

CHROMIUM TETRAFLUORIDE AND RELATED COMPOUNDS

by

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ABSTRACT

The present investigation was concerned with a study of the preparation and properties of chromium tetrafluoride and its complexes; magnetic properties and X-ray structures were also studied. Attempts to prepare the pentafluoride of chromium using fluorinating agents other than fluorine were unsuccessful.

Chromium tetrafluoride was prepared by the action of fluorine on the heated metal, the products being involatile chromium trifluoride, volatile chromium tetrafluoride, and more volatile fluorides which were condensed at -78°C . The best yields of chromium tetrafluoride were obtained at 350°C and with a moderate flow-rate of fluorine.

Chromium tetrafluoride is a glassy solid which forms blue vapours when heated. It does not dissolve in the usual organic solvents and is hydrolysed readily in moist air. It is paramagnetic, the moment corresponding to two unpaired electrons, and has a Weiss Constant of -70° .

Chemically, chromium tetrafluoride is surprisingly inert and at room temperature does not react with ammonia, pyridine, sulphur dioxide, sulphur trioxide, iodine pentafluoride, bromine trifluoride, bromine pentafluoride, chlorine trifluoride, or selenium tetrafluoride. However, it reacts instantaneously with water giving Cr^{+3} and CrO_4^{-2} ions in solution. When heated with bromine trifluoride for longer periods, reaction occurs to give $\text{CrF}_3 \cdot 0.5\text{BrF}_3$. On heating with a mixture of bromine trifluoride and bromine pentafluoride, a wine-coloured solution was obtained, and the residue after distillation of volatile materials was $\text{CrOF}_3 \cdot 0.25\text{BrF}_3$. The reaction of selenium tetrafluoride with chromium tetrafluoride at 120°C yielded two compounds, $\text{CrF}_3 \cdot \text{SeF}_4$ and $\text{CrF}_2 \cdot \text{SeF}_4$.

Complexes of the type ACrF_5 , where $\text{A} = \text{K}, \text{Rb}, \text{or Cs}$, were prepared for the first time, by heating the respective alkali metal chloride and chromium tetrafluoride in a 1:1 molar ratio in bromine trifluoride. The resulting complex compounds contained half a

molecule of bromine trifluoride per molecule of the complex, if the removal of excess bromine trifluoride, after the reaction, was carried out at 100°C . However, if removal was carried out at 160°C , the pure complexes were obtained.

Complexes of the type A_2CrF_6 , where $\text{A} = \text{K}, \text{or Cs}$, were prepared in bromine trifluoride solutions. The presence of extra bromine trifluoride in the molecule of the complex compound affected the structure seriously in potassium complexes but had no effect on cesium complexes. Thus $\text{K}_2\text{CrF}_6 \cdot 0.5\text{BrF}_3$ was tetragonal and on heating at 160°C in vacuo yielded the cubic modification of pure K_2CrF_6 ; $\text{Cs}_2\text{CrF}_6 \cdot 0.5\text{BrF}_3$ and Cs_2CrF_6 were both cubic.

Reactions of chromium trioxide with bromine trifluoride, bromine pentafluoride, and chlorine trifluoride were also investigated. With bromine fluorides, the products obtained were the corresponding adducts of CrOF_3 . These are very reactive and sensitive to moist air. The compounds are paramagnetic.

The reaction with chlorine trifluoride was very interesting because the appearance of the product depended on the experimental conditions. If the reaction was carried out at ordinary temperature, the product was a buff-coloured powdery mass, but if the reaction was performed by passing chlorine trifluoride vapour over heated chromium trioxide ($100\text{--}120^{\circ}\text{C}$), the product was a brick-red substance. Chemical analyses and magnetic measurements indicated that both these products were identical and had the composition $\text{CrOF}_3 \cdot 0.25\text{ClF}_3$. The brick-red product could be converted into the light buff-coloured powdery mass by heating at 70°C in vacuo.

Reactions of potassium dichromate with bromine trifluoride, bromine pentafluoride, and chlorine trifluoride were also investigated. Potassium dichromate reacted with these smoothly at room temperature and the product of reaction in each case was KCrOF_4 .

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The compounds investigated in the present research are tabulated below.

<u>Compound</u>	<u>Magnetic Moment</u>		<u>Crystal Structure</u>
	μ_{294} (B.M.)	(θ)	
$\text{CrF}_2 \cdot \text{SeF}_4$	5.34		complex
$\text{CrF}_3 \cdot \text{SeF}_4$
$\text{CrF}_3 \cdot 0.5\text{BrF}_3$	3.96	
$\text{CrF}_3 \cdot \text{BrF}_3$	3.67	
CrF_4	3.02	(-70°)
KCrF_5	3.15		hexagonal
RbCrF_5	3.17	(-32°)	hexagonal
CsCrF_5	3.20		cubic
$\text{KCrF}_5 \cdot 0.5\text{BrF}_3$	3.22	(-80°)	tetragonal
$\text{CsCrF}_5 \cdot 0.5\text{BrF}_3$. . .		cubic
$\text{K}_2\text{CrF}_6 \cdot 0.5\text{BrF}_3$	3.06		tetragonal
K_2CrF_6	3.06		cubic
$\text{Cs}_2\text{CrF}_6 \cdot 0.5\text{BrF}_3$	3.14		cubic
$\text{CrOF}_3 \cdot 0.25\text{BrF}_3$	2.02	
$\text{CrOF}_3 \cdot 0.25\text{BrF}_5$	1.85	
$\text{CrOF}_3 \cdot 0.25\text{ClF}_3$	1.83	
$\text{KCrOF}_4 \cdot 0.5\text{BrF}_3$	1.73	($+4^\circ$)	orthorhombic
$\text{KCrOF}_4 \cdot 0.5\text{BrF}_5$	1.75		complex

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I. INTRODUCTION

The element fluorine, the most reactive halogen, was isolated in 1886 by Moissan (1). Because of its highly reactive nature, its isolation was delayed, and its chemistry is less well known than those of other halogens, since unless considerable care is taken a study of its behaviour will always lead to fluorination of the apparatus. However, with the development of many fluorine-resistant materials and with the availability of fluorine commercially, rapid progress has been made in recent years, and research in this field is currently very intense. The present activity encompasses all aspects of fluorine chemistry and has resulted not only in the preparation of many new, simple and complex compounds, some of which are indeed unique, such as O_2PtF_6 (2), XeF_4 (3), and $XePtF_6$ (4), but also in the re-examination of previously reported compounds, e.g. a compound reported to be osmium octafluoride has been shown to be, in reality, osmium hexafluoride (5). Excellent reviews (6,7,8) have also appeared in recent years.

Fluorine is the lightest halogen and like first members of other periodic groups, it possesses unusual properties. The outermost shell of the fluorine atom ($n=2$) contains only p electrons and no d electrons, the electronic configuration being $1s^2 2s^2 2p^5$. This shell can be completed by forming one σ -bond, (i.e. covalent bond

formation), or by transfer of an electron to it resulting in the formation of a fluoride ion. The chemistry of fluorine, therefore, is limited to the reactions of fluoride ions and of its σ -bonded covalent compounds. The outermost shells of the other halogen atoms, on the other hand, contain d orbitals and can form $d\pi$ bonds.

Another important feature of fluorine chemistry originates in fluorine's small size ($R = 1.36 \text{ \AA}$) and high electronegativity. Its small size makes it sterically possible to pack relatively large numbers of fluorine atoms around a given atom. This together with the high electronegativity of fluorine, results in the formation of many fluorides in which the elements show high (though not necessarily the highest) oxidation states. It also results in many inorganic fluorides having structures quite different from those of the corresponding chlorides, bromides, and iodides. On the other hand, the radii of the oxide and hydride ions are close to that of the fluoride ion; crystallographic resemblances between fluorides and oxides have long been known and those between fluorides and hydrides have also been pointed out (9).

