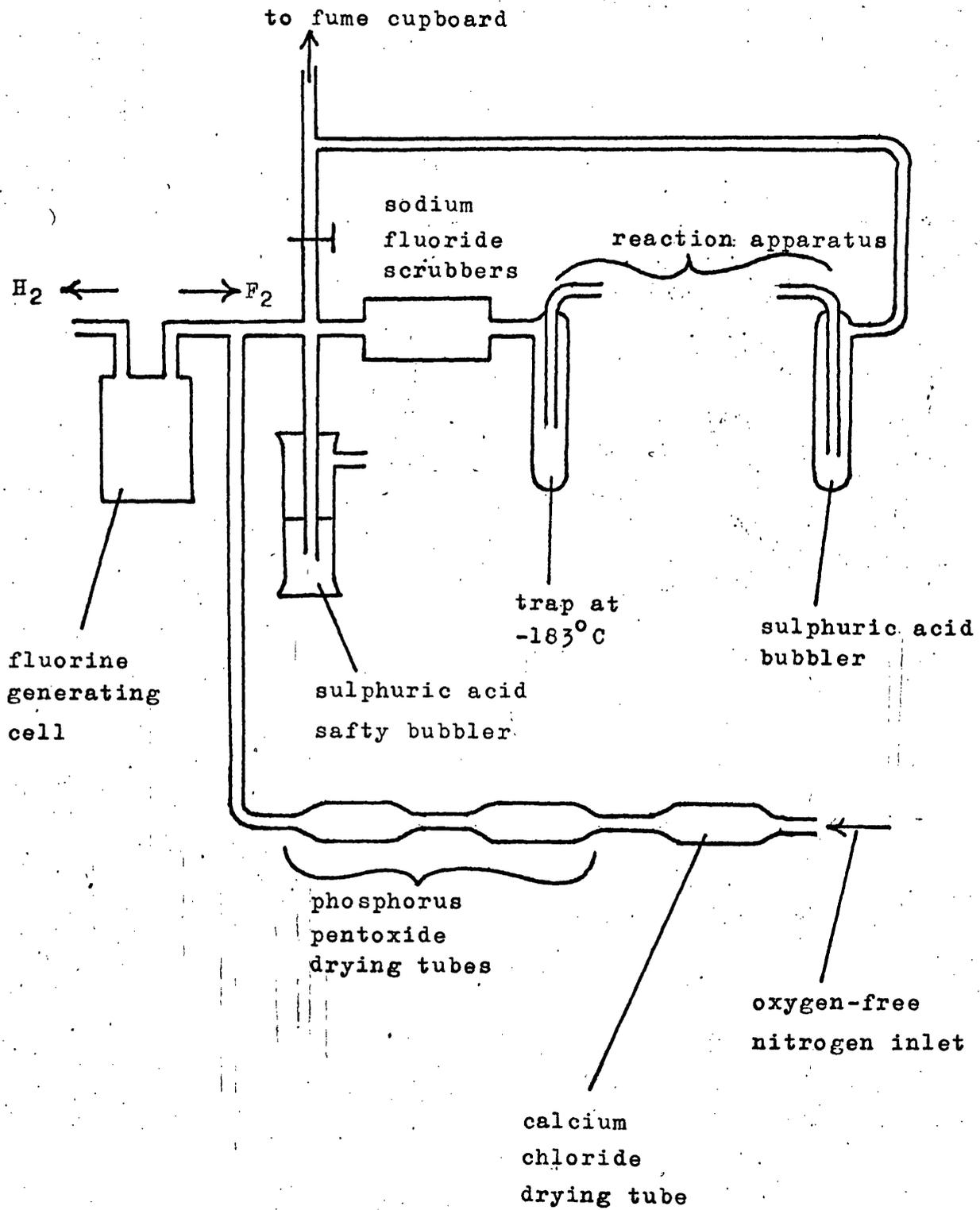


FIGURE 5.1.3(b) Fluorine Generating and Purification System.



5.2. Preparations.

5.2.1. Preparation of Volatile Transition Metal Hexafluorides.

The volatile transition metal hexafluorides WF_6 , MoF_6 , ReF_6 and OsF_6 were all prepared by the same general method of fluorinating the metal⁹.

Immediately before each preparation any oxide impurities were removed from the metal ^{by} heating the metal to dull red heat in a stream of hydrogen for $1\frac{1}{2}$ hours and allowing it to cool in the hydrogen stream. (see Figure 5.2.1(a).)

The previously dried apparatus (Figure 5.2.1(b).) was assembled on the standard fluorine generating system (Section 5.1.3). Trap B contained anhydrous sodium fluoride over which the hexafluorides are generally stored. Trap A was cooled in liquid oxygen ($-183^\circ C$) and dry oxygen free nitrogen was passed through the apparatus overnight.

The fluorine generator was switched on and the current slowly increased to 20A (giving 15g fluorine per hour). A mixture of fluorine and nitrogen was passed slowly through the system. Trap B was cooled with liquid oxygen. The reaction was initiated and maintained at various times through the reaction by externally heating the nickel reactor. The volatile hexafluoride condensed in Trap B. When the reaction was complete (i.e. after allowing sufficient time for the passage of $1\frac{1}{2}$ times the required amount of fluorine plus one extra hour) the fluorine generator was turned off. The apparatus was then purged with dry nitrogen for 1 to 2 hours. With the nitrogen off and tap T closed the apparatus

FIGURE 5.2.1(a) - Reduction of Oxide Impurities in Metal Reactants.

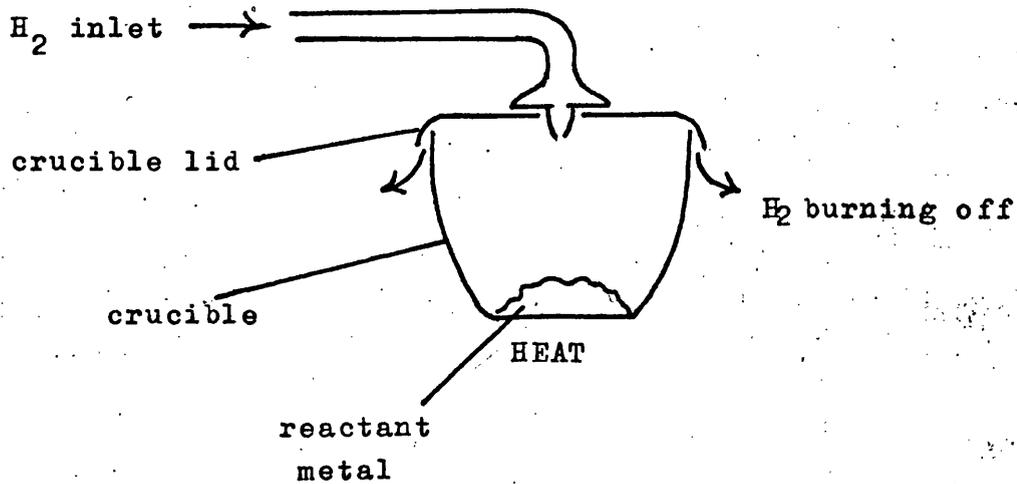


FIGURE 5.2.1(b) - Apparatus for the Preparation of Volatile Hexafluorides.

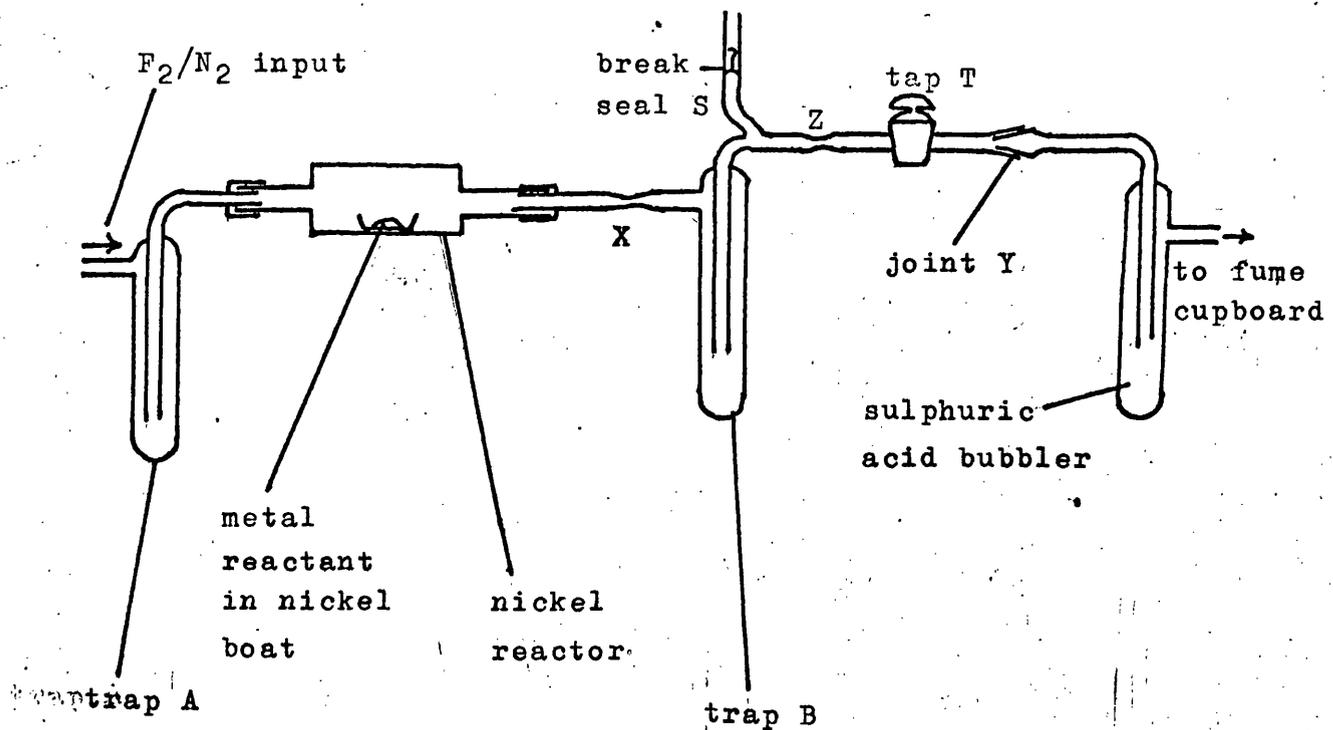
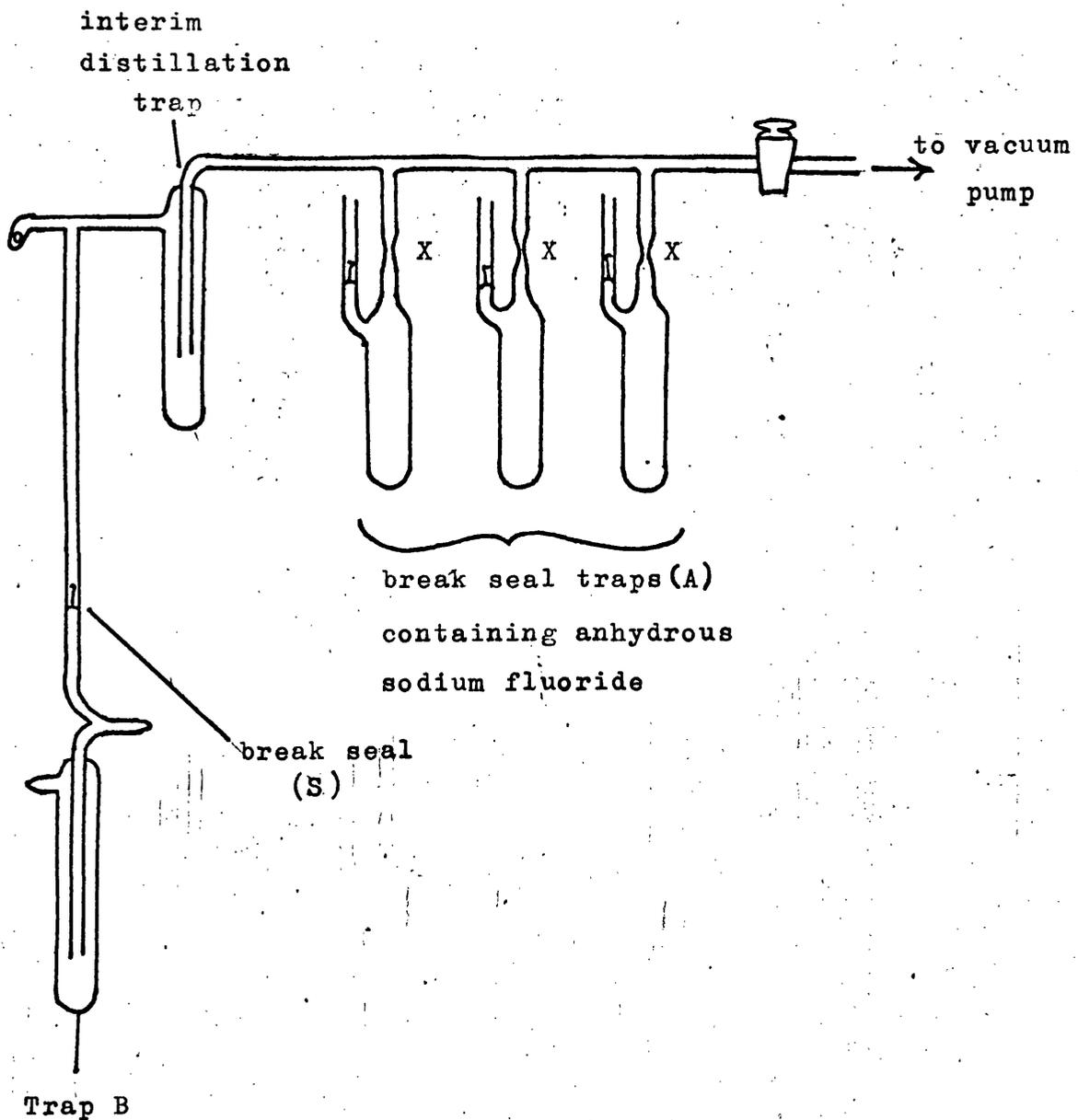


FIGURE 5.2.1(c) - Apparatus for the redistillation of the Volatile Hexafluorides.



was sealed off at X. Joint Y was connected to a vacuum system and the apparatus sealed at Z.

Using a standard, previously dried, vacuum apparatus (Figure 5.2.1(c).) the hexafluoride was purified by distillation into break seal traps (A) containing anhydrous sodium fluoride. Each trap was pumped at -78°C for a few minutes (to remove any silicon tetrafluoride) before being sealed at X and stored (at -30°C) ready for use.

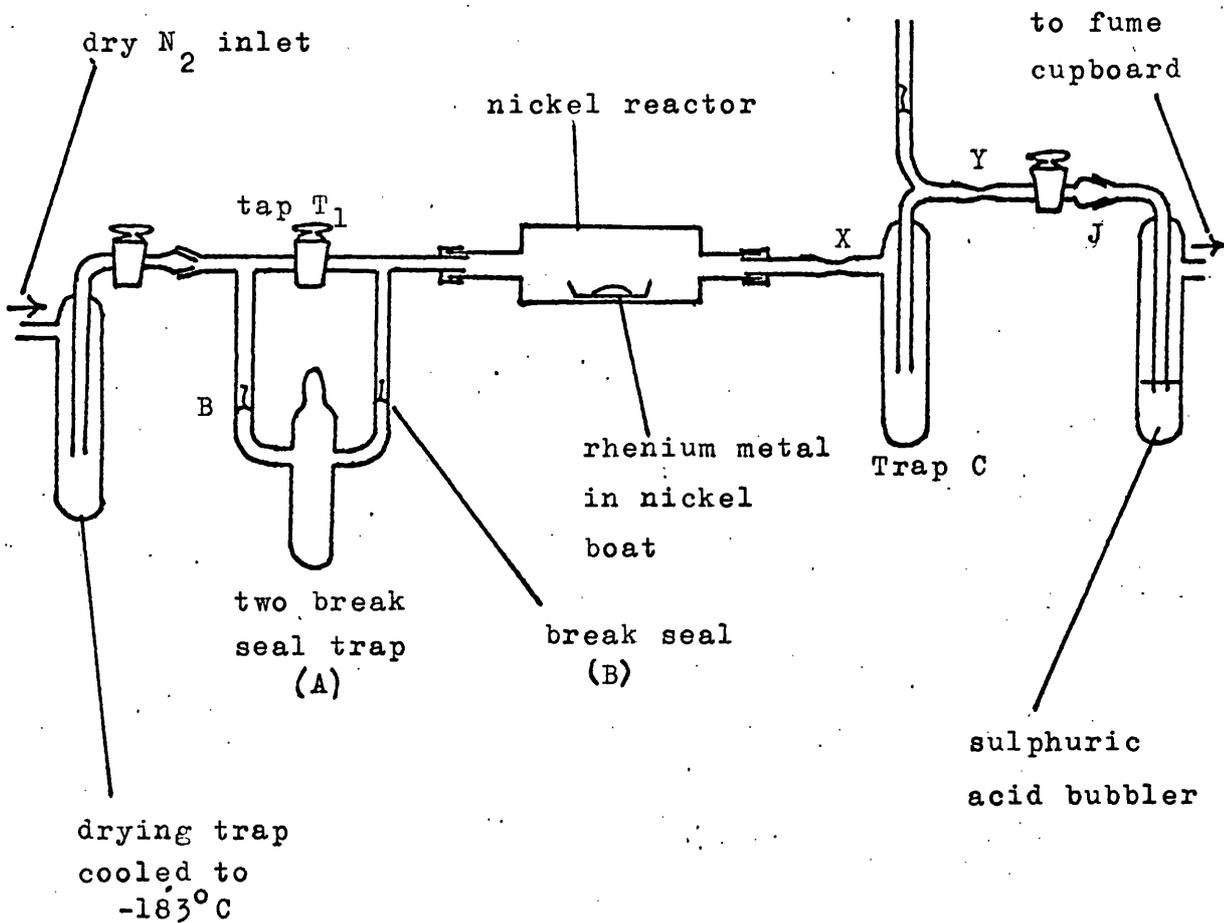
5.2.2 Further Purification of Rhenium Hexafluoride.

Rhenium hexafluoride prepared by this method (previous section) was contaminated with rhenium heptafluoride¹⁸. The impure hexafluoride was purified by passing over heated rhenium metal (from which oxide impurities had just been removed) in a stream of dry nitrogen.

The $\text{ReF}_6/\text{ReF}_7$ mixture was distilled into a special two break seal trap(A), which was then built into the purification apparatus. (Figure 5.2.2). Dry nitrogen was passed through the apparatus overnight. After flaming out the apparatus, the break seals (B) were broken, tap T_1 was closed and the $\text{ReF}_6/\text{ReF}_7$ was swept over the heated rhenium, with a slow stream of dry nitrogen, into trap C which was cooled with liquid oxygen. On completion of the purification, trap C was sealed at X, connected to a vacuum line (at joint J), pumped out for a few minutes at -78°C and sealed off at Y. The hexafluoride in trap C was then ready for purification by vacuum distillation (see previous Section) and storage over anhydrous sodium fluoride in pyrex break seal vessels at -30°C .

As well as reducing ReF_7 to ReF_6 , this purification procedure also reduces any volatile ReOF_5 impurity to the less volatile ReOF_4 . The ReOF_4 was then separated in the subsequent distillation.

FIGURE 5.2.2. - Apparatus for the Purification of Rhenium Hexafluoride.



5.2.3 Preparation and Purification of Tungsten Pentafluoride.

Tungsten pentafluoride was prepared from tungsten hexafluoride and heated tungsten wires using the method of Schröder and Grewe⁶.

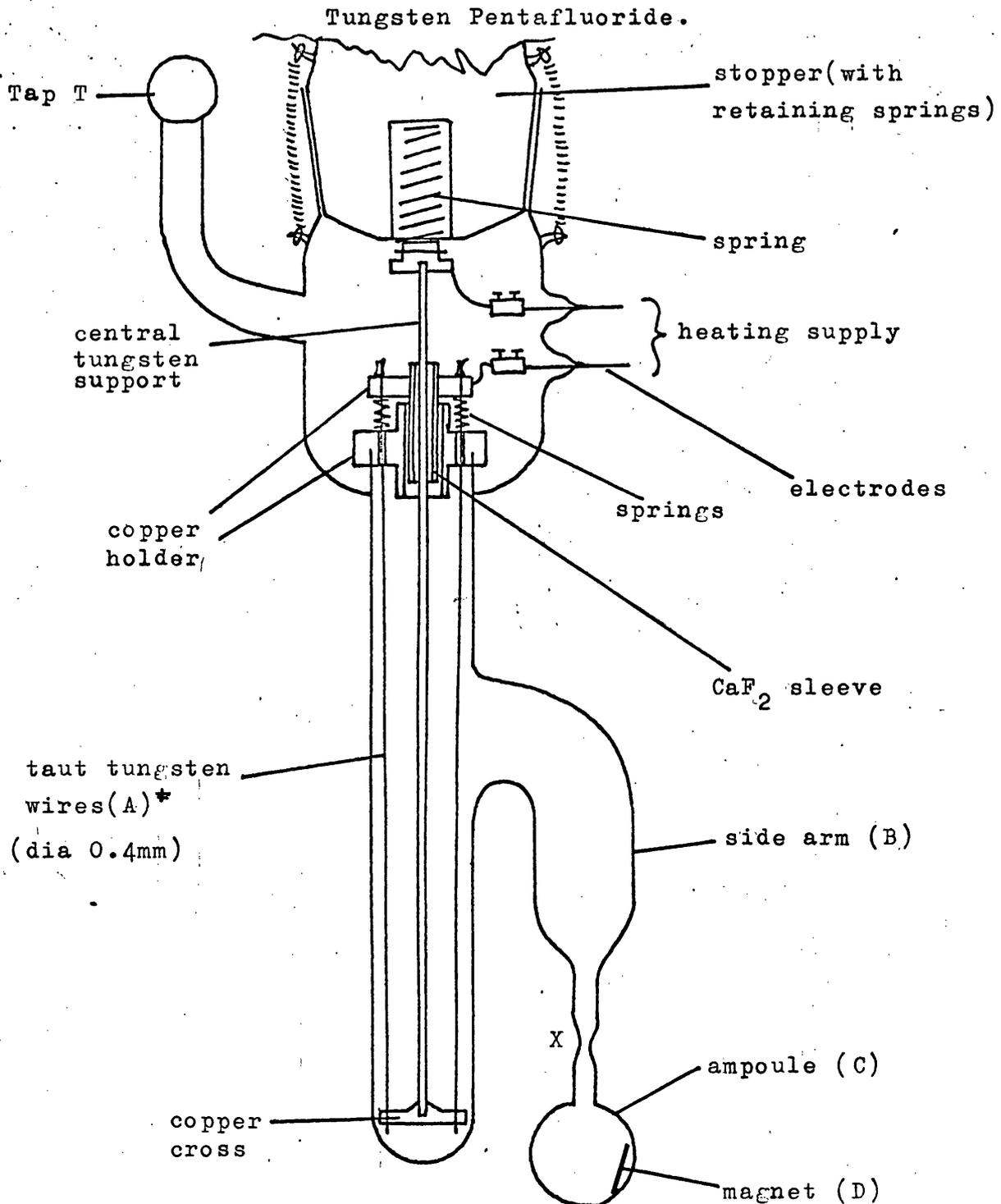
The special quartz apparatus (supplied by Dr Schröder) was set up as shown in Figures 5.2.3(a) and (b), evacuated, flamed out and the tungsten wires briefly brought to red heat. The apparatus was filled with between 250 and 400 torr of tungsten hexafluoride and tap T closed. A large Dewar vessel containing cooling liquid (at -60°C) was brought up to the electrodes. The wires (A) were heated by passing an AC current of $\sim 15-17\text{A}$ at 2.6 Volt. The wires were only allowed to reach a dull red glow. As the reaction proceeded and the wires became hotter the heating voltage was reduced. The cooling bath was maintained at -55 to -65°C throughout the reaction. Tungsten pentafluoride was condensed on the cold walls of the reaction vessel.

The end of the synthesis (usually after about 7 hour) was determined either by the consumption of the hexafluoride or by the burning through of the wires.

After switching off the heater current and removing the vessel large Dewar, the side arm (B) of the apparatus was cooled to -196°C . The tungsten pentafluoride was then sublimed into the side arm. This purified tungsten pentafluoride was scraped into the ampoule (C) with the magnet (D), the excess of

tungsten hexafluoride was pumped away and the ampoule was sealed off (after cleaning the sealing off point) at X.