One of the most important achievements in fluorine chemistry has been the preparation and study of the halogen fluorides. Their physical properties and general chemical behaviour have been reviewed recently (10). The halogen fluorides have found numerous uses as fluorinating agents,

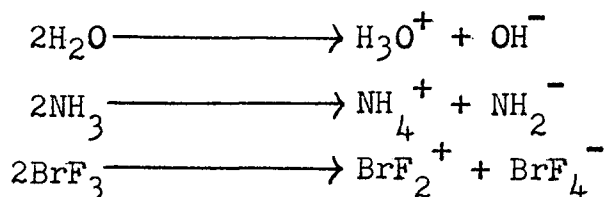
and in this respect they complement the behaviour of elemental fluorine, inasmuch as fluorinations involving elemental fluorine usually are vigorous and result in oxidation to the higher oxidation states of the elements, while the fluorinating powers of the halogen fluorides cover a range of reactivity and need not always result in oxidations of lower states. In addition, fluorinations in the liquid phase are possible with halogen fluorides. An order of their reactivity can be derived from the magnitude of the partial negative charge on the fluorine atom in these compounds. Since the driving force for fluorinating reactions is to increase this partial negative charge, the compounds with low numerical value of partial negative charge will be the strong fluorinating agents. The value of the partial negative charge (11) on the fluorine atom in each compound is as follows:

Compound	ClF_3	BrF_5	IF_7	BrF_3	IF_5	ClF	BrF
Partial negative charge on fluorine atom	0.04	0.05	0.06	0.07	0.08	0.09	0.13

One would expect ClF_3 with the lowest partial negative charge on fluorine to be the strongest fluorinating agent and this is indeed observed; chlorine trifluoride is as strong a fluorinating agent as elemental fluorine. Chlorine monofluoride and bromine monofluoride have not been used for fluorinating purposes; the former has a

very low freezing point and boiling point and the latter is highly unstable (10).

In addition to the fluorinating properties of the halogen fluorides, their use as non-aqueous solvents and hence as media for the preparation of complex fluorides has been much studied (12). Bromine trifluoride has been mostly used for this purpose. The remarkable solvent properties of bromine trifluoride are related to its association and ionization and are consistent with the high value of Trouton's constant (13) and its other physical properties. In this respect bromine trifluoride resembles ammonia and water.



The specific conductivity of bromine trifluoride at 25°C is $8.0 \times 10^{-3} \text{ ohm}^{-1} \text{ cm.}^{-1}$ in contrast to 10^{-6} for chlorine trifluoride and 2×10^{-5} for iodine pentafluoride (10).

Base analogues in this solvent system and the corresponding acids containing BrF_2^+ have been prepared. Bromine trifluoride may thus act as a fluoride ion donor or acceptor in an acid-base type solvent system in which fluoride ion plays a role similar to that of the proton in water.

Another important field of fluorine chemistry in which rapid progress has been made in recent years is in the study of fluorine derivatives of transition metals. These may be ionic, covalent, or polymeric. Ionic fluorides usually contain elements in their lower oxidation states and are characterized by high melting points, e.g. trifluorides of the first transition metal series. Fluorides containing metals in high oxidation states are usually gases or volatile liquids or solids, resembling the covalent fluorides of non-metals. In a few fluorides, macromolecular structures seem to occur, e.g. TiF_4 , BeF_2 .

The element chromium forms a number of fluorides in which the oxidation number of chromium may be +2, +3, +4, or +5. Chromium (II) fluoride and chromium (III) fluoride have been known since 1894 (14) and are prepared by the action of hydrogen fluoride on the respective chlorides, but their crystal structures have been determined only recently. Chromium (II) fluoride (15) has a distorted rutile type structure with four neighbours at 2.01 Å and two neighbours at 2.43 Å. The green chromium (III) fluoride (16) possesses a vanadium trifluoride structure. Many complexes derived from both of these fluorides are known.

The +4 oxidation state for chromium is not a common one; rather, it is exhibited in only a few cases. The known compounds are chromium tetra-*t*-butoxide,

chromium tetrafluoride, chromium tetrachloride, and chromium dioxide. Chromium tetra-*t*-butoxide was obtained (17) by heating bis-benzene chromium with di-*t*-butyl peroxide in a sealed tube. Chromium dioxide was first described by Mauss (18) who maintained that it could not be regarded as an oxide of tetrapositive chromium. Its magnetic properties have been studied (19) and found dependent on the mode of preparation (20). The +4 oxidation state in the dioxide has recently been questioned (21) and it has been suggested that it is an acid chromium (III) compound, $(\text{CrO})_2\text{CrO}_4$. Chromium tetrachloride has been reported by von Wartenberg (22) and probably exists only in the gaseous state. Chromium tetrafluoride was prepared by von Wartenberg (23) by the action of fluorine at 300--500°C on chromium, chromium trichloride, or chromium trifluoride. He also observed that chromium tetrafluoride formed steel-blue vapours.

Apart from this, no work has previously been reported on the properties of chromium tetrafluoride. However, complexes containing tetrapositive chromium have recently been prepared: K_2CrF_6 by Klemm and Huss (24), and Rb_2CrF_6 and Cs_2CrF_6 by Bode and Voss (25).

A fire-red pentafluoride of chromium has been reported to form in small quantities simultaneously with chromium tetrafluoride (23), or to be formed by thermal decomposition of hexafluorochromates (25). Recently a

series of oxyfluoride complexes containing chromium in the +5 oxidation state has been described (26), e.g. KCrOF_4 , AgCrOF_4 .

Thus, the work reported to date on the higher fluorides of chromium is scanty and no systematic investigation seems to have been carried out. This was noticed by Sharpe (27) when he remarked that the higher fluorides of chromium merit further investigation.

It was therefore decided to investigate further the fluorination of chromium metal and to study the preparation and properties of these higher fluorides; in the following pages a report is given of the preparation and properties of chromium tetrafluoride and of complexes derived from it.

II. THE PREPARATION AND PHYSICAL PROPERTIES OF CHROMIUM TETRAFLUORIDE

A. PREPARATION

The +4 oxidation state of chromium in chromium tetrafluoride suggests two methods of preparation--oxidative and reductive. Oxidative methods would involve the fluorination of compounds containing chromium in 0, +2, or +3 oxidation states. The reductive methods would demand a compound containing chromium in an oxidation state higher than +4 and then reducing it to the desired oxidation state and fluorinating it simultaneously. For reductive methods chromium trioxide would be a very suitable compound and is easily available in a very pure grade. Its fluorination reactions have been studied and are described in a later section. In oxidative methods chromium metal would be an ideal starting material since it is readily available in a very pure form (99.9%), and can be handled easily. Compounds of +2 and +3 chromium would have to be obtained anhydrous and are more difficult to handle than the metal. Fluorination of chromium or chromium (III) trifluoride has been reported by von Wartenberg (23) to yield chromium tetrafluoride and small amounts of chromium pentafluoride. In the present work, the tetrafluoride of chromium was always prepared by fluorination of the metal at a temperature of 350°C; the details are given in the experimental section of this thesis.

The direct fluorination of chromium metal has been observed to give involatile chromium (III) trifluoride, volatile chromium tetrafluoride, and more volatile fluorides which are condensed at -78°C . The best yields of chromium tetrafluoride have been obtained at a temperature of approximately 350°C and with a moderate flow-rate of fluorine.

At lower temperatures or with a low flow-rate of fluorine, the yield is very poor while on the other hand, at higher temperatures or with a high flow-rate, fluorination occurs too vigorously and so much heat is liberated that the nickel reactor tube becomes dull-red and is attacked by the stream of fluorine, leading to contamination of the product.

During the preparation it was always observed that dense yellow vapours were produced which condensed in the trap cooled to -78°C . The solid was chromyl fluoride as indicated by the chromium analysis, and by the fact that a small amount of the compound was sufficient to ignite benzene, a property previously described for chromyl fluoride (28).

The formation of chromyl fluoride results from the availability of oxygen during the fluorination reaction. Oxygen may be available from the metal which is usually covered with an oxide layer, or from the fluorine itself. In order to reduce the yield of chromyl fluoride

during fluorination, it was decided to pass hydrogen over the heated metal prior to fluorination to reduce any oxide layer present. A few fluorinations were carried out in which the metal was heated in a stream of hydrogen gas and then fluorinated. This resulted in a decreased yield of chromyl fluoride. However, the formation of chromyl fluoride could not be altogether stopped due to the fact that a small amount of oxygen was always present as impurity in the fluorine itself.

Much care had to be exercised while handling chromium tetrafluoride. Because of its ready decomposition with moisture, it needed to be handled in a dry-box. It could be stored in well dried glass apparatus without any reaction. A sample was sealed in vacuo in a small pyrex glass tube and recovered unchanged after several months, indicating that no reaction occurred with glass.

B. PHYSICAL PROPERTIES

The preparation and some physical properties of chromium tetrafluoride were reported in 1941 by von Wartenberg (22). He observed this compound to be cinnamon-coloured, and amorphous with a density equal to 2.9 g/cc. He also noticed that it formed blue vapours and attacked glass when heated to 150°C.