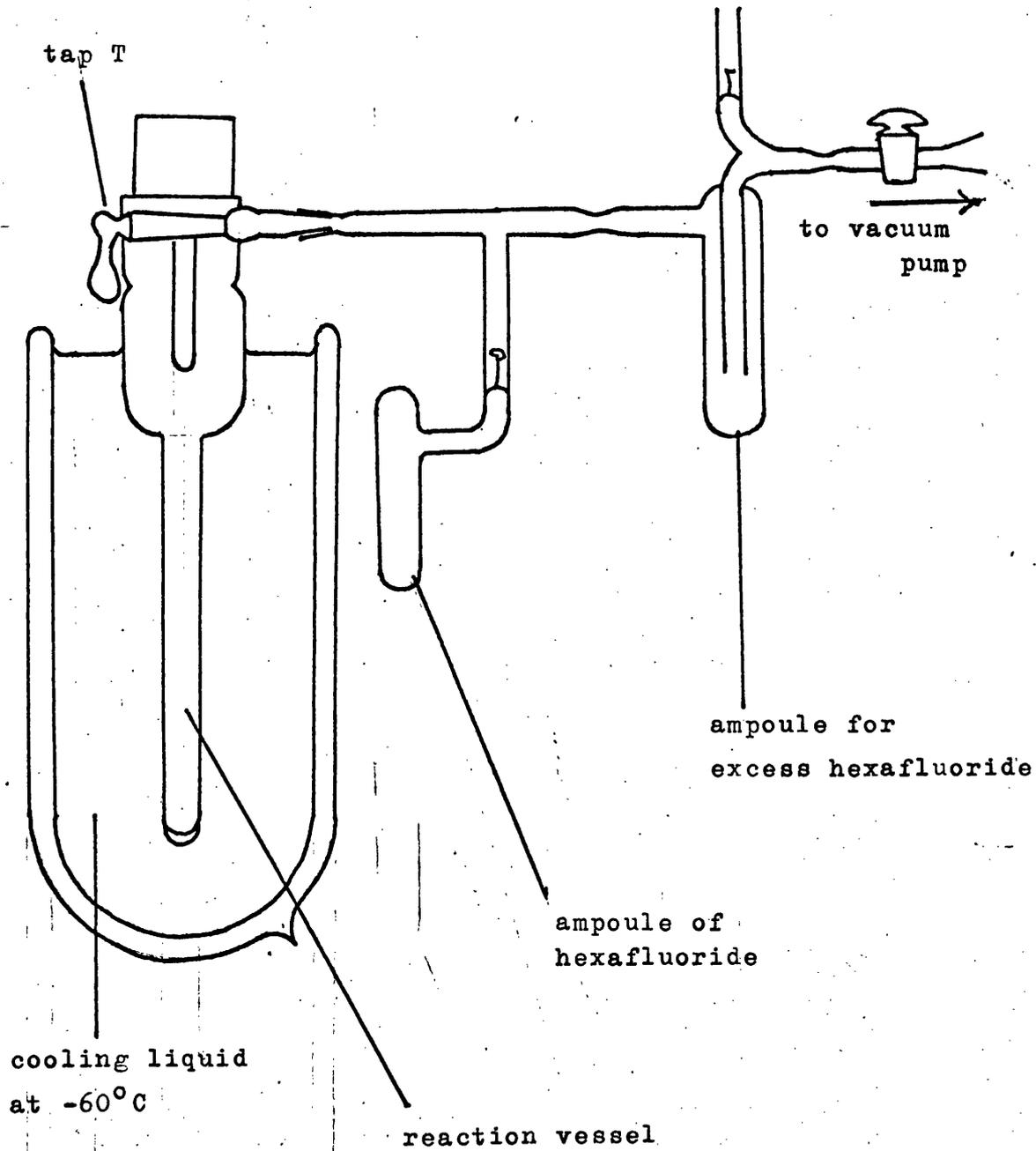
FIGURE 5.2.3(a) - Apparatus for the Preparation of



Footnote †

For modification in Section 2.5.4(b): these are replaced by molybdenum wires in the preparation of molybdenum pentafluoride.

FIGURE 5.2.3(b) - Vacuum System for the Preparation of Tungsten Pentafluoride.



5.2.4 Preparation and Purification of Molybdenum Pentafluoride.

Molybdenum pentafluoride was first prepared by the reaction of elementary fluorine with molybdenum hexacarbonyl at -75°C ¹⁵². It has since been prepared by the reduction of the hexafluoride with molybdenum carbonyl or tungsten carbonyl at 25°C ¹⁵³, by the reduction of the hexafluoride with molybdenum powder at $300-400^{\circ}\text{C}$ ¹⁵³, and by the reaction of dilute fluorine with molybdenum powder at 400°C ¹⁵³. The reduction of the hexafluoride with molybdenum powder has been used as the standard method of preparation of molybdenum pentafluoride in this thesis. Another method of preparation of molybdenum pentafluoride, involving the reduction of molybdenum hexafluoride by heated molybdenum wires, has been developed.

(a) Standard Method of Preparation of Molybdenum Pentafluoride.

Molybdenum pentafluoride was prepared by the reduction of the hexafluoride with molybdenum powder at $300-400^{\circ}\text{C}$.

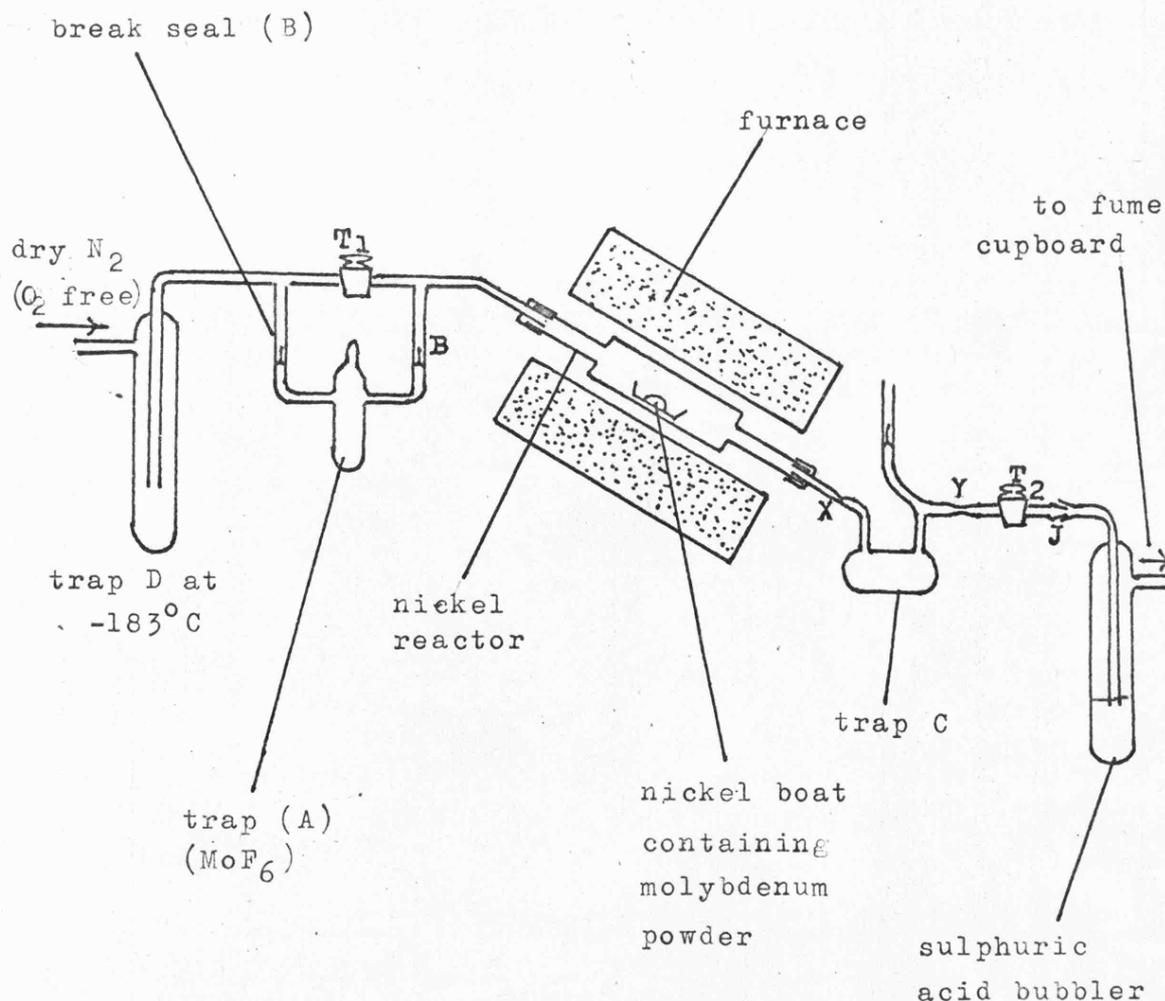
Immediately before the preparation, any oxide impurities were removed from the molybdenum powder by heating the metal at dull red heat in a stream of hydrogen for $1\frac{1}{2}$ hr and allowing to cool in the hydrogen stream (see Section 5.2.1). Using the molybdenum hexafluoride in a special 'two break-seal' trap (A), the apparatus (Figure 5.2.4) was made up, dried and assembled. With tap T_1 open, dry oxygen-free nitrogen was passed through the apparatus overnight. The furnace was set at $300-400^{\circ}\text{C}$. The break seals (B) were

broken, tap T_1 closed and the molybdenum pentafluoride swept slowly over the heated molybdenum in a slow stream of dry nitrogen. Molybdenum pentafluoride ran down the sloping nickel tube into trap C (at -78°C).

On completion of the reaction, the nitrogen supply was turned off and trap C was sealed at X, connected to a vacuum system (at joint J), pumped out at room temperature and sealed off at Y.

The pentafluoride in trap C was purified by vacuum sublimation.

FIGURE 5.2.4 - Apparatus for the Preparation of Molybdenum Pentafluoride by the Standard Method.



(b) New Preparation of Molybdenum Pentafluoride.

The method of Schröder and Grewe⁶, for the preparation of tungsten pentafluoride, has been slightly modified to enable molybdenum pentafluoride to be prepared.

The new method differed only in detail from that used in the preparation of tungsten pentafluoride (Section 2.5.3) Using the standard apparatus (Figures 2.5.3(a) and (b)) ~ 400 torr of molybdenum hexafluoride was reduced by molybdenum wires (diameter 0.02") heated at dull red heat. The cooling bath around the apparatus was maintained at -40 to -50°C. The synthesis was usually complete after 5 to 6 hours. Purification was effected by sublimation of the molybdenum pentafluoride (heated at 40 to 50°C) into the side arm (at -196°C).

Molybdenum pentafluoride has also been prepared by the reduction of ~ 400 torr of molybdenum hexafluoride with heated tungsten wires under the same conditions. Analysis of the products of this latter reaction for tungsten in the presence of molybdenum (by the method of Yagoda and Fales¹⁵⁴) showed that tungsten was not present.

5.2.5 Preparation and Purification of Oxytetrafluorides.

Tungsten and molybdenum oxytetrafluorides were prepared by the oxyfluorination of their respective powdered metals³⁷. Since the oxytetrafluorides can also be prepared by fluorination of the metal oxides¹⁵⁵, it was unnecessary to remove any oxide impurities from the powdered metals before the synthesis.

The previously dried apparatus (Figure 5.2.5) was

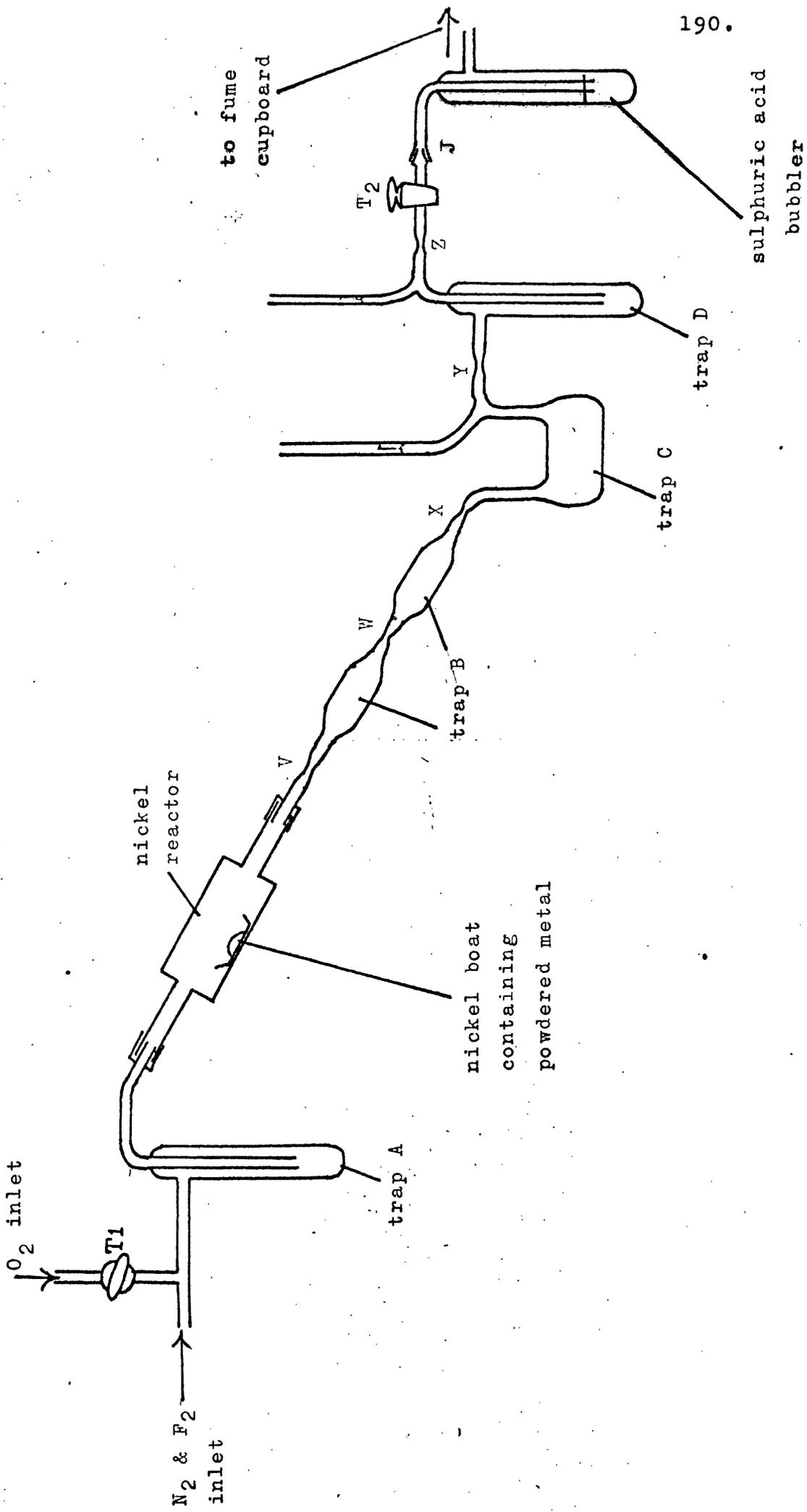
assembled on the standard fluorine generating system (Section 5.1.3). Trap D, which was for the final collection of any hexafluoride formed in the synthesis, contained some anhydrous sodium fluoride. Usually, 20-30g of powdered metal were used in the synthesis. With trap A at -183°C , dry nitrogen was passed through the apparatus overnight. After starting to pass a slow stream of oxygen through tap T_1 , the fluorine generator was slowly turned up to 20A (giving 15g of fluorine per hour) After allowing sufficient time for the fluorine to pass through to the reactor, it (the reactor) was heated with a low gas/oxygen flame in order to initiate the reaction.

The oxytetrafluoride produced ran down the sloping reactor and was collected in traps B and C (the latter being cooled at -183°C). Any hexafluoride produced was also collected in trap C. It was sometimes necessary to clear blockages in trap B with an industrial hot air blower. Sufficient time for reaction was estimated by allowing time for the passage of $1\frac{1}{2}$ times excess fluorine plus 1 hour. After this time the fluorine generator and the oxygen supply were turned off and the system was purged with a slow stream of dry nitrogen for 1 to 2 hours.

With the nitrogen off and tap T_2 closed, the apparatus was sealed at V. Joint J was connected to a vacuum line and the apparatus evacuated. With trap C at room temperature and trap D at -183°C , any hexafluoride was distilled into trap D. The apparatus was then sealed at W, X, Y and Z.

Traps B and C contained impure oxytetrafluoride which was stored at room temperature until required. Purification was carried out as required by vacuum sublimation at approximately 100°C .

FIGURE 5.2.5. - Apparatus for the Preparation of Oxytetrafluorides.



5.2.6 Preparation of Potassium Hexafluorotungstate(V) and Potassium Hexafluoromolybdate(V).

The salts KWF_6 and $KMoF_6$ were prepared by the reduction of the hexafluoride with potassium iodide in liquid sulphur dioxide (solvent)⁷⁶ thus $KI + MF_6 \rightarrow KMF_6 + \frac{1}{2}I_2 \uparrow$.

AnalaR potassium iodide was dried at $100^\circ C$ under vacuum and known masses were loaded into previously dried bulbs (Figure 5.2.6(a)) in the dry box (Section 5.1.2). These bulbs (A and B) were stoppered, removed from the dry box and built into the previously dried apparatus (Figure 5.2.6(b)). Ampoule C contained a known mass (two to three times excess) of the hexafluoride. The apparatus (including bulbs A and B) was evacuated and flamed out. The bulbs A and B were sealed off at Q.

Break seal D was broken and the hexafluoride distilled into bulb A (at $-196^\circ C$). Dry sulphur dioxide (about 20ml) was also distilled into bulb A. The apparatus was sealed off at X. With tap T_1 closed bulb A was slowly allowed to warm up until the sulphur dioxide melted and reaction occurred (liberating iodine). By adjusting tap T_1 and controlling the temperature of bulb A, the sulphur dioxide and excess hexafluoride were distilled into bulb B (at $-196^\circ C$). The reaction process was repeated with the solvent and excess hexafluoride being distilled back into bulb A. The solvent and excess hexafluoride were distilled between bulbs A and B several times to ensure complete reaction.

FIGURE 5.2.6(a) Bulbs for Loading with Potassium Iodide.

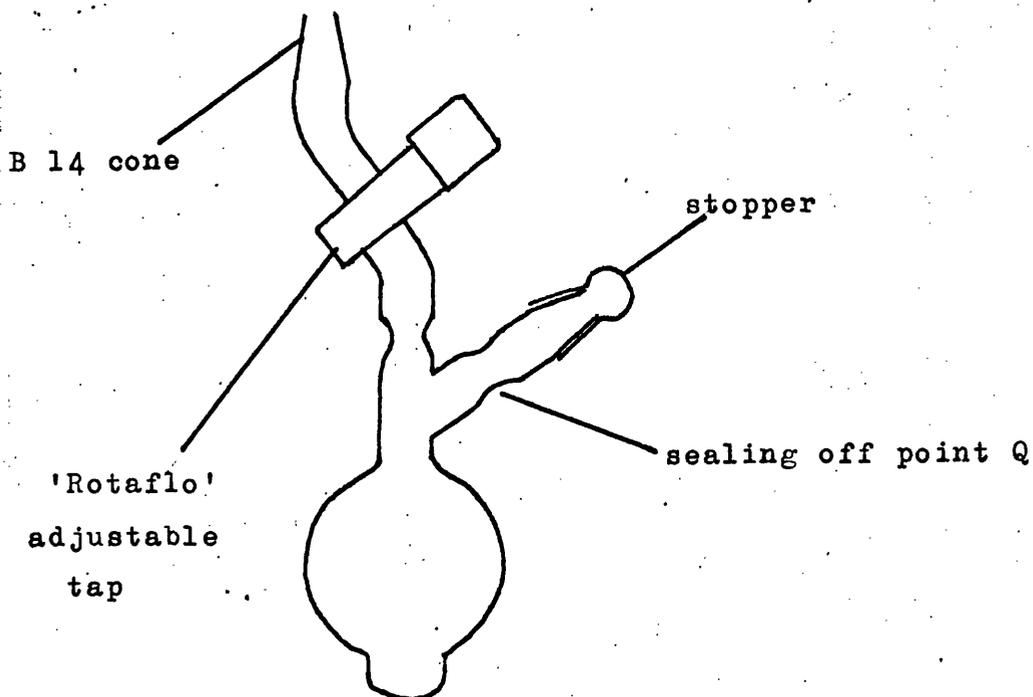
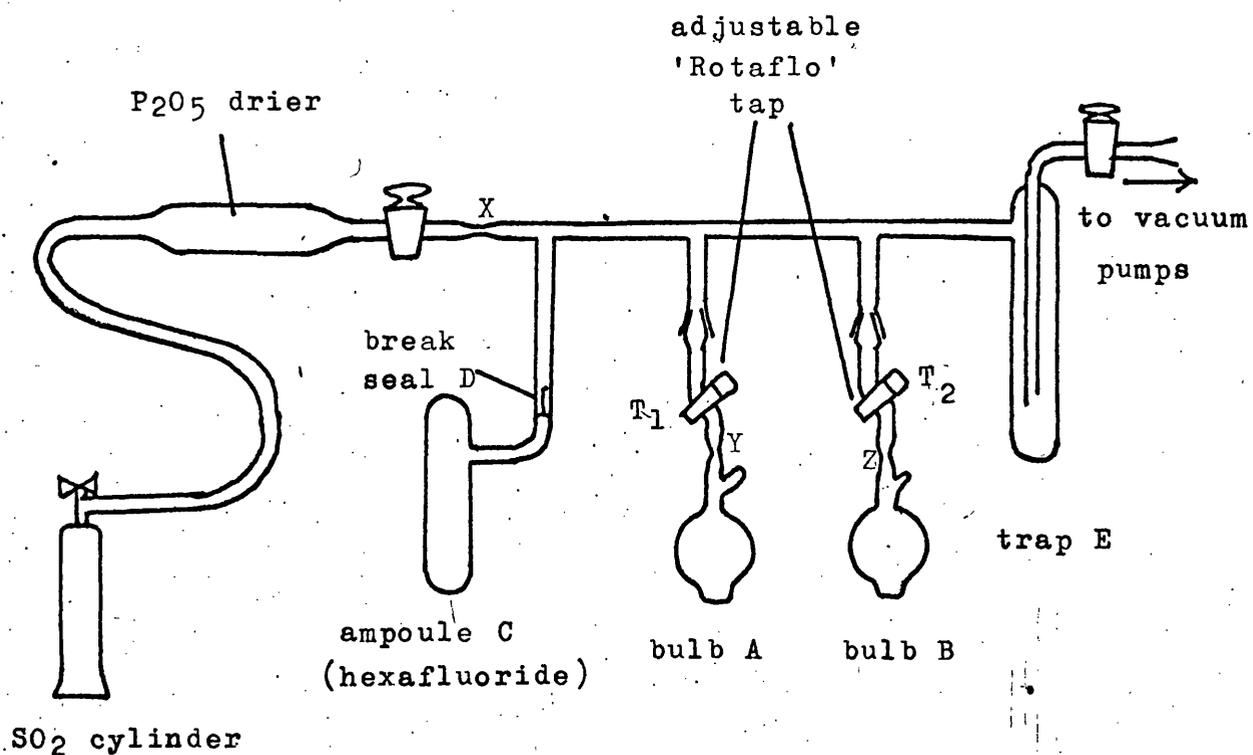


FIGURE 5.2.6(b) Apparatus for the Preparation of Potassium Hexafluorotungstate(V) and Potassium Hexafluoromolybdate(V).



The solvent, excess hexafluoride and some iodine were then distilled into trap E (at -196°C)

Bulbs A and B, containing the potassium salt and iodine, were heated to 100°C under vacuum for one to two days to completely remove the iodine. The bulbs were then sealed off at Y and Z.

It was not possible to purify the potassium hexafluoro molybdate and tungstate but analysis for fluorine and molybdenum or tungsten showed them to be $> 95\%$ pure.

5.2.7. Preparation of Potassium Hexachlorotungstate(IV).⁸¹

Finely ground potassium iodide (1-2g) was introduced into a dry Carius tube. The tube was heated in an oven at 130°C overnight. While still hot, the tube was stoppered and transferred into the dry box. Tungsten hexachloride[‡] in a sealed ampoule was also introduced into the dry box.

An excess of tungsten hexachloride was introduced into the Carius tube. The Carius tube was stoppered, removed from the dry box, evacuated, sealed off, and then heated at 130°C for four days. After this time, the Carius tube was opened, attached to a vacuum line and evacuated. By heating the Carius tube at 280°C under vacuum the liberated iodine and excess tungsten hexachloride were removed. The Carius tube, containing the dark red potassium hexachlorotungstate(IV), was sealed off. No further purification of the product was

Footnote ‡

The tungsten hexachloride was supplied by Koch-Light Laboratories Ltd. It was resublimed before use.

possible

5.3. Analyses.

5.3.1 Introduction.

The heats of hydrolysis of several compounds have been determined (Chapter 2). It has been necessary to analyse these compounds as a demonstration of their purity. The methods of analysis are described in the following sections. AnalaR chemicals were used throughout.

5.3.2 Analysis for Tungsten¹⁵⁶.

Tungsten was determined by precipitation of the cinchonine-tannin complex and ignition to tungstic oxide.

(a) Procedure.

A known mass of the compound was dissolved in a small amount of dilute sodium hydroxide (10ml) - or a 10ml aliquot of a larger solution was used. If necessary, the tungsten was oxidised to W(VI) by gently warming with a few drops of concentrated nitric acid. Any precipitate of tungstic oxide was re-dissolved by adding dilute sodium hydroxide solution. The volume was adjusted to 200ml. 4N ammonium hydroxide (5ml) was added, the solution heated to 60°C, and tannin (1g dissolved in a little water) added. 1:1 hydrochloric acid was added dropwise until the solution was just acid (indicated by the colour change). Powdered cellulose and 5% cinchonine hydrochloride solution (5ml) were stirred in. The precipitate was allowed to stand overnight, filtered (Whatman No. 41 filter paper), washed

three times with cinchonine wash solution, returned to the original beaker with a small amount of wash liquid, and refiltered on the same paper. The precipitate and filter paper were dried, by the gentle pumping of the filter pump, before being transferred to a tared crucible. The precipitate and filter paper were charred and the crucible heated at 800°C until constant mass was attained. Tungsten was determined from the mass of tungstic oxide obtained.

(b) Preparation of Reagents.

Cinchonine hydrochloride solution was prepared by dissolving cinchonine (5g) in concentrated hydrochloric acid (27ml) and water (63ml). The wash solution was prepared by diluting this solution by thirty.

157,158.

5.3.3 Analysis for Molybdenum.

Molybdenum was determined gravimetrically as the oxine complex.

60% perchloric acid (1ml) was added to a known mass of the compound (or a 10ml aliquot of solution) in a platinum dish. Too much perchloric acid would ruin the determination. The solution was evaporated to dryness under an infra-red lamp and heated over a micro-burner to expel the excess perchloric acid (which removed fluoride and oxidised the molybdenum to Mo(VI)). The residue was redissolved in a slight excess of dilute sodium hydroxide solution. The solution (in a 250ml beaker) was neutralised to methyl red and acidified with a few drops of 2N sulphuric acid. 2N ammonium acetate (5ml) was added. The solution was diluted

to 150ml and heated to nearly boiling. The molybdenum was precipitated by the dropwise addition of a 3% solution of oxine[†] in dilute acetic acid. The mixture was boiled for 3 minutes, allowed to cool to room temperature, and filtered through a tared sintered glass crucible. The precipitate (of oxine complex) was well washed with hot water until free from the reagent, and dried at 130°C to constant mass. Molybdenum was determined from the mass of oxine complex, $\text{MoO}_2(\text{C}_9\text{H}_6\text{ON})_2$, obtained.

5.3.4 Analysis for Tungsten and Molybdenum in the Same Sample.

The analysis for tungsten and molybdenum in a sample containing both was carried out by the method of Yagoda and Fales¹⁵⁴.

The following reagents were prepared: 2M formic acid, 30% W/V tartaric acid, 50% W/V ammonium formate, distilled water saturated with hydrogen sulphide at 0°C and a cinchonine solution (12.5g of cinchonine dissolved in 50ml of 1.19 S.G. hydrochloric acid and 50ml of distilled water).