Chromium tetrafluoride, as obtained in the present study, is a brown-greenish solid, insoluble in the usual organic solvents. When heated in a dry glass vessel

in vacuo, it sublimes at 150°C, condensing in the cooler part of the tube as a deep-green deposit. At higher temperatures, in air, it forms blue vapours and decomposition occurs with the formation of chromyl fluoride, and reaction with glass also occurs. In air it becomes covered very quickly with a brown crust and therefore must be handled under dry-box conditions.

The X-ray picture of the powder showed no lines despite many attempts to obtain a crystalline product. The samples were then taken in glass or silica tubes and sealed under vacuum. The tubes were heated for different intervals of time at different temperatures. Temperatures in the region of 140--170°C caused reaction with the glass container and decomposition products were obtained. Long intervals of time at lower temperatures also resulted in reaction with the tubes. Annealing at temperatures in the region of 80°C did not give products which showed diffraction lines. However, in one case a sample heated at 100°C for seventy-two hours gave a few broad lines which could be indexed on a tetragonal lattice ($a = 9.350 \text{ \AA}$; $c = 13.34 \text{ \AA}$). It was not possible to decide if these lines were due to some product of decomposition or due to the tetrafluoride.

Hückel (29) has classified halogen compounds as being volatile, non-volatile, (or of intermediate type), depending on whether their boiling points lie below 300°C

or are very high or in the neighbourhood of 300°C. Volatile halides are characterized by forming molecular lattices while the involatile halides possess coordination lattices. A molecular lattice is formed if the coordination number of the central atom in the isolated molecule is the same as in the lattice, while in a coordination lattice the coordination number of the central atom in the lattice is a multiple of that of the central atom in the isolated molecule. Molecular lattices are formed if:

- (i) the central atom is well shielded by the surrounding ligands, i.e. the coordination number of the central atom is high
- (ii) the bonds to the central atom are weakly polarizable and the interaction between molecules will not affect the bonding in the individual molecule
- (iii) the bonds are weakly polar

In transition metal fluorides of the first series which contain large fluoride ions ($R_F = 1.36 \text{ \AA}$) surrounding transition metal cations which are quite small, the cation will be well shielded and the compounds might be expected to be volatile having molecular lattices, especially if the molecule contains more than three atoms of fluorine per atom of the metal. Thus we might expect the fluorides of the compositions MF_4 , MF_5 , MF_6 , and still higher fluorides to

form molecular lattices and possess high volatility. This is indeed true as the majority of hexafluorides are volatile (boiling below 60°C) (7), so also are pentafluorides (7), boiling below 300°C. The trifluorides possess ionic lattices as is shown by their high melting points.

Tetrafluorides deserve special mention since they occupy a unique position between the two extreme types. Formation of an ionic coordination lattice in their case will require a coordination number of at least eight for the central atom. If consideration is given to the first transition series only, it can safely be said that the possibility of a coordination number of eight for the central atom is unlikely. The maximum possible coordination number is six, for which there is ample evidence since anionic complexes of these elements in which the central atom has a coordination number of six are well known. Thus, from a consideration of coordination numbers, the formation of a purely ionic lattice in tetrafluorides is highly unlikely, especially for those of the first transition series-- Ti, V, Cr, Mn, Fe, Co, Ni, and Cu. In this series, only the elements Ti, V, Cr, and Mn form tetrafluorides, of which the first three are better known (7) while the last one has been isolated very recently and little is yet known about it (30).

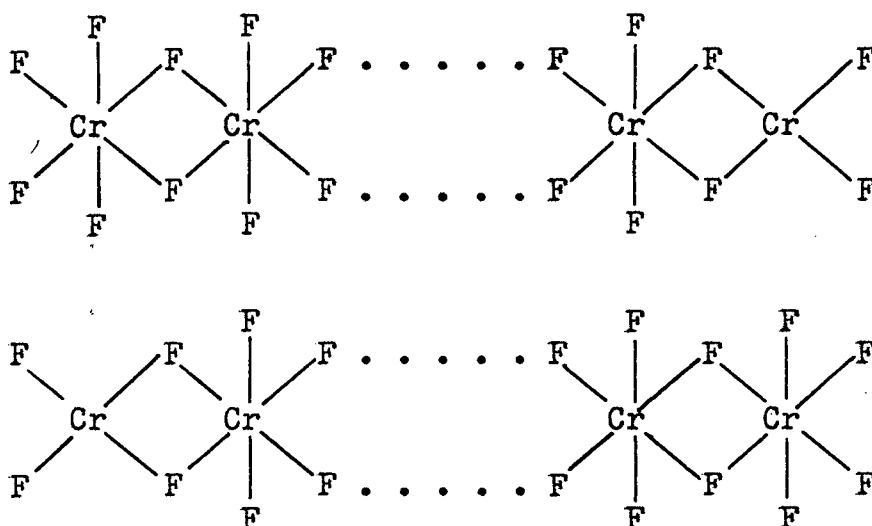
That the tetrafluorides of titanium and tin also do not form molecular lattices was suggested by Hückel (29) who observed that the densities of these two fluorides were

greater than those of the corresponding tetrachlorides. This should not be the case if both types of halides form molecular lattices. In order to account for this discrepancy in density, he suggested a chain structure for titanium tetrafluoride, formed from condensed TiF_6 octahedra in which each titanium atom has acquired a coordination number of six, except the one at the end of the chain which has the coordination number four only. This will make the chain polar but if the neighbouring chains are arranged such that one chain has the titanium atom with coordination number four at one end and its neighbour has this atom at the other end, the crystal will not possess a polar axis.

The similar volatilities of titanium, vanadium, and chromium tetrafluorides and the tendency of these elements to achieve a maximum coordination number of six suggest that the tetrafluorides of these elements are polymers of condensed octahedra making contact along one edge. Such a structure for vanadium tetrafluoride has already been suggested (31). This is supported by the fact that the density of vanadium tetrafluoride is higher than that of vanadium tetrachloride: for VF_4 $d = 3.15$ g/cc, for VCl_4 $d = 1.84$ g/cc. Chromium tetrafluoride may also be assumed to have formed from condensed CrF_6 octahedra.

The suggested chain structure for titanium tetrafluoride has been supported by recent studies of the specific heat of titanium tetrafluoride (32). The attainment of

coordination number six in vanadium tetrafluoride and chromium tetrafluoride is supported by their magnetic moments which are higher than the spin-only values, suggesting an orbital contribution characteristic of ions in an octahedral environment. This is discussed in detail later. The chain structure of tetrafluorides is also in harmony with the ease of sublimation of these compounds. The proposed structure is:



C. COORDINATION NUMBER OF CHROMIUM (IV)

The coordination number of an atom or ion is a very important property of the ion as it gives an insight into the structure of the compounds and the arrangement of atoms within the structure. The coordination number of an atom is a function of both electrostatic interactions and of size factors.

1. Electrostatic Considerations

Kossel (33) used electrostatic concepts to explain

the phenomenon of complex formation and showed that the systems arising from the attraction between oppositely charged ions and possessing minimum potential energy did not as a rule correspond to the addition of n monovalent anions to an ion of $+n$ charge. In an anionic complex there are two types of forces at work, forces of attraction between cations and anions, and forces of repulsion between anions. Magnus (34) computed the coefficients expressing the ratio between the forces of attraction and repulsion for a series of complex ions with varying numbers of coordinated anions and their varying geometrical arrangements. These coefficients are called screening constants. The general expression (35) for the energy of formation (U) of the complex ion, will take the form

$$U = p(n - sp) \frac{e^2}{r}$$

where p = number of coordinated anions

n = charge on the central metal ion

r = radius of the metal ion

sp = screening constant, its value depending on p

For a constant r , the value of U will be proportional to $p(n - sp)$. If we compute the value of U for varying p (for constant charge n and radius r) of the central ion, we find that U at first increases, passes through a maximum, and then decreases. For an ionic charge of $+4$ on the central ion, the values of $p(n - sp)$ for different values of p are

given below.

	<u>n = 4</u>					
p	4	5	6	7	8	
p(n - sp)	12.32	13.12	14.04	11.90	12.24	

It is seen in the above that the most likely coordination number for an ion in a +4 oxidation state surrounded by negative ions each of unit charge, is six. Similar electrostatic considerations lead to the following maximum coordination numbers (36) for different charges on the central ion and singly charged negative ions.

charge on central ion	1	2	3	4	5	6	7	8
maximum coordination number for singly charged negative ions	2	4	5	6	8	8	8	12

The above considerations are, of course, based on the assumption that four groups are arranged tetrahedrally and six, octahedrally.