A known mass of the sample being analysed was added to a solution of sodium hydroxide. Hydrogen peroxide (20vol) was added slowly until the brown precipitate which had been obtained was completely dissolved and a yellow solution of the metal peroxide was obtained. The solution was boiled to decompose the peroxide and a colourless solution was obtained which was made up to 100ml in a volumetric flask.

Footnote [†]

Oxine is 8 - hydroxyquinoline ($\text{C}_9\text{H}_7\text{ON}$).

To an aliquot of the solution was added 50% ammonium formate (10ml), 30% tartaric acid (10ml), water saturated with hydrogen sulphide at 0°C (100ml) and 2M formic acid (10ml). The mixture was heated on a water bath at 60°C for 1 hour, a small quantity of ashless filter paper pulp added, and the precipitation of molybdenum sulphide completed with concentrated formic acid (10ml). The mixture was heated on a water bath for a further 30 minutes. When the solution had cooled, the precipitate was filtered through an ashless filter paper. The precipitate was washed with five portions (10ml each) of a wash solution (prepared from 5ml of 50% ammonium formate, 5ml of concentrated formic acid and 100ml of distilled water). Both the precipitate and filtrate were retained.

The precipitate and filter paper were transferred to a silica crucible which had previously been heated to 500°C and cooled to constant mass. The contents of the crucible were dried in a drying oven, the filter paper partially ashed over a very small bunsen flame and the crucible transferred to a furnace at 500°C for 1 hour. After cooling, the mass of the crucible and contents (MoO_3) were determined to constant mass. Molybdenum was determined from the mass of molybdic oxide obtained.

The filtrate was evaporated (to 15ml) and allowed to cool. Concentrated nitric acid (25ml) was added to remove ammonium salts. When gases ceased to be evolved, the mixture was diluted with distilled water (100ml) and cinchonine solution (5ml). The mixture was boiled for two hours (the volume was maintained) and filtered through an ashless filter

paper. The precipitate (of tungstic acid) was washed, dried and ignited at 750°C in a crucible of known mass.

Tungsten was determined from the mass of tungstic oxide obtained.

5.3.5 Analysis for Rhenium¹⁵⁸ in Rhenium Hexafluoride.

Rhenium was analysed gravimetrically as nitron perrhenate.[‡]

A known mass of the hexafluoride was added to an excess of dilute sodium hydroxide. The mixture was evaporated to dryness in a platinum dish and the solid obtained was fused with an excess of sodium carbonate containing a little sodium peroxide (to oxidise the rhenium to the heptavalent state). The melt was extracted with water (50ml). The solution obtained was transferred to a beaker, neutralised with 2N sulphuric acid and buffered to pH 7 by the addition of sodium acetate (1g). The solution was heated to boiling and the rhenium precipitated by the dropwise addition of a pre-calculated excess of 5% nitron acetate. The solution was stirred frequently as it cooled to room temperature. After standing for one hour the solution was cooled to 0°C for a further hour and then filtered through a tared sintered glass crucible. The precipitate was washed with small portions of an ice cold saturated solution of nitron perrhenate containing 1% of nitron acetate, and then with ice cold distilled water (only a few ml). The precipitate of nitron perrhenate was dried to constant mass at 110°C . The rhenium content of the hexafluoride was determined from the mass of nitron perrhenate precipitate.

Footnote [‡]

Nitron is a strong organic base 4,5-dihydro -1,4 diphenyl - 3,5 phenylimino - 1,2,4 triazole.

5.3.6 Analysis for Fluoride.

(a) Distillation of fluorosilicic acid.¹⁵⁹

Heavy metals interfere with analysis for fluorine. Therefore, it is necessary, in the fluorine analyses of this work, to separate the fluorine from the heavy metals. The method used was the steam distillation of fluorosilicic acid. The subsequent analysis involved the precipitation of lead chlorofluoride and the determination of the chloride content of this precipitate by Volhard's method.

A known mass[#] of ^{the} compound to be analysed was added to flask A of the distillation apparatus (Figure 5.3.6). 85% phosphoric acid (20ml) and a few soft glass beads were also added. Flask A was attached to the distillation apparatus. Immersion heater B and heater C were switched on. When steam reached flask A, the steam super heater D was switched on (this automatically reduced the output of heater B) A solution of fluorosilicic acid was collected in flask E.

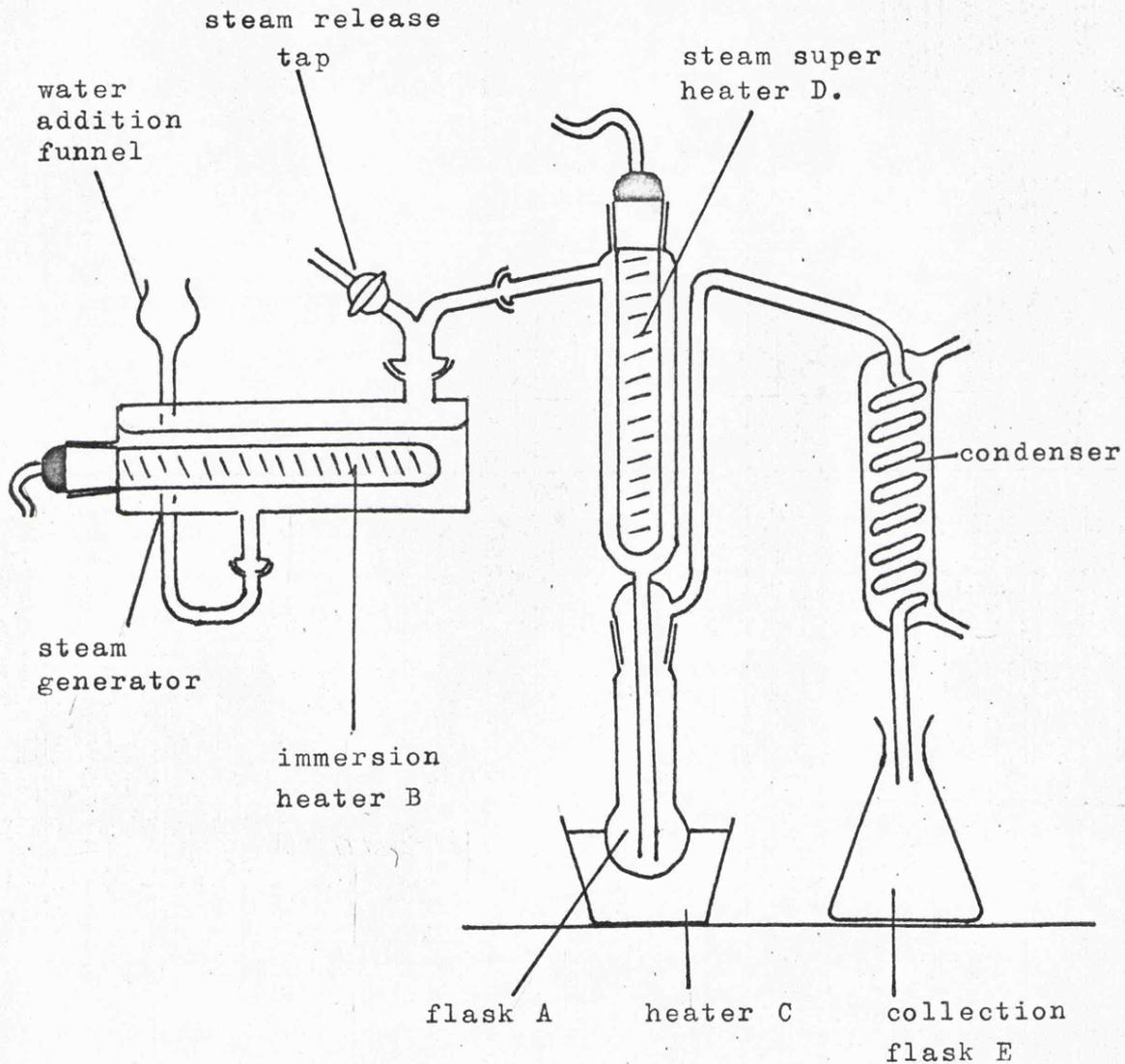
Footnote[#]

In this work with moisture sensitive compounds, two methods of loading the flask A were used:

1. With non-volatile samples the stoppered flask A was loaded in a dry box.
2. With volatile samples the sample was contained in a frangible glass bulb (as in Section 2.3.2). The frangible glass bulb, at the bottom of flask A, was broken when the flask was attached to the distillation apparatus.

The distillation was continued until the distillate was no longer acidic (to litmus).

FIGURE 5.3.6 - Apparatus for the Distillation of Fluorosilicic Acid.[#]



Footnotes ≠

1. Standard Normag apparatus according to Prof Seel.
2. It was necessary to wrap the steam generator, steam super heating section and flask A with heat insulating asbestos rope in order to retain heat.

(b) Analysis of Distillate.¹⁵⁷

A few drops of bromophenol blue indicator were added to the distillate followed by dilute sodium hydroxide solution until the colour just turned blue. 1:1 hydrochloric acid (2ml) was added and the solution heated on a steam bath for five minutes. Lead nitrate (5g) was added with stirring. Immediately this had dissolved crystallised sodium acetate (5g) was added, with vigorous stirring, to precipitate lead chlorofluoride. The precipitate was digested on a steam bath for 30 minutes and allowed to stand overnight.

The precipitate of lead chlorofluoride was filtered (Whatman No. 42 filter paper), washed five times with a saturated wash solution of lead chlorofluoride and finally washed once with ice cold water.

The precipitate and filter paper were transferred back to the beaker in which the precipitation had taken place and 5% nitric acid (100ml) was added. The mixture was heated on a steam bath until the precipitate had dissolved.

Standardised (c 0.1N) silver nitrate (exactly 25ml) was added and the precipitate (silver chloride) digested on the steam bath for 30 minutes. After cooling to room temperature (in darkness), the precipitate was filtered (Whatman No. 40 filter paper) and washed with cold water. The filtrate (and washings) were titrated against standard 0.1N ammonium thiocyanate using ferric alum indicator (1ml).

This back titration gave (by subtraction) the amount of silver nitrate required to combine with the chloride from the lead chlorofluoride precipitate and hence the amount of fluoride in the original compound (1ml N AgNO_3 \equiv 0.019g F).

(c) Preparation of Reagents.

The wash solution of lead chlorofluoride was prepared by adding lead nitrate (10g) in water (200ml) to a solution (100ml) containing sodium fluoride (1g) and concentrated hydrochloric acid (2ml). The mixture was thoroughly mixed and the precipitate of lead chlorofluoride allowed to settle. The supernatant liquid was decanted and discarded. The precipitate was washed with water (5 portions of 200ml) and then made up to 1 litre. The mixture was shaken at intervals during one hour, and the precipitate allowed to settle. The liquid was filtered. The filtrate was the wash solution. The precipitate of lead chlorofluoride could be used to make further wash solutions.

The ferric alum indicator was a cold saturated solution (approximately 40%) of ferric ammonium sulphate to which a few drops of 6N nitric acid had been added.

5.3.7 Analysis for Chloride in Tungsten Chlorides.¹⁵⁷

Chlorides were determined by Volhard's method.

A known mass of the compound to be analysed was added to a small volume of dilute sodium hydroxide solution in a beaker. The beaker was covered by a wetted watch glass in order to minimise the loss of chloride as hydrogen chloride. The mixture was made just acid with nitric acid and heated on a steam bath for one hour to oxidise the tungsten to the insoluble trioxide. The cooled filtered solution was made just alkaline with sodium hydroxide solution and made up in a volumetric flask.

6N nitric acid (5ml) and an excess of standard (0.1N) silver nitrate (30ml) were added to an aliquot of the chloride

solution. The suspension was boiled for a few minutes (on a steam bath). The precipitate of silver chloride was filtered, and washed with very dilute (1:100) nitric acid. Ferric alum indicator[#] (1ml) was added to the filtrate and washings. The residual silver nitrate was titrated with standard (0.1N) ammonium thiocyanate. The back titration gave (by subtraction) the amount of silver nitrate which had reacted with the chloride from the original compound.

5.3.8 Analysis of Hypochlorite Solution.¹⁵⁷

It was necessary to keep a check on the sodium hypochlorite solution used in the determination of enthalpies of oxidative hydrolysis (Chapter 2). This was carried out using standard iodometric titrations.

(a) Procedure

An aliquot of a diluted volumetric solution of the sodium hypochlorite was transferred to a conical flask. Iodate free potassium iodide (2g) and glacial acetic acid. (10ml) were added with shaking. The hypochlorite was determined by titration of the liberated iodine with standard (0.1N) sodium thiosulphate using starch solution as the indicator when the iodine colour had almost disappeared.

(b) Preparation of Reagents.

The starch solution was prepared from a paste of soluble starch (1g) in water, stirred into boiling water

Footnote[#]

For the preparation of ferric alum indicator solution see previous section.

(100ml), and boiled for 1 minute. After cooling, potassium iodide (2-3g) and mercuric iodide (5mg) were added.

5.3.9 The Use of ^{19}F NMR. Spectroscopy for Identification of Reaction Products.

^{19}F NMR. spectroscopy has been used (Section 4.4) in the identification of the products of the preparations and attempted preparations of halide fluorides of tungsten(VI).