2. Size Factor

In addition to electrostatic considerations, the other important factor governing the coordination number and hence the stereochemical arrangement is the relative magnitude of the sizes of the cation and the anions. The values of maximum coordination numbers produced from electrostatic interactions are valid insofar as spatial factors do not play a role--for example a large central ion. Increasing the number of coordination ions will bring them

in contact with one another and will at one stage result in no contact with the central ion. Actually a critical radius ratio can be calculated for each coordination number. The critical radius ratio is that value of the ratio of the radii of the central ion and coordinated ions for which the coordinated ions will touch each other as well as the central ion. In these calculations the ions are assumed to be spherical. The ratios for different coordination numbers are given below (36).

maximum coordination number	2	3	4	6	8	10
r^+ / r^-	-	0.15	0.22	0.41	0.73	1.00

The radius of Cr^{+4} is 0.56 Å (37) which gives a value of radius ratio $\text{Cr}^{+4}:\text{F}^-$ equal to 0.41, equal to the minimum characteristic of octahedral configuration.

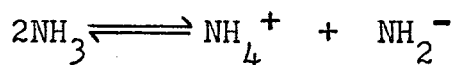
Thus, from the consideration of electrostatic and size factors, an octahedral coordination is suggested for chromium in the +4 oxidation state, and is consistent with the proposed chain structure.

III. CHEMICAL PROPERTIES OF CHROMIUM TETRAFLUORIDE

Chromium, like other transition metals, shows many oxidation states, of which +2, +3, and +6 are well known. The oxidation state of +4 is not characteristic for chromium and is exhibited in only a few cases, e.g. chromium tetrabutoxide, the oxide CrO_2 , and chromium tetrafluoride. Chromium in the +4 oxidation state has the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$ containing two unpaired electrons in the d orbitals. It has, therefore, vacant d orbitals and may be expected to form coordination compounds by accepting electrons from donor molecules. Chromium in the +3 state has an extraordinarily great tendency to form complex compounds, a tendency exceeded by no other element and equalled perhaps only by tripositive cobalt and tetrapositive platinum. Dipositive chromium also forms a variety of complex compounds but the great majority of these are strong reducing agents. The maximum coordination number of chromium in these complexes is six, as is also the case for the other members of the first transition metal series. The coordinated groups may be neutral molecules, negative ions, or a combination of these. Neutral groups which have been used as ligands include nitrogen bases-- ammonia, pyridine, etc.--and oxides such as sulphur dioxide, nitric oxide, nitrogen dioxide, and carbon monoxide. The ligands vary considerably in their strength to form coordination compounds.

A. REACTION WITH AMMONIA

Ammonia, the simplest and most easily available electron-donor molecule, is a base in the Lewis sense. Besides combining with protonic acids, ammonia forms addition compounds with nonprotonic electronically unsaturated molecules like boron trifluoride and sulphur trioxide and with many other metal ions. In both cases the reaction may be regarded as neutralization in the Lewis sense. Interaction with electronically unsaturated molecules leads to the formation of molecular addition compounds, e.g. $\text{H}_3\text{N}:\text{BF}_3$, and reaction with metal ions to ammoniated cations, e.g. $\text{Cr}(\text{NH}_3)_6^{+3}$, $\text{Pt}(\text{NH}_3)_4^{++}$, etc. In addition to being an electron-donor, ammonia is also well known as an acid-base solvent system. It ionizes to form acidic and basic ionic species, according to the equation



$$K_{\text{ion}} = 1.9 \times 10^{-33} \text{ at } -50^\circ\text{C} \quad (38)$$

Thus, solvolysis can occur in liquid ammonia in addition to the formation of donor-acceptor complexes. Compounds which are soluble in liquid ammonia are often solvolysed existing as hypothetical acids or bases. However, it may be pointed out that fluorides have a low tendency to solvolyse. For example, vanadium tetrachloride is solvolysed in liquid ammonia (39) but vanadium tetrafluoride forms an adduct (31). Similarly, tungsten hexachloride (40) and niobium penta-

chloride (41) are solvolysed, but their respective fluorides form coordination compounds (42,43). When excess dry liquid ammonia was reacted with chromium tetrafluoride, the starting materials were recovered unchanged, indicating that no reaction had taken place.

Another well known nitrogen base used to form coordination compounds is pyridine, which has also received some attention as a solvent (44) and which possesses a lone electron pair on nitrogen which can be donated to acceptor molecules. Many coordination compounds with pyridine as donor molecule are known. However, chromium tetrafluoride did not show any reaction with pyridine either.

The possibility of forming an ammine can be followed from a consideration of the lattice energies (45). The formation of an ammine involves a change in the distance between the cation and the anion in the original compound to the value characteristic of the lattice of the ammine. The process of separating the ions is accompanied by an expenditure of energy (E) and this will be greater the larger the lattice energy of the original compound. On the other hand, the process of adding the ammonia molecule to the cation will evolve energy, (A). Thus the heat of formation (Q) of the ammine is given by

$$Q = A - E.$$

The probability of ammine formation is determined by the relative values of A and E. In the case where E is large,

the energy (A) evolved by the addition of ammonia to the cation is insufficient to make up for E and the ammine is not formed.

Lattice energies of tetrafluorides increase from titanium to chromium (46) and therefore the tendency towards ammine formation will decrease. Also, it follows that the tendency towards ammine formation will be least in fluorides and oxides for which the lattice energies are large compared to the values for other halides.

B. REACTIONS WITH SULPHUR DIOXIDE AND SULPHUR TRIOXIDE

The reactions of chromium tetrafluoride with sulphur dioxide and trioxide were studied firstly to examine the reactivity of chromium tetrafluoride towards simple oxides, and secondly because many transition metal fluorides react in a very interesting manner with these oxides. In addition to its donor properties, sulphur dioxide has also been used as a solvent system for chemical reactions.

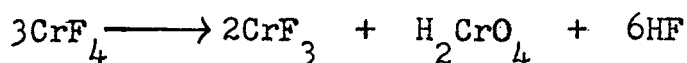
Sulphur dioxide was condensed on to a sample of chromium tetrafluoride and the reactants were allowed to mix at room temperature. There were no signs of any reaction taking place and after the removal of excess sulphur dioxide, the residue was found to be unchanged chromium tetrafluoride.

In another experiment sulphur trioxide was allowed to melt in the presence of chromium tetrafluoride,

and the residue, after removal of the excess of sulphur trioxide, was found to be unchanged chromium tetrafluoride. Thus chromium tetrafluoride does not react with either sulphur dioxide or sulphur trioxide, and resembles vanadium tetrafluoride in this respect (31).

C. REACTION WITH WATER

The reaction of chromium tetrafluoride with water has previously been studied by von Wartenberg (22) who was able to characterize the fluorination product of chromium as chromium tetrafluoride by using this hydrolysis reaction. He assumed the reaction,



to occur and confirmed that the ratio of Cr^{+6} to the total chromium corresponded to the above equation. In the present investigation, this hydrolysis has also been confirmed. Dissolution of chromium tetrafluoride in water gave a yellowish-green solution containing chromium in the +6 and +3 oxidation states. The ratio of $\text{Cr}^{+6}:\text{Cr}^{+3}$ was found to be 1:2, as indicated by the above equation for hydrolysis.

Many tetrahalides can be regarded as salts of very weak bases and are expected to be extensively hydrolysed. Thus chromium tetrafluoride and all the complexes derived from it are immediately hydrolysed by water; the same is true for vanadium tetrafluoride and its complexes.

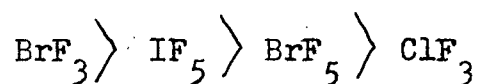
IV. REACTIONS OF CHROMIUM TETRAFLUORIDE WITH HALOGEN FLUORIDES AND SELENIUM TETRAFLUORIDE

The study of the reactions of halogen fluorides with metallic fluorides has led to the preparation of many new compounds. Bromine trifluoride and pentafluoride, iodine pentafluoride, and chlorine trifluoride have been most frequently used for this purpose. Of these, bromine trifluoride and iodine pentafluoride have been the most widely used because of their large liquid ranges and their high molar energies of vaporization (47). In addition, they are not as reactive as bromine pentafluoride and chlorine trifluoride and can be handled more safely in glass apparatus. During reactions with bromine pentafluoride, reaction with the connecting glass tubes was frequently observed.