A Varian DA60 high resolution nuclear magnetic resonance spectrometer (operated at 56.4 MHz) was used. Measurements were by a standard side band technique¹⁵⁰. Spectra were recorded at temperatures down to -60°C .

All samples were prepared on a vacuum line and sealed into 15cm long, thick walled tubes accurately machined to 4.5mm O.D. and supplied by Jencons Scientific Co. A liquid sample of about 3cm depth was required to fill the probe area. In certain cases, small samples were increased in volume by the addition of arcton 11 (CFCl_3).

APPENDIX 1. - THE 'INVERSION TEMPERATURE' OF THE TUNGSTEN
FLUORINE REGENERATIVE CYCLE.

Using known thermochemical data (Table 6.1.1), the Gibbs free energies of various equilibria, involving tungsten, fluorine and tungsten hexafluoride, have been calculated over a large range of temperatures. The results, expressed in terms of the free energies of decomposition of the tungsten hexafluoride, are shown in Table 6.1.2 and Graph 6.1.1.

The free energies indicate that the decomposition of tungsten hexafluoride is unfavourable at low temperatures (i.e. the Gibbs free energies, ΔG° , of the decompositions are positive) whilst at high temperatures the decompositions become favourable (ΔG° for the decompositions become negative). The lowest temperature at which a decomposition reaction becomes favourable, called the 'inversion temperature', is $\sim 3360\text{K}$. Above this temperature tungsten hexafluoride will decompose to give gaseous fluorine atoms and solid tungsten (deposited) - see also Chapter 3.

TABLE 6.1.1. Known Thermochemical Data.(a) Enthalpies of formation (ΔH_f°)

Temperature (K)	Enthalpy of formation (kcal mol ⁻¹)				
	of F(g)	of F ₂ (g)	of W(s)	of W(g)	of WF ₆ (g)
298	18.86	0	0	203.40	-411.50
1000	19.572	0	0	204.386	-409.482
2000	20.044	0	0	206.224	-406.825
3000	20.327	0	0	205.109	-405.967

All these enthalpies of formation are taken from the JANAF Thermochemical Tables⁴⁵.

(b) Absolute entropies (S°)

Temperature (K)	Entropy (cal deg ⁻¹ K mol ⁻¹)				
	of F(g)	of F ₂ (g)	of W(s)	of W(g)	of WF ₆ (g)
298	37.917	48.447	7.806	41.349	84.22
1000	44.277	52.553	15.237	50.109	124.958
2000	47.767	57.246	20.142	56.427	150.674
3000	49.791	60.427	23.540	59.405	165.893

All these entropies, with the exception of those of WF₆(g), are taken from the JANAF Thermochemical Tables⁴⁵. The entropies of WF₆(g) are taken from Appendix 2.

TABLE 6.1.2. Free Energies of Decomposition of Gaseous Tungsten Hexafluoride.

(a) Enthalpies of decomposition, ΔH_T° .

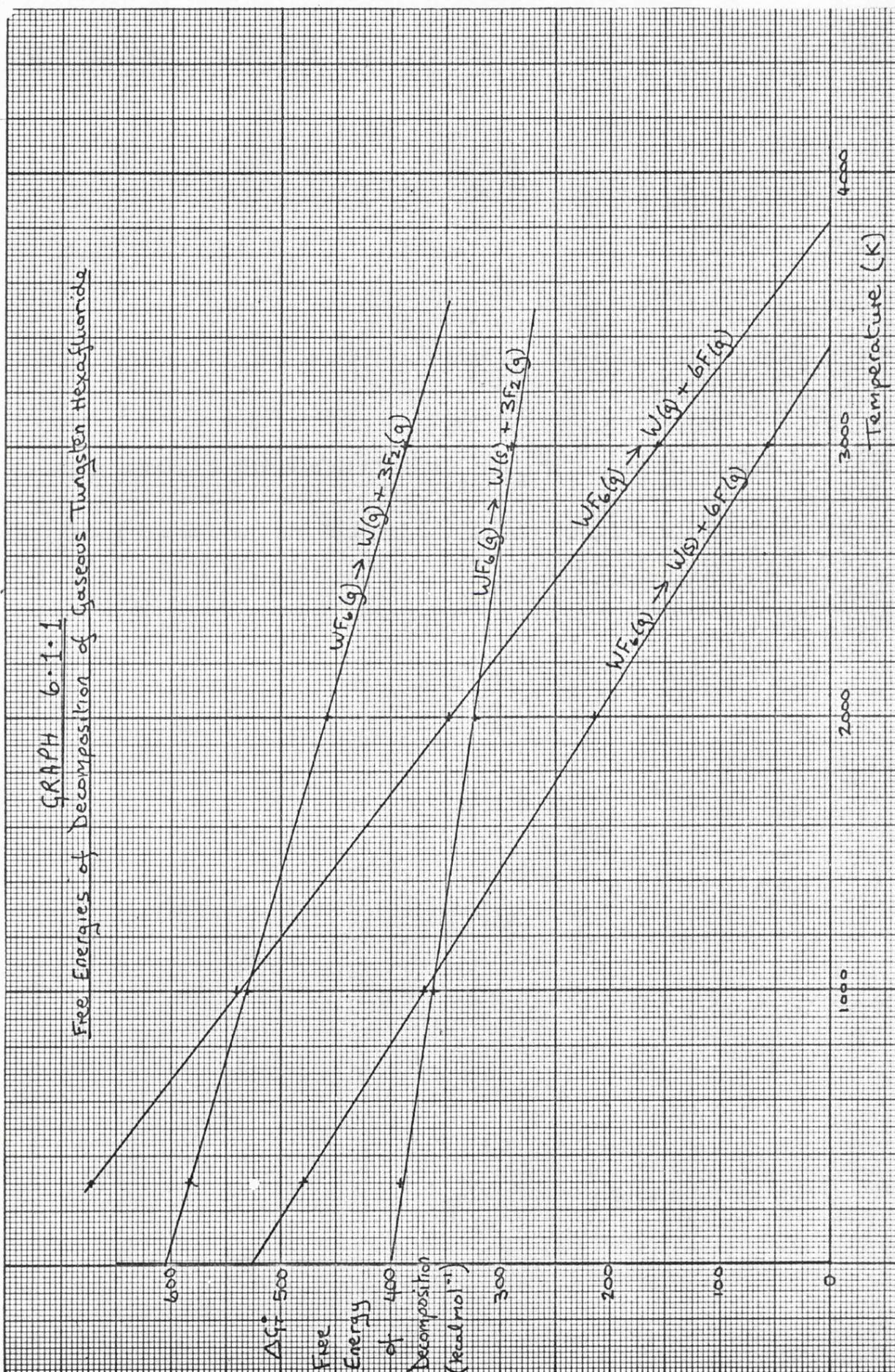
Temperature (K)	Enthalpy of the decomposition (kcal mol ⁻¹)			
	$WF_6(g) \rightarrow W(s) + 6F(g)$	$WF_6(g) \rightarrow W(l) + 6F(g)$	$WF_6(g) \rightarrow W(s) + 3F_2(g)$	$WF_6(g) \rightarrow W(l) + 3F_2(g)$
298	+ 524.66	+ 728.06	+ 411.5	+ 614.9
1000	+ 526.914	+ 731.30	+ 409.482	+ 613.868
2000	+ 527.089	+ 733.313	+ 406.825	+ 613.049
3000	+ 527.929	+ 733.04	+ 405.967	+ 611.076

(b) Entropies of decomposition, ΔS_T°

Temperature (K)	Entropy of the decomposition (cal deg ⁻¹ C mol ⁻¹)			
	$WF_6(g) \rightarrow W(s) + 6F(g)$	$WF_6(g) \rightarrow W(l) + 6F(g)$	$WF_6(g) \rightarrow W(s) + 3F_2(g)$	$WF_6(g) \rightarrow W(l) + 3F_2(g)$
298	+ 151.085	+ 184.628	+ 68.924	+ 102.467
1000	+ 155.941	+ 190.813	+ 47.938	+ 82.81
2000	+ 156.070	+ 192.355	+ 41.206	+ 77.491
3000	+ 156.393	+ 192.258	+ 38.928	+ 74.793

(c) Gibbs free energies of decomposition, ΔG_T°

Temperature (K)	Gibbs free energy of decomposition (kcal mol ⁻¹)			
	$WF_6(g) \rightarrow W(s) + 6F(g)$	$WF_6(g) \rightarrow W(l) + 6F(g)$	$WF_6(g) \rightarrow W(s) + 3F_2(g)$	$WF_6(g) \rightarrow W(l) + 3F_2(g)$
298	+ 479.638	+ 673.036	+ 390.959	+ 584.365
1000	+ 370.973	+ 540.487	+ 361.544	+ 531.078
2000	+ 214.949	+ 348.603	+ 324.413	+ 458.067
3000	+ 56.75	+ 156.296	+ 289.183	+ 386.697



APPENDIX 2. - HIGH TEMPERATURE THERMODYNAMIC FUNCTIONS
OF HEXAFLUORIDES.

In order to calculate the 'inversion temperatures' (Chapter 3 and Appendix 1) it was necessary to use high temperature thermodynamic properties (in particular the entropy) of gaseous tungsten hexafluoride.

Gaunt¹⁶⁰ used statistical mechanics and the then available infra-red spectroscopic and bond length data to determine thermodynamic properties (C_p° , S° and $-(G^\circ - E_0^\circ)/T$) for some hexafluorides over the temperature range 100 to 500K.

Using standard statistical thermodynamic methods and recent spectroscopic and structural data the thermodynamic properties (C_p° , S° and $-(G^\circ - E_0^\circ)/T$) of some hexafluorides have been computed.* A rigid rotator and harmonic oscillator model has been assumed. The necessary input data and sources of this data are summarised in Table 6.2.1. The moments of inertia of the hexafluorides were calculated from the known M-F bond lengths in MF_6 and the atomic weight of fluorine.

The computed thermodynamic properties of the hexafluorides from 100 to 3000K are given in Table 6.2.2.

Nagarajan and Brinkley¹⁶¹ have very recently[‡] published similar tables for the hexafluorides over the temperature range 200 to 2000K.

Footnotes.

* The computer program (Algol) used in this work was kindly supplied by Dr D.M. Adams.

‡ Since the completion of this work.

The recent JANAF Thermochemical Tables⁴⁵ also include the thermochemical properties of sulphur, molybdenum and tungsten hexafluorides to 3000K. A comparison of the standard entropies at 298K (Table 6.2.3) shows fairly close agreement.

TABLE 6.2.1.1.-Data Used in the Computation of the Thermodynamic Properties of the Hexafluorides.

Fluoride	Number of fundamental frequencies	Molecular Weight	Symmetry ¹ Number	Bond Length(\AA)	Moment of ² Inertia	Fundamental frequencies ³ (degeneracy in brackets) (cm^{-1})					
						1	2	3	4	5	6
SF ₆	6	146.06	24	1.56 ³	184.95	770(1), 640(2), 939(3), 614(3), 522(3), 349(3).					
SeF ₆	6	192.96	24	1.67 ³	211.96	708(1), 661(2), 780(3), 437(3), 403(3), 262(3).					
TeF ₆	6	241.6	24	1.84 ³	257.31	701(1), 674(2), 752(3), 325(3), 313(3), 195(3).					
MoF ₆	6	209.94	24	1.84 ³	257.31	741(1), 643(2), 741(3), 262(3), 312(3), 122(3).					
WF ₆	6	297.85	24	1.826 ⁴	253.41	771(1), 673(2), 711(3), 258(3), 315(3), 134(3).					
TcF ₆	6	213	24	(1.84)	257.31	712(1), 639(2), 748(3), 265(3), 297(3), 174(3).					
ReF ₆	6	300.23	24	(1.83)	254.52	775(1), 671(2), 715(3), 257(3), 295(3), 193(3).					
RuF ₆	6	215.1	24	(1.83)	254.52	675(1), 624(2), 735(3), 275(3), 283(3), 186(3).					
OsF ₆	6	304.2	24	1.830 ⁴	254.52	733(1), 668(2), 720(3), 272(3), 276(3), 205(3).					
RhF ₆	6	216.91	24	(1.83)	254.52	634(1), 592(2), 724(3), 283(3), 269(3), 189(3).					
IrF ₆	6	306.2	24	1.833 ⁴	255.35	701(1), 646(2), 719(3), 276(3), 258(3), 206(3),					
PtF ₆	6	309.09	24	1.83 ³	254.52	665(1), 600(2), 705(3), 273(3), 242(3), 211(3).					
UF ₆	6	352.03	24	1.994 ⁴	302.18	667(1), 535(2), 624(3), 186(3), 201(3), 140(3).					
NpF ₆	6	351	24	1.981 ⁴	298.25	648(1), 528(2), 624(3), 199(3), 208(3), 165(3).					
PuF ₆	6	356	24	1.969 ⁴	286.49	628(1), 523(2), 616(3), 206(3), 211(3), 173(3).					

Footnotes to Table 6.2.1.

1. Herzberg.¹⁶²
2. Calculated from the bond length and atomic weight of fluorine.
3. Kim, Souder and Claassen.¹⁶³
4. Weinstock and Malm.¹⁶⁴

*
TABLE 6.2.2. Thermodynamic Properties of Gaseous Hexafluorides,
#

(a) Entropy, S°.

Species	Entropy (S° cal.mol ⁻¹ deg ⁻¹ K) at										
	100K	273.15K	298.15K	500K	1000K	1500K	2000K	2500K	3000K		
SF ₆	53.262	67.663	69.632	83.710	107.022	121.744	132.394	140.719	147.548		
SeF ₆	55.097	72.632	74.887	90.270	114.368	129.259	139.971	148.326	155.169		
TeF ₆	57.604	77.898	80.309	96.301	120.698	135.649	146.382	154.745	161.595		
MoF ₆	59.412	81.258	83.737	99.981	124.499	139.474	150.215	158.583	165.434		
WF ₆	60.016	81.748	84.223	100.456	124.971	139.946	150.687	159.054	165.906		
TcF ₆	58.026	79.488	81.959	98.187	122.701	137.676	148.416	156.784	163.635		
ReF ₆	58.732	80.052	82.516	98.712	123.209	138.180	148.920	157.287	164.138		
RuF ₆	57.799	79.279	81.766	98.078	122.649	137.636	148.382	156.751	163.604		
OsF ₆	58.582	79.831	82.298	98.513	123.028	138.002	148.743	157.111	163.963		
RhF ₆	57.815	79.502	82.016	98.454	123.103	138.107	148.858	157.231	164.085		
IrF ₆	58.704	80.189	82.676	98.983	123.551	138.538	149.283	157.653	164.505		
PtF ₆	58.819	80.684	83.210	99.695	124.376	139.386	150.140	158.513	165.367		
UF ₆	62.751	87.385	90.058	107.149	132.143	147.217	157.993	166.377	173.238		
NpF ₆	61.714	85.905	88.568	105.633	130.620	145.693	156.470	164.854	171.714		
PuF ₆	61.314	85.379	88.056	105.134	130.139	145.216	155.994	164.378	171.239		

* The values were computed from 100 to 3000K in 100K steps and at 273.15 and 298.15K but only a selection of values are included in these tables.

Ideal gas state at a pressure of 1 atmosphere.

TABLE 6.2.2 Continued.

(b) Heat Capacity, C_p°

Species	Heat Capacity (C_p° cal.mol ⁻¹ deg ⁻¹ K) at										
	100K	273.15K	298.15K	500K	1000K	1500K	2000K	2500K	3000K		
SF ₆	9.242	21.734	23.234	30.725	35.690	36.803	37.211	37.402	37.507		
SeF ₆	11.090	25.081	26.410	32.570	36.284	37.081	37.370	37.505	37.579		
TeF ₆	13.813	26.968	28.094	33.326	36.496	37.178	37.424	37.540	37.603		
MoF ₆	16.068	27.784	28.812	33.634	36.581	37.216	37.446	37.554	37.613		
WF ₆	15.864	27.738	28.773	33.624	36.579	37.216	37.446	37.554	37.613		
TcF ₆	15.190	27.697	28.745	33.621	36.579	37.216	37.446	37.553	37.613		
ReF ₆	14.958	27.607	28.662	33.579	36.567	37.210	37.443	37.552	37.612		
RuF ₆	15.004	27.875	28.927	33.750	36.623	37.236	37.458	37.562	37.618		
OsF ₆	14.762	27.634	28.696	33.614	36.580	37.216	37.446	37.554	37.613		
RhF ₆	15.059	28.181	29.225	33.933	36.682	37.264	37.499	37.572	37.625		
IrF ₆	14.963	27.868	28.919	33.743	36.621	37.235	37.457	37.561	37.618		
PtF ₆	15.200	28.321	29.354	34.001	36.703	37.273	37.479	37.575	37.628		
UP ₆	18.912	30.090	30.959	34.781	36.931	37.378	37.538	37.613	37.654		
U ₂ P ₆	18.047	29.966	30.861	34.759	36.927	37.377	37.538	37.613	37.654		
PuF ₆	17.716	29.998	30.902	34.798	36.941	37.383	37.541	37.616	37.656		

TABLE 6.2.2 continued.

(c) Free Energy Function $-\frac{(G^{\circ}-E_0^{\circ})}{T}$

Species	Free Energy Function (cal.mol ⁻¹ deg ⁻¹ K)											
	100K	273.15K	298.15K	500K	1000K	1500K	2000K	2500K	3000K			
SF ₆	45.081	54.904	56.057	64.492	80.458	91.920	100.769	107.956	114.003			
SeF ₆	46.442	57.644	58.996	68.677	86.085	98.153	107.331	114.725	120.912			
TeF ₆	48.015	60.887	62.415	73.054	91.387	103.810	113.174	120.683	126.948			
MoF ₆	48.440	62.842	64.491	75.737	94.609	107.230	116.696	124.268	130.575			
WF ₆	49.261	63.474	65.112	76.301	95.127	107.732	117.191	124.758	131.062			
TcF ₆	47.871	61.573	63.179	74.233	92.959	105.530	114.972	122.528	128.826			
ReF ₆	48.755	62.285	63.879	74.867	93.533	106.081	115.511	123.060	129.353			
RuF ₆	47.785	61.383	62.989	74.061	92.836	105.433	114.890	122.456	128.760			
OsF ₆	48.729	62.142	63.730	74.695	93.353	105.901	115.332	122.882	129.175			
RhF ₆	47.803	61.461	63.081	74.246	93.142	105.792	115.278	122.862	129.178			
IrF ₆	48.781	62.324	63.927	74.987	93.751	106.344	115.798	123.363	129.666			
PtF ₆	48.821	62.359	64.167	75.388	94.345	107.019	116.518	124.111	130.433			
UF ₆	50.743	66.861	68.695	80.999	100.979	114.044	123.748	131.466	137.874			
NpF ₆	50.316	65.844	67.639	79.761	99.600	112.617	122.296	130.000	136.398			
PuF ₆	50.125	65.454	67.238	79.316	99.133	112.146	121.824	129.527	135.925			

TABLE 6.2.3. A Comparison of the Standard Entropies of the Hexafluorides from the Three Recent Sources.

Fluoride	Standard Entropy at 298.15K, S_{298}° (cal mol ⁻¹ deg ⁻¹ K)		
	This thesis	1971 JANAF Thermochemical Tables ⁴⁵	Nagarajan & Brinkley ¹⁶¹
SF ₆	69.632	69.713	69.708
SeF ₆	74.887	-	74.964
TeF ₆	80.309	-	80.238
MoF ₆	83.737	83.76	83.869
WF ₆	84.223	81.504	84.508
TcF ₆	81.959	-	83.414
ReF ₆	82.516	-	84.367
RuF ₆	81.766	-	81.912
OsF ₆	82.298	-	82.405
RhF ₆	82.016	-	82.011
IrF ₆	82.676	-	82.524
PtF ₆	83.210	-	83.106
UF ₆	90.058	-	89.936
NpF ₆	88.568	-	88.597
PuF ₆	88.056	-	88.210

REFERENCES.

1. W.M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solution" 2nd Ed. (Prentice Hall, 1952).
2. H. Moissan, "Le Fluor et ses composés" (Monograph, Paris, 1900).
3. O. Ruff and F. W. Tschirch, Ber., 1913, 46, 929.
4. B. Weinstock and J. G. Malm, J. Amer. Chem. Soc., 1958, 80, 4466.
5. (a) O. Ruff and W. Kwasnik (with E. Asher), Z. anorg. allg. Chem., 1932, 209, 113.
(b) O. Ruff and J. Fischer, Z. anorg. Chem., 1929, 179, 174.
6. J. Schröder and F.J. Grewe, (a) Chem. Ber., 1970, 103, 1536.
(b) Angew. Chem. (Int. Ed.), 1968, 7, 132.
7. T.A. O'Donnell and D.F. Stewart, Inorg. Chem., 1966, 5, 1434.
8. G.H. Cady and G.B. Hargreaves, J. Chem. Soc., 1961, 1563.
9. J.H. Canterford and R. Colton, "Halides of the Second and Third Row Transition Metals" (Wiley-Interscience, 1968).
10. V. Gutmann, "Halogen Chemistry" Volume 3 (Academic Press, 1967).
11. J.H. Canterford, R. Colton and T.A. O'Donnell, Reviews of Pure and Applied Chem., 1967, 17, 123.
12. (a) L. Brewer, L.A. Bromley, P.W. Gilles and N.L. Lofgren, Papers 6 and 8 from "The Chemistry and Metallurgy of Miscellaneous Materials. Thermodynamics", Ed. L.L. Quill, National Energy Series Div 1V, Vol 19B. (McGraw Hill, 1950).

12. (b) A. Glassner, At. En. Comm. (U.S.A.), Rep. ANL 5750, (1957)..
13. O.E. Myers and A.P. Brady, J. Phys Chem., 1960, 64, 591.
14. P.A.G. O'Hare and W.N. Hubbard, J. Phys. Chem., 1966, 70, 3353.
15. K.F. Zmbov, O.M. Uy and J.L. Margrave, J. Phys. Chem., 1969, 73, 3008.
16. S.A. Shchukarev, G.I. Novikov, I.V. Vasil'kova, A.V. Suvorov, N.V. Andreeva, B.N. Sharupin, and A.K. Baev, Russ. J. Inorg. Chem., 1960, 5, 802.
17. S.A. Shchukarev and G.A. Kokovin, Russ. J. Inorg. Chem., 1964, 9, 715.
18. J.G. Malm and H. Selig, J. Inorg. Nucl. Chem., 1961, 20, 189.
19. O. Ruff and W. Kwasnik, Z. anorg. Chem., 1934, 219, 65.
20. J.P. King and J.W. Cobble, J. Amer. Chem. Soc., 1960, 82, 2111.
21. R.H. Busey, K.H. Gayer, R.A. Gilbert and R.B. Bevan Jr., J. Phys. Chem., 1966, 70, 2609.
22. R.C. Weast, "CRC Handbook of Chemistry and Physics", 49th Ed. (The Chemical Rubber Co., 1968-9).
23. G.J. Ewing and C.J. Mazac, Anal. Chem., 1966, 38, 1575.
24. E. Lange and R.M. Fosse, Z. Physik. Chem., 1927, 125, 431.
25. R.J. Irving and I. Wadsö, Acta Chemica Scandinavica, 1964, 18, 195.
26. J.O. Hill, G. Öjelund and I. Wadsö, J. Chem. Thermodynamics, 1969, 1, 111.

27. J.L. Settle, H.M. Feder and W.N. Hubbard, *J. Phys. Chem.*, 1961, 65, 1337.
28. J. Schröder and F.J. Sieben, *Chem. Ber.*, 1970, 103, 76.
29. National Bureau of Standards (Washington D.C.), *Technical Note 270-3* (1968).
30. J.E. McDonald, J.P. King, and J.W. Cobble *J. Phys. Chem.*, 1960, 64, 1345.
31. National Bureau of Standards (Washington D.C.), *Technical Note 270-4* (1969).
32. R.L. Graham and L.G. Hepler, *J. Amer. Chem. Soc.*, 1956, 78, 4846.
33. G.E. Boyd, J.W. Cobble and W.T. Smith Jr., *J. Amer. Chem. Soc.*, 1953, 75, 5783.
34. O. Kubaschewski, E.Ll. Evans and C.B. Alcock, "Metallurgical Thermochemistry" 4th Ed. (Pergamon Press, 1967).
35. D.W. Osborne, F. Schreiner, J.G. Malm, H. Selig and L. Rochester, *J. Chem. Phys.*, 1966, 44, 2802.
36. (a) O. Ruff, *Angew. Chem.*, 1933, 46, 239. (b) O. Ruff and W. Kwasnik, *Z. anorg. allg. Chem.*, 1934, 220, 96.
37. G.H. Cady and G.B. Hargreaves, *J. Chem. Soc.*, 1961, 1568.
38. S. Blanchard, French Atomic Energy Commission Report CEA-R3194 (1967).
39. A.J. Edwards, G.R. Jones and B.R. Steventon, *Chem. Comm.*, 1967, 462.
40. B.G. Ward and F.E. Stafford, *Inorg. Chem.*, 1968, 7, 2569.
41. I.R. Beattie, K.M.S. Livingston, D.J. Reynolds and G.A. Ozin, *J. Chem. Soc.(A)*, 1970, 1210.
42. K.F. Zmbov and J.L. Margrave, 1967, private communication included in *J.A.N.A.F. Thermochemical Tables*, 1971, NSRDS. NBS 37.45.

43. D.V. Korol'kov and G.N. Kudryashova, Russ. J. Inorg. Chem., 1970, 15, 1759.
44. S.A. Shchukarev, I.V. Vasil'kova and G.I. Novikov, Zh. Neorg. Khim., 1958, 3, 2642.
45. J.A.N.A.F. Thermochemical Tables, D.R. Stull et al., Dow Chemical Co., Midland, Mich., 1971, NSRDS. NBS37.
46. E. Greenberg, C.A. Natke and W.N. Hubbard, J. Phys. Chem., 1965, 69, 2089.
47. H.A. Porte, E. Greenberg and W.N. Hubbard, J. Phys. Chem., 1965, 69, 2308.
48. H. Schafer and F. Kahlenberg, Z. anorg.allg. Chem., 1958, 294, 242.
49. D.N. Tarasenkow and A.V. Komandin, Zh. Obshch. Khim., 1940, 10, 1319.
50. V.M. Amosov, Izv. Vysskikh.Uchebn. Zavedenii, Tsvetn. Met., 1963, 6, 103.
51. P. Gress, C. Hayman, D.L. Levi and G.L. Wilson, Trans. Faraday Soc., 1960, 56, 318.
52. National Bureau of Standards (Washington D.C.), Technical Note 270-5.(1971).
53. L.A. Reznitskii, Zh. Fiz. Khim., 1967, 41, 1482.
54. S.A. Shchukarev, M.A. Oranskaya and T.S. Shemyakina, Russ. J. Inorg. Chem., 1960, 5, 1036.
55. S.A. Shchukarev, I.V. Vasil'kova and B.N. Sharupin, Vestn. Leningr. Univ., 14, Ser. Fiz. i. Khim., 1959, 73.
56. S.A. Shchukarev and A.V. Suvorov, Russ. J. Inorg. Chem., 1961, 6, 763.