These covalent fluorides can react with the metal fluorides in the following two ways:

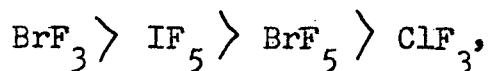
- (i) dissolution and/or adduct formation
- (ii) oxidation and fluorination

The formation of adducts or complexes with metal fluorides is well known and has been observed for all of these halogen fluorides. The tendency to form such adducts decreases in the order



Thus, the adducts formed from bromine trifluoride are very stable, as also are those formed from iodine pentafluoride (7). The transition metal fluoride adducts are unstable

as compared to those of alkali metal fluorides; in fact iodine pentafluoride does not appear to form any transition metal fluoride adducts. Since the order of stability of the adducts is the same as the apparent order of the strength of intermolecular fluorine bonding in the liquids,



it has been suggested that fluoride ions play a role analogous to that of the proton in hydrogen bonding, and the formation of a complex would require the presence of a stable vacant orbital on the central atom (48). The stability of the adduct will also depend on the nature of the metal atom and increases with an increase in the radius of the metal.

A wide range of bromine trifluoride adducts has been prepared and these fall into two categories--one in which two molecules of bromine trifluoride are present per molecule of the metal fluoride, and the other in which the metal fluoride and bromine trifluoride are in a 1:1 molar ratio. For example, auric fluoride forms a 1:1 adduct, $\text{AuF}_3 \cdot \text{BrF}_3$, while platinum tetrafluoride forms a 1:2 adduct, $\text{PtF}_4 \cdot (\text{BrF}_3)_2$, which decomposes at 200°C to give pure PtF_4 (49). In contrast to the stable adduct formed by platinum tetrafluoride, the titanium tetrafluoride adduct, also a 1:2 type, is highly unstable and decomposes in vacuo at room temperature (50). Rhodium tetrafluoride dissolves in bromine trifluoride and can be recovered

after distillation of bromine trifluoride, and forms no adduct. Thus it is observed that the tetrafluorides react with bromine trifluoride apparently by simple dissolution, as well as by forming adducts of both types, namely 1:1 and 1:2 adducts.

The possibility of the second type of reaction, that is, the oxidation and fluorination of the metal fluoride to a higher fluoride, will depend on the nature and reactivity of the halogen fluoride and also on the oxidation state of the metal in the metal fluoride. If the metal fluoride contains a metal that can exist in a higher oxidation state, then there is a great possibility of this type of reaction occurring. This possibility will be greater the more reactive the halogen fluoride; thus, iodine pentafluoride, which is the least reactive of the halogen fluorides, very often leaves the oxidation state of the metal unchanged, while reactive bromine trifluoride usually yields products containing the metal in the highest oxidation state.

The reactions of chromium tetrafluoride with these fluorides were studied in the hope of preparing a higher fluoride of chromium, and of determining the reactivity of chromium tetrafluoride towards these fluorinating agents. Chromium tetrafluoride did not react with any of these fluorides at room temperature, and therefore the reactions at high temperatures (i.e. the boiling points of the halogen

fluorides) were investigated.

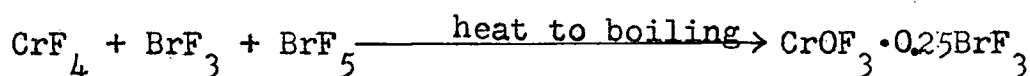
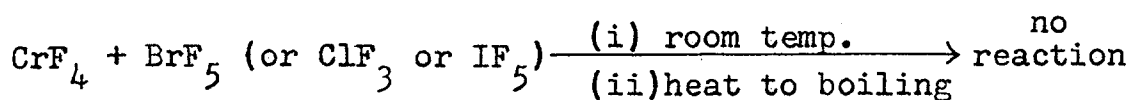
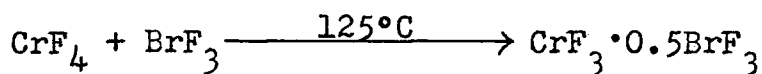
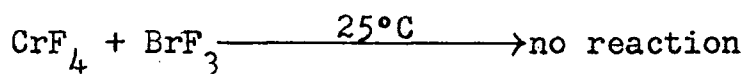
When chromium tetrafluoride was reacted with boiling bromine trifluoride, the colour of the residue in the silica reaction vessel was green, resembling that of chromic compounds. Magnetic susceptibility measurements were carried out at room temperature and the computed value of the magnetic moment corresponded to the presence of three unpaired electrons, indicating that chromium in the product had an oxidation number of +3. Chemical analysis and equivalent weight determination showed that the green reaction product was a bromine trifluoride adduct, with the formula $\text{CrF}_3 \cdot 0.5\text{BrF}_3$.

On the other hand, no reaction occurred between chromium tetrafluoride and either bromine pentafluoride or chlorine trifluoride. Because of the low boiling points of these two and also their low heats of vaporization, when they were heated with chromium tetrafluoride their rates of evaporation were very rapid and unchanged chromium tetrafluoride remained at the end of each experiment.

Since in none of the preceding reactions a product containing chromium in an oxidation state higher than four was obtained, it was decided to react chromium tetrafluoride with a mixture of bromine trifluoride and bromine pentafluoride. This mixture would allow the reactants to be heated to a higher temperature than is possible with bromine pentafluoride and would act as a stronger fluorinating agent than pure bromine trifluoride. The reaction was

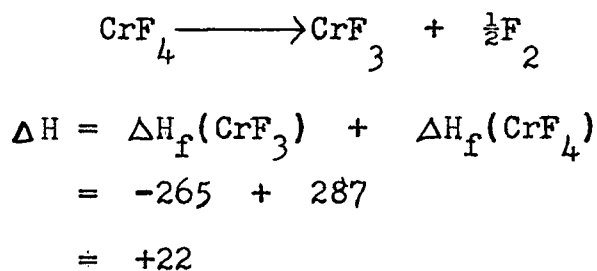
carried out in a silica tube and after the removal of excess bromine fluorides at 100°C, a reddish-brown product was obtained. The product was paramagnetic and the calculation of the magnetic moment gave a value for the moment $\mu_{294} = 2.01$ B.M., indicating the presence of one unpaired electron. The percentage of chromium was 34.2% and an equivalent weight determination was carried out to determine whether the compound was an oxyfluoride or a pure fluoride. The compound reacted vigorously with water and a solution containing Cr^{+6} and Cr^{+3} was obtained. An equivalent weight determination showed that the product was an oxyfluoride and the magnetic measurement and chemical analysis suggested the formula $\text{CrOF}_3 \cdot 0.25\text{BrF}_3$.

Chromium tetrafluoride did not react with either iodine pentafluoride or chlorine trifluoride on heating. The reactions of chromium tetrafluoride with the halogen fluorides can therefore be summarized as follows:



It is not clear why chromium tetrafluoride does not form adducts. Titanium tetrafluoride, as mentioned earlier, forms adducts while vanadium tetrafluoride on

reacting with bromine trifluoride immediately yields vanadium pentafluoride (31). On the other hand, the reaction product of chromium tetrafluoride with bromine trifluoride at 125°C was $\text{CrF}_3 \cdot 0.5\text{BrF}_3$, containing chromium in an oxidation state lower than in the starting material. It appears highly unlikely that chromium tetrafluoride will be able to oxidize bromine trifluoride and be itself reduced to chromium trifluoride. The alternative explanation would require just the thermal decomposition of chromium tetrafluoride to chromium trifluoride, followed by adduct formation by the latter. The decomposition of chromium tetrafluoride into chromium trifluoride is exothermic (46).

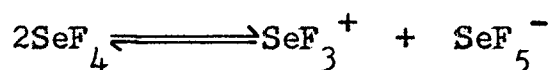


The reaction will naturally be facilitated by heat and the heat of formation of an adduct by chromium trifluoride may also favour the decomposition.

REACTION OF CHROMIUM TETRAFLUORIDE WITH SELENIUM FLUORIDE

Selenium tetrafluoride is another covalent fluoride which has frequently been used to study the reactions of metal fluorides. Like the halogen fluorides, it has

remarkable solvent properties and has a fairly large liquid range (melting point: -19.3°C ; boiling point: 106°C) but is not as reactive nor such a vigorous fluorinating agent. Its solvent properties have recently been discussed (51) and alkali metal complexes of the type ASeF_5 isolated, indicating an ionization of the type



An important difference between selenium tetrafluoride and other fluoride solvents, such as bromine trifluoride, is that the latter are oxidizing agents and tend to raise an element to its highest oxidation state, whereas the former either leaves the element in its original oxidation state or even acts as a reducing agent. For example, vanadium tetrafluoride is immediately oxidized by bromine trifluoride to form vanadium pentafluoride, while with selenium tetrafluoride, vanadium tetrafluoride forms an adduct (31). Bromine trifluoride also oxidizes thallous compounds to thallic fluoride (52). Selenium tetrafluoride forms $\text{PdF}_3 \cdot \text{SeF}_4$, which on heating yields pure PdF_2 (53). The reducing properties of selenium tetrafluoride originate in its ready oxidation to selenium hexafluoride, which is a gas at room temperature. The occurrence of reduction will of course also depend on the reactivity of the metal fluoride.

The stabilities of adducts formed by bromine

trifluoride and selenium tetrafluoride are widely different. Whereas the "acid" adducts of bromine trifluoride, e.g. $\text{BrF}_2^+ : \text{AuF}_4^-$, are not very stable to heat and usually decompose at 120--150°C, selenium tetrafluoride forms very stable adducts (7). Adducts containing one or two molecules of selenium tetrafluoride per molecule of metal fluoride are known.

The reaction of chromium tetrafluoride with selenium tetrafluoride was investigated to see if adduct formation occurred. At first the reaction was studied at room temperature but no reaction occurred. In a second experiment, chromium tetrafluoride and selenium tetrafluoride were heated together. Reaction was observed to occur and appeared to be complete in about fifteen minutes. The residue after the removal of selenium tetrafluoride at room temperature consisted of two phases--one pink and the other buff-coloured. When an attempt was made to distil off more selenium tetrafluoride from this heterogeneous reaction product at 100°C, it was unexpectedly observed that the buff-coloured portion of the product was carried into the cold trap, presumably with some vapours of selenium tetrafluoride, leaving the pure pink product in the reaction vessel. This step fortunately afforded a method of separating the two compounds. The pink compound in the reaction vessel was found on chemical analysis to correspond to $\text{CrF}_2 \cdot \text{SeF}_4$, containing dipositive

chromium. The oxidation state was confirmed by a magnetic moment measurement at room temperature, which gave a value of $\mu_{294} = 5.34$ B.M., corresponding to four unpaired electrons, suggesting Cr^{++} in a low field situation (high spin).

The chemical analysis of the buff-coloured compound gave the formula $\text{CrF}_3 \cdot \text{SeF}_4$. This compound was very light and not as reactive as the pink compound. It could be stored for longer periods of time without any noticeable change. The magnetic susceptibility measurement on the buff-coloured compound gave a low value for the magnetic moment, which was not satisfactory, since the compound was very light and could not be easily and uniformly packed into the magnetic moment tube.

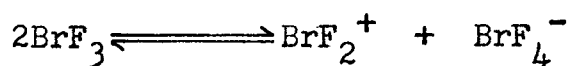
Thus selenium tetrafluoride and chromium tetrafluoride when heated together yield 1:1 selenium tetrafluoride adducts of CrF_2 and CrF_3 . This is another example of a reaction in which selenium tetrafluoride acts as a reducing agent.

V. COMPLEXES DERIVED FROM CHROMIUM TETRAFLUORIDE

It was decided to prepare alkali metal complexes containing chromium in the +4 oxidation state. Two types of complex fluoride derivatives seem to be possible for tetrapositive chromium.

- (i) complexes which contain an alkali metal and chromium in a 1:1 atomic ratio, i.e. of the type $ACrF_5$ --e.g. $KCrF_5$, $RbCrF_5$, etc.
- (ii) complexes which contain two atoms of alkali metal per atom of chromium, i.e. of the type A_2CrF_6 --e.g. K_2CrF_6 , Cs_2CrF_6 , etc.

During the present investigation, complexes were prepared in a bromine trifluoride medium. After the discovery of bromine trifluoride in 1949, its potential use as a non-aqueous solvent was brought to light when the physical properties were studied. Emeleus and Woolf (54) proposed that bromine trifluoride can act as an ionizing solvent according to the equilibrium



and this therefore has been considered the parent substance of a new acid-base solvent system. Bromine trifluoride has a high value for its Trouton's constant, indicative of association, and it also possesses a high specific conductivity (55). It is true that useful solvent properties

are possessed by other fluorides (e.g. iodine pentafluoride and selenium tetrafluoride) but bromine trifluoride has many advantages, such as its large liquid range and high reactivity. For the preparation of the complexes of tetra-positive chromium, bromine trifluoride was selected, since in this medium the possibility of reduction of Cr^{+4} will be the least. Bromine trifluoride has been used to prepare the fluoro-complexes of the platinum metals (56), gold (57), vanadium (58), and phosphorus, arsenic, antimony, boron, tantalum, and bismuth (59).

In the present work, the complexes were prepared by heating together the alkali metal chlorides and chromium tetrafluoride in the correct molar ratio in bromine trifluoride.

A. COMPLEXES OF THE TYPE ACrF_5 WHERE A = K, Rb, OR Cs.

1. Potassium pentafluorochromium (IV)

Chromium tetrafluoride and potassium chloride in a 1:1 molar ratio were reacted together in bromine trifluoride. The reaction was carried out by heating the reactants for a short time and excess bromine trifluoride was then removed by distillation in vacuo. Depending upon the temperature at which the distillation was carried out, two products were obtained. If the excess bromine trifluoride was removed at 100°C , the residue was a bromine trifluoride adduct, shown by chemical analysis to be $\text{KCrF}_5 \cdot 0.5\text{BrF}_3$. The oxidation number of chromium was confirmed by the observed magnetic

moment of 3.22 B.M., which showed the presence of two unpaired electrons. If, however, the removal of excess bromine trifluoride was carried out at 160°C, the product did not contain any bromine trifluoride; chemical analysis showed the compound to be KCrF_5 .

2. Rubidium pentafluorochromium (IV) and cesium pentafluorochromium (IV)

These were similarly prepared by heating chromium tetrafluoride and the respective alkali metal chloride in bromine trifluoride, and removing excess bromine trifluoride at 160°C to obtain a pure product. The following compounds were thus obtained.

<u>complex</u>	<u>magnetic moment (B.M.)</u>	<u>crystal structure</u>	<u>lattice constants</u>
$\text{KCrF}_5 \cdot 0.5\text{BrF}_3$	3.22	tetragonal	$a = 9.168 \text{ \AA}$ $c = 13.49 \text{ \AA}$
KCrF_5	3.16	hexagonal	$a = 8.739 \text{ \AA}$ $c = 5.226 \text{ \AA}$
RbCrF_5	3.17	hexagonal	$a = 6.985 \text{ \AA}$ $c = 12.12 \text{ \AA}$
$\text{CsCrF}_5 \cdot 0.5\text{BrF}_3$	3.09	cubic	$a = 8.107 \text{ \AA}$
CsCrF_5	3.09	cubic	$a = 8.107 \text{ \AA}$

The complexes obtained contain five atoms of fluorine per atom of chromium. They do not contain free potassium fluoride as can be shown by their diffraction patterns which contain no lines characteristic of potassium fluoride. At least from their formulae these salts contain penta-coordinate chromium. However, coordination number five in

complexes is rare, as is indicated by the fact that very few complexes of the type A_nMX_5 are known, especially for those containing a tetrapositive central atom. The only such complex containing M^{+4} known at the start of this work was that of manganese (IV), $KMnF_5$, prepared from potassium permanganate and bromine trifluoride (26). A few other examples that may be cited are Tl_2AlF_5 , Cs_3CoCl_5 , and $(NH_4)_3ZnCl_5$.

Many neutral molecules are known which contain five ligands per central atom, e.g. pentahalides of molybdenum and tantalum, etc. In various of these compounds where the stoichiometry might suggest a coordination number of five, the true coordination number is either higher or lower, apparently depending upon the oxidation number of the central atom. For the pentahalides of niobium and tantalum and for molybdenum pentachloride, it has been established that in the vapour state these are monomers with a trigonal bipyramidal structure. However, there is evidence that in the solid state they all exist as dimers, M_2X_{10} , consisting of two octahedral MX_6 groups sharing an edge. Similarly, in the case of PF_5 , PCl_5 , and PF_3Cl_2 , the molecules have been shown to exist as trigonal bipyramidal molecules in the vapour state (60). However, a study of the phosphorus pentachloride molecule in the solid state by Clark, Powell, and Wells (61) shows that the trigonal bipyramidal arrangement does not persist in the solid state. Thus the various observations of MX_5 molecules indicate that a

coordination number of five is unusual in the solid state.