57. G.L. Gal'chenko, D.A. Gedakyan, B.I. Timofeev, S.M. Skuratov, T.I. Serebryakova and G.W. Samsonov, Dokl. Akad. Nauk. SSSR, 1966, 170, 132.
58. H. Schafer and F. Kahlenberg, Z. anorg. Chem., 1960, 305, 178.
59. S.A. Shchukarev, E.K. Smirnova, I.V. Vasil'kova and L.I. Lappo, Vestn. Leningr. Univ., 15, Ser. Fiz. i. Khim., 1960, 113.
60. C.J.W. Fraser, Ph.D. Thesis, Leicester (1970).
61. J.H. Junkins, R.L. Farrar Jr., E.J. Barber and H.A. Bernhardt, J. Amer. Chem. Soc., 1952, 74, 3464.
62. R.N. Goldberg and L.G. Hepler, Chem. Rev., 1968, 68, 229.
63. F.J. Keneshea, D. Cubicciotti, G. Withers and H. Eding, J. Phys. Chem., 1968, 72, 1272.
64. Y. Saeki and R. Matsuzaki, Denki Kagaku, 1965, 33, 155.
65. Y. Saeki, R. Matsuzaki, M. Yanai and K. Funaki, Kogyo Kagaku Zasshi, 1968, 71, 350.
66. S.A. Shchukarev, G.I. Novikov and N.V. Andreeva, Vest. Leningr. Univ., 14, No4, Ser. Fiz. i. Khim., Nol, 1959, 120.
67. H.H. Claassen and H. Selig, Isreal. J. Chem., 1969, 7, 499.
68. D.S. Dyer and R.O. Ragsdale, Chem. Comm., 1966, 601.
69. D.S. Dyer and R.O. Ragsdale, Inorg. Chem., 1967, 6, 8.
70. L.E. Orgel, "An Introduction to Transition-Metal Chemistry. Ligand Field Theory". 2nd Ed., (Methuen, 1966).
71. N. Bartlett, Angew. Chem. (Int. Ed.), 1968, 7, 433.
72. N. Bartlett, S.P. Beaton and N.K. Jha, Chem. Comm., 1966, 168.

73. J.R. Geichman, E.A. Smith, S.S. Trond and P.R. Ogle, *Inorg. Chem.*, 1962, 1, 661.
74. F.P. Gortsema and R.H. Toenskoetter, *Inorg. Chem.*, 1966, 5, 1217.
75. S.A. Shchukarev, I.V. Vasil'kova, V.M. Drozdova and N.S. Martynova, *Russ. J. Inorg. Chem.*, 1959, 4, 13.
76. G.B. Hargreaves and R.D. Peacock, *J. Chem. Soc.*, 1957, 4212.
77. J. Burgess, I. Haigh and R.D. Peacock, *Chem. Comm.*, 1971, 977.
78. T.C. Waddington, *Adv. Inorg. Chem. Radiochem.*, 1959, 1, 157.
79. N.D. Zaitseva, *Russ. J. Inorg. Chem.*, 1963, 8, 1239.
80. A.F. Kapustinskii, *Quart. Rev.*, 1956, 10, 283. (and earlier references).
81. C.D. Kennedy and R.D. Peacock, *J. Chem. Soc.*, 1963, 3392.
82. A.F. Clifford, H.C. Beachell and W.M. Jack, *J. Inorg. Nucl. Chem.*, 1957, 5, 57.
83. G.A. Olah, E.B. Baker, J.C. Evans, W.S. Tolgyesi, J.S. McIntyre and I.J. Bastien, *J. Amer. Chem. Soc.*, 1964, 86, 1360.
84. I.V. Vasil'kova, N.D. Zaitseva and V.A. Petrova, *Russ. J. Inorg. Chem.*, 1968, 8, 124.
85. N. Bartlett and D.H. Lohmann, *Proc. Chem. Soc.*, 1962, 277.
86. N. Bartlett and D.H. Lohmann, *J. Chem. Soc.*, 1962, 5253.
87. F.H. Field and J.L. Franklin, "Electron Impact Phenomena", (Academic Press, New York, 1957).

88. N. Bartlett, Proc. Chem. Soc., 1962, 218.
89. J.R. Geichman, E. A. Smith and P.R. Ogle, Inorg. Chem., 1963, 2, 1012.
90. J.H. Canterford, T. A. O'Donnell and A.B. Waigh, Aust. J. Chem., 1971, 24, 243.
91. N. V. Sidgwick, "The Chemical Elements and their Compounds", P1034 (Oxford Univ. Press, 1950).
92. A.B. Burg, "Fluorine Chemistry", 1, 112 (Academic Press, 1950).
93. T.A. O'Donnell and D.F. Stewart, J. Inorg. Nucl. Chem., 1962, 24, 309.
94. J.H. Canterford and T.A. O'Donnell, Inorg. Chem., 1967, 6, 541.
95. J.H. Canterford and T.A. O'Donnell, Inorg. Chem., 1966, 5, 1442.
96. T.A. O'Donnell, D.F. Stewart and P. Wilson, Inorg. Chem., 1966, 5, 1438.
97. P.R. Hammond, J. Phys. Chem., 1970, 74, 647.
98. P.R. Hammond and R.R. Lake, Chem. Comm., 1968, 987.
99. P.R. Hammond and W.S. McEwan, J. Chem. Soc. (A), 1971, 3812.
100. R.R. McLean, D.W.A. Sharp and J.M. Winfield, J. Chem. Soc.(D), 1970, 452.
101. R.R. McLean, D.W.A. Sharp and J.M. Winfield, J. Chem. Soc. (Dalton Trans.), 1972, 676.
102. D.D. Gibler, unpublished.
103. B.C. Korshunov and V.N. Beznevskaya, Zh. Neorg. Khim., 1967, 12, 3280.

104. P.M. Boorman, N.N. Greenwood, M.A. Hildon and R.V. Parish, *Inorg. Nucl. Chem. Letters*, 1966, 2, 377.
105. L.A. Woodward and M.J. Ware, *Spectrochim. Acta*, 1963, 19, 775.
106. M. Mercer, T.J. Ouellette, C.T. Ratcliffe and D.W.A. Sharp, *J. Chem. Soc.(A)*, 1969, 2532.
107. J.C. Fuggle, D.W.A. Sharp and J.M. Winfield, *J. Fluorine Chem.*, 1971/2, 1, 427.
108. T.A. Edison, U.S. Patent 223898 (1880).
109. A. Rabenau, *Angew. Chem. (Int. Ed.)*, 1967, 6, 68.
110. Coolidge, J. *Amer. Inst. Elect. Eng.*, 1910, 953.
111. I. Langmuir, (a) *Proc. Amer. Inst. Elect. Engrs.*, 1912, 31, 1011. (b) *Phys. Rev.*, 1912, 34, 501. (c) *Trans. Amer. Electrochem. Soc.*, 1913, 23, 299.
112. W. Geiss, *Philips Techn. Rev.*, 1936, 1, 97.
113. E.A. Scribner, U.S. Patent 254780 (1882).
114. I. Langmuir, *J. Amer. Chem. Soc.*, 1915, 37, 1139.
115. O. Neunhoefffer and P. Schulz, *Ger. Patent* 841307 (1949).
116. E.G. Zubler and F.A. Mosby, *Illuminating Eng.*, 1959, 54, 734.
117. J.M. Rees, *Thorn Lighting Ltd. Techn. Conf.*, 1970, 5.
118. G.R. T'jampens and M.H.A. Van de Weijer, *Philips Techn. Rev.*, 1966, 27, 173.
119. J. Schröder, U.S. Patent 3263113 (1966).
120. G.M. Neumann and W. Knatz, *Z. Naturforsch.*, 1971, 26A, 863.

121. JANAF. Thermochemical Tables and Addenda I-III, Ed. D.R. Stull, Dow Chemical Co., Midland, Mich. (1965-8).
122. G.M. Neumann and W. Knatz, Z. Naturforsch., 1971, 26A, 1046.
123. J. Schröder, Philips Techn. Rev., 1964, 25, 359.
124. J. Schröder, Philips Techn. Rev., 1965, 26, 111.
125. A.C. Chapman and N.L. Paddock, J. Chem. Soc., 1962, 635.
126. M.K. Wilson and S.R. Polo, J. Chem. Phys., 1952, 20, 1716.
127. P.J.H. Woltz and A.H. Nielsen, J. Chem. Phys., 1952, 20, 307.
128. E.A. Jones, J.S. Kirby-Smith, P.J.H. Woltz and A.H. Nielsen, J. Chem. Phys., 1951, 19, 242.
129. J. Heiken and V. Knight, Spectrochem. Acta, 1964, 20, 295.
130. R.A. Svehla, NASA Tech. Report R-132 (1961).
131. J.C. de Vos, Physica, 1954, 20, 690.
132. O.C. Jones, J. Phys. (D), 1970, 3, 1967.
133. B.J. McBride, S. Hermel, J.G. Erhler and S. Gordon, NASA SP-3001 (1963).
134. K.S. Vorres and F.B. Dutton, J. Amer. Chem. Soc., 1955, 77, 2019.
135. V.L. Kolditz, V. Neumann and G. Kilch, Z. anorg. Chem., 1963, 325, 275.
136. V.L. Kolditz and G. Frucht, Z. anorg. Chem., 1961, 312, 11.
137. V.L. Kolditz, G. Kurschner and V.S. Calov, Z. anorg. Chem., 1964, 329, 172.

138. G.B. Hargreaves and R.D. Peacock, *J. Chem. Soc.*, 1960, 2618.
139. B. Cohen, A.J. Edwards, M. Mercer and R.D. Peacock, *Chem. Comm.*, 1965, 322.
140. G.W. Fraser, M. Mercer and R.D. Peacock, *J. Chem. Soc. (A)*, 1967, 1091.
141. G.W. Fraser, C.J.W. Gibbs and R.D. Peacock, *J. Chem. Soc. (A)*, 1970, 1708.
142. R.D. Peacock and D.F. Stewart, *Inorg. Nucl. Chem. Letters*, 1967, 3, 255.
143. L. Kolditz and V. Calov, *Z. Chem.*, 1966, 6, 431.
144. A.A. Opalovskii and K.A. Khaldoyanidi, *Russ. J. Inorg. Chem.*, 1968, 13, 310.
145. G.W. Fraser, R.D. Peacock and P.M. Watkins, *Chem. Comm.*, 1968, 1257.
146. B. Cohen and A.G. MacDiarmid, *Chem. Ind.*, 1962, 1866.
147. C.I. Merrill, M. Lustig and G.H. Cady, *OTS. US. Dept. Commerce*, AD285205 (1962). (See also *Chem. Abs.*, 1964, 60, 6463.).
148. H.L. Roberts and N.L. Ray, *J. Chem. Soc.*, 1960, 665.
149. C.J. Schack, R.D. Wilson and J.F. Hon, *Inorg. Chem.*, 1972, 11, 209.
150. J.W. Emsley, J. Feeney and L.H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy" 2 volumes (Pergamon Press, 1966).
151. A.M. Noble and J.M. Winfield, *Chem. Comm.*, 1969, 151.

152. R.D. Peacock, Proc. Chem. Soc., 1957, 59.
153. A.J. Edwards, R.D. Peacock and R.W.H. Small, J. Chem. Soc., 1962, 4486.
154. H. Yagoda and H.A. Fales, J. Amer. Chem. Soc., 1936, 58, 1494.
155. D.W. Sherwood and G.C. Banikiotes, U.S. Patent 2695214 (1954).
156. Lambie, Analyst, 1945, 70, 124.
157. A.I. Vogel, "Quantitative Inorganic Analysis including Elementary Instrumental Analysis" 3rd Edition. (Longmans, 1961).
158. G.B. Hargreaves, Ph.D. Thesis (Univ. of London, 1959).
159. (a) H.H. Willard and O.B. Winter, Ind. Eng. Chem., Anal. Ed., 1933, 5, 7. (b) F. Seel, Angew. Chem. (Int. Ed.), 1964, 3, 424.
160. J. Gaunt, Trans. Faraday Soc., 1953, 49, 1122.
161. G. Nagarajan and D.C. Brinkley, Z. Naturforsch., 1971, 26A, 1658.
162. G. Herzberg, "Molecular Spectra and Molecular Structure 11. Infra red and Raman Spectra of Polyatomic Molecules" (D. Van Nostrand, New York, 1960).
163. H. Kim, P.A. Souder and H.H. Claassen, J. Mol. Spec., 1968, 26, 46.
164. B. Weinstock and J.G. Malm, Proc. 2nd U.N. Int. Conf. on peaceful uses of At. En., Geneva, 1958, 28, 125.