The avoidance of odd coordination numbers has been demonstrated by Menzies (62), who suggested that heavy metals might even show an unusual effective atomic number to avoid odd coordination numbers. Sidgwick's statement (62) that the relation of an odd coordination number to the next higher even value is that of unsaturation, and Bossett's (62) explanation of the structure of a number of complex lithium compounds in which the lithium tends to attain a coordination number of two or four, are indications that the tendency towards an even coordination number is displayed through all the periodic table. Furthermore, geometric considerations also show that, in general, if there is space for five ligands around the central atom then six ligands can be equally well accommodated. There is, therefore, no preference for five coordination as far as spatial considerations are concerned.

Crystal structure studies on various complex compounds of the type A_nMX_5 have revealed that in almost every case an even coordination number--six in general--has been attained. A few complexes of this type which can be prepared in aqueous solution form monohydrates, e.g. $K_2FeCl_5 \cdot H_2O$, and it may be reasonably supposed that these contain ions such as $[FeCl_5 \cdot H_2O]^{-2}$, in which the central atom has attained hexa-coordination. Powell and Wells (63) investigated the structure of anhydrous

Cs_3CoCl_5 and found that it contained tetrahedral $[\text{CoCl}_4]^{-2}$ ions together with separate chloride ions and cesium ions. Similarly, the compound $(\text{NH}_4)_3\text{ZnCl}_5$ contains tetrahedral $[\text{ZnCl}_4]^-$ groups and free chloride and ammonium ions. The compound Tl_2AlF_5 has been shown to contain infinite chains of AlF_6^{-3} octahedra, in which two corners of each octahedron are shared with others to preserve the stoichiometry (64). Thus the above-mentioned structure determinations demonstrate that penta-coordination in the solid state very rarely occurs for complexes, and in all those cases where the stoichiometry might suggest it, a coordination number of four or six has actually been attained--four if the oxidation number of the central atom was two, and six if it was three.

Complexes of the type AMX_5 containing a tetrapositive central metal have only recently been prepared, and so far no detailed structure determinations have been carried out. The existence of coordination number six for manganese in KMnF_5 has been suggested (65) based on the observed similarity of its infrared spectrum with that of K_2MnF_6 , in which hexa-coordination has been established.

Knowing that atoms tend to attain their maximum coordination number avoiding odd values, and that the oxidation number of chromium in these complexes of the type ACrF_5 is +4, it can reasonably be assumed that these complexes contain CrF_6^{-2} octahedral groups, each of which

shares two corners with neighbouring groups to obtain the observed stoichiometry. Detailed structural studies would be very informative. Magnetic moments of these complexes, which will be discussed later, also lead to the view that chromium has attained a coordination number of six in these compounds.

B. COMPLEXES OF THE TYPE A_2CrF_6

These complexes of tetrapositive chromium were known previously. The potassium complex K_2CrF_6 was prepared by Huss and Klemm (24) by fluorinating a mixture of potassium chloride and chromium chloride. Using the same method, Bode and Voss (25) prepared analogous rubidium and cesium complexes and investigated their crystal structure. Their investigations showed that the potassium and rubidium complexes existed in two crystalline forms, hexagonal and cubic, while the cesium complex formed only cubic crystals. Their results are given below.

<u>lattice constants</u>		
K_2CrF_6	cubic	$a = 8.15 \text{ \AA}$
	hexagonal	$a = 5.69 \text{ \AA}; c = 9.34 \text{ \AA}$
Rb_2CrF_6	cubic	$a = 8.506 \text{ \AA}$
	hexagonal	$a = 5.94 \text{ \AA}; c = 9.67 \text{ \AA}$
Cs_2CrF_6	cubic	$a = 9.004 \text{ \AA}$

In the present investigation, experiments were carried out to prepare these complexes in a bromine trifluoride solvent. Only potassium and cesium complexes

were investigated.

1. Potassium hexafluorochromium

Chromium tetrafluoride and potassium fluoride in a 1:2 molar ratio were refluxed in bromine trifluoride, and excess bromine trifluoride was distilled in vacuo at 100°C. Chemical analysis of the product suggested that it was a bromine trifluoride adduct of the composition $K_2CrF_6 \cdot 0.5BrF_3$. The tetrapositive state of chromium was confirmed by the observed magnetic measurement $\mu_{eff} = 3.03$ B.M., which corresponded to two unpaired electrons. An X-ray diffraction photograph of the sample was taken and the pattern was indexed on a tetragonal unit cell with $a = 4.339 \text{ \AA}$, $c = 5.500 \text{ \AA}$. The reported structures for pure K_2CrF_6 were either hexagonal or cubic, which suggested that the presence of bromine trifluoride in the lattice seriously affected the structure. An attempt was therefore made to see if this tetragonal compound could be transformed into one of the previously reported structures. Small amounts of $K_2CrF_6 \cdot 0.5BrF_3$ powder were sealed in vacuo in glass tubes and heated to different temperatures. X-ray pictures of the heated products were found to be different from that of the starting material. All the heated samples showed the presence of the same phase, which on indexing was found to be cubic with $a = 8.104 \text{ \AA}$. Thus the tetragonal adduct $K_2CrF_6 \cdot 0.5BrF_3$ on heating decomposed to the cubic K_2CrF_6 .

2. Cesium hexafluorochromium

Similarly $\text{Cs}_2\text{CrF}_6 \cdot 0.5\text{BrF}_3$ was prepared and had a magnetic moment of 3.14 B.M. An X-ray photograph of the sample was indexed on a cubic lattice with $a = 8.916 \text{ \AA}$. A sample of this adduct was heated to 135°C , when bromine trifluoride distilled off. The residue on analysis was found to be pure Cs_2CrF_6 . The results of the present investigation are summarized below.

<u>compound</u>	<u>magnetic moment (B.M.)</u>	<u>crystal structure</u>	<u>lattice constants</u>
$\text{K}_2\text{CrF}_6 \cdot 0.5\text{BrF}_3$	3.06; 3.30	tetragonal	$a = 4.339 \text{ \AA}$ $c = 5.500 \text{ \AA}$
K_2CrF_6	3.06; 3.30	cubic	$a = 8.104 \text{ \AA}$
$\text{Cs}_2\text{CrF}_6 \cdot 0.5\text{BrF}_3$	3.14	cubic	$a = 8.916 \text{ \AA}$
Cs_2CrF_6	3.14	cubic	$a = 8.916 \text{ \AA}$

The values reported by Bode and Voss (24) for the lattice constants of cubic modifications of K_2CrF_6 and Cs_2CrF_6 are higher than the values obtained in this work. Their preparations always contained some alkali fluoride in excess which was not discernible in X-ray patterns. The excess alkali fluoride was presumably present as solid solution and may be responsible for the slightly higher values of the lattice constants.

Many complex fluorides of the type A_2MF_6 are known; in fact almost every element which forms a tetrahalide gives such complexes. The complexes in which $\text{A} = \text{lithium}$ or sodium are difficult to form and do not crystallize in

the same types of structures (66) as do the complexes in which A = potassium, rubidium, or cesium. These latter complexes usually crystallize in three types of structures--cubic, hexagonal, or trigonal--and contain discrete MX_6^{-2} octahedra. At the present time, the factors governing the occurrence of these structures are unknown. It has been repeatedly remarked that these three structures possess the same energy and are equally favoured from energetic considerations. However, the calculations of the energies of these structures contain many approximations and therefore may not indicate subtle differences in energy. The fact that the metals of the first transition series do not all show the same modifications evenly distributed suggests that the structures do depend on both the cations present in the molecule. The observed structures for A_2MF_6 complexes of the first transition series and the ratio of radii of alkali metal to radii of transition metal are given below.

<u>metal</u>	<u>structure</u>	$\frac{r_{\text{M}^{+4}}}{r_{\text{K}^+}}$	<u>structure</u>	$\frac{r_{\text{M}^{+4}}}{r_{\text{Rb}^+}}$	<u>structure</u>	$\frac{r_{\text{M}^{+4}}}{r_{\text{Cs}^+}}$
Ti	C H T	0.51	C H T	0.46	C - T	0.40
V	- H T	0.465	- H T	0.42	C - T	0.366
Cr	C H -	0.42	C H -	0.378	C - -	0.331
Mn	C H T	0.405	C H T	0.354	C - -	0.319
C = cubic H = hexagonal T = trigonal						

It is seen in the table that potassium salts always

exist in either two or three crystalline forms, while cesium salts exist at the most in two forms, indicating that the relative sizes of the cations are important. It is apparent from the table that for low radius ratios, i.e. equal to or less than 0.331, the complex crystallizes only in the cubic form. As the value of the radius ratio increases, other structures also occur. Thus, at radius ratios between 0.42 and 0.311, complexes exist in two modifications. For radius ratios between 0.46 and 0.51, all the three structures may occur. One might expect that with a further increase in the radius ratio cubic structure will disappear, and at still higher ratios one might expect only one structure. It is indeed observed for similar compounds of heavier elements, as lead, tin, platinum, and ruthenium, which will give higher radius ratio values, that the trigonal modification is the only observed structure (67).

The case of vanadium is intriguing. The modification that has not been isolated is the cubic. This is surprising and suggests that further research is necessary. It should be possible to prepare a cubic modification of K_2VF_6 certainly and of Rb_2VF_6 quite probably. The other prominent absence is a trigonal variety of K_2CrF_6 , and one would expect this to exist.

If these general correlations are correct, then one would expect only the cubic modification of a potassium complex for which the ratio $\frac{r_{M^{+4}}}{r_{K^{+}}}$ is less than 0.33. One

example of an element which gives a radius ratio less than 0.33 is tetrapositive silicon (radius = 0.41 \AA , $\frac{r_{\text{Si}^{+4}}}{r_{\text{K}^{+}}} = 0.308$),

and this forms a potassium complex which is known to exist only in the cubic form. (67).

VI. MAGNETIC PROPERTIES

The magnetic properties of a substance are characterized by its magnetic moment, which for a simple dipole is proportional to the strength of the poles and the distance between them. For a complex system, the observed magnetic moment is the resultant of elementary moments, ultimately of the electrons themselves. These magnetic moments either are intrinsic properties of the electron, corresponding to the spin, or result from the orbital motion of the electron. Thus, the magnetic moment in general consists of two parts, namely the "orbital" and "spin" portions.

If an atomic system contains unpaired electrons, their spin and orbital moments are not completely cancelled and there remains a permanent magnetic moment. When an external magnetic field is applied, the permanent moment tends to orient itself parallel to the field. This orienting tendency is opposed by the usual thermal motion: the extent of alignment therefore must decrease with rising temperature.

The quantum mechanical treatment of the interaction between the elementary moment and the applied field yields for the molar susceptibility χ_M the result (68)

$$\chi_M = \frac{N \bar{\mu}^2}{3RT} + N \bar{L}^2$$

where $\overline{\mu^2}$ = statistical mean square of the moment
 $N\overline{\mathcal{L}}$ = the joint contribution of the high frequency
 elements of the paramagnetic moment
 (temperature independent) and of the
 diamagnetic effect

N, k, and T have their usual significance

This expression, derived by Van Vleck (68), is identical to one derived by Langevin, except for the addition of the term $N\overline{\mathcal{L}}$.

Among transition metal compounds, different types of magnetic behaviour have been observed (69) and different expressions for the magnetic moment have been obtained, depending on the spacing of degenerate spin levels in comparison to kT. For example, if the spacing is large as compared to kT, the moment μ is given by the expression

$$\mu = g\sqrt{J(J+1)} \text{ B.M.}$$

and if the spacing is small as compared to kT, then

$$\mu = \sqrt{4S(S+1) + L(L+1)} \text{ B.M.},$$

when S, L, and J are the resultant spin, resultant orbital angular momentum, and total angular momentum respectively, and g is the Lande splitting factor, a known explicit function of S, L, and J.

$$S = \sum s_i, L = \sum l_i$$

$$g = \frac{1 + J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

Clearly, both spin and orbital contribution are included in the expression and must generally be considered. Neighbouring ions in the crystalline or liquid state or in solution interact strongly with one another. If the interactions are so strong that the orbital angular momentum cannot be oriented by an applied magnetic field, the orbital contribution to the magnetic moment does not appear and is said to be quenched. In the case of ions of short transition series elements in which the unpaired electrons are near the surface and are almost entirely unscreened from the fields of neighbouring ions, the orbital contributions are almost entirely quenched and indeed it has long been known (70) that the magnetic moments of the elements of the first transition series are best given by the spin-only formula $\mu = \sqrt{4S(S+1)}$ B.M., the whole of the orbital contribution being neglected. However, it may be pointed out that the quenching of this orbital contribution is often incomplete and this deviation can be used to assist in determining the stereochemistry as discussed later.

TEMPERATURE DEPENDENCE OF MAGNETIC SUSCEPTIBILITY

Thermal motions retard the alignment of permanent moments and thus decrease the value of the susceptibility with rising temperature. The idealized form of behaviour for the magnetic susceptibility of a paramagnetic substance with temperature T is given by the Curie Law

$$\chi_M = \frac{C}{T} \text{ and } \mu = 2.84\sqrt{\chi_M T},$$

where C = Curie Constant, and χ_M = molar susceptibility. If the Curie Law is obeyed, μ is independent of temperature. The Curie Law is obeyed with considerable accuracy by a few systems, e.g. $[\text{FeF}_6]^{-3}$, but for a majority of cases there are deviations. One cause of deviations in one unpaired electron systems is the temperature independent paramagnetism arising from the second order Zeeman effect from higher ligand fields. This has been allowed for in the Langevin-Debye formula by introducing the term $N\bar{\alpha}$ (68). However, the molar susceptibility of many compounds deviates from the requirement of the Curie Law in a way which may be described by a simple modification of this law, the Curie-Weiss Law,

$$M = \frac{C}{T + \theta} \quad (\theta = \text{Weiss Constant})$$

Chromium, like other transition metals, can exist in various oxidation states ranging from one to six; of these only two, three, four, five, and six are realized in fluorides and oxyfluorides. Magnetic properties of chromium compounds containing chromium in different oxidation states have been studied extensively at room temperature, but data on their temperature dependence is not complete. The magnetic behaviour for different oxidation states are

described below for a few selected compounds.

1. Cr^+

The ground state is ${}^6\text{S}_{5/2}$ and five d electrons are present. From ligand-field theory applications, the expected magnetic moment in an octahedral environment is 5.92 B.M. in a weak field case and 1.73 B.M. in a strong field case.

2. Cr^{++}

The ground state of this ion is ${}^5\text{D}_0$ and it has four d electrons. In an octahedral environment the expected magnetic moment will correspond to four unpaired electrons in a weak field case and to two unpaired electrons in a strong field case. Both types of coordination compound are known (71).

In the present work, the compound CrF_2SeF_4 has been prepared and the value of its magnetic moment was found to be 5.34 B.M. This is higher than the calculated spin-only value of 4.90 B.M., indicating a large orbital contribution. This will be discussed in the following section.

3. Cr^{+3}

The ground state of terpositive chromium is ${}^4\text{F}_{3/2}$ and it possesses three electrons in a d shell responsible for magnetic moment. The magnetic moment in an octahedral environment will be due to three unpaired electrons in both weak and strong fields.

The octahedral complexes of terpositive chromium are well known and the observed magnetic moments correspond

closely to the spin-only values (71).

The compound $\text{K}_2\text{CrF}_5 \cdot \text{H}_2\text{O}$ (72) has a magnetic moment of 3.79 B.M., while CrF_3 has a magnetic moment of 3.9 (73).

It is unfortunate that data on the variation of magnetic susceptibility with temperature is so meagre. The magnetic susceptibilities of a few compounds of chromium at low temperatures have been measured. In Cr_2O_3 , the observed value of the magnetic moment is 3.61 B.M., with the Weiss Constant equal to -405° (19).

In the present investigation, the following compounds were prepared and their magnetic moments measured.

<u>compound</u>	<u>μ_{294} (Curie Law)</u>
$\text{CrF}_3 \cdot 0.5\text{BrF}_3$	3.96 B.M.
$\text{CrF}_3 \cdot \text{BrF}_3$	3.67 B.M.

4. Cr^{+4}

The ground state of tetrapositive chromium is $^3\text{F}_2$ and the ion has two electrons in the d shell. The expected magnetic moment corresponds to two unpaired electrons in an octahedral environment, whether due to weak field ligands or to strong field ligands. Tetrapositive chromium compounds have been mostly studied in the present investigation and therefore will be discussed in detail.

Chromium shows an oxidation number of four only in chromium tetra-t-butoxide, chromium dioxide, and chromium tetrafluoride, and in the complexes derived from them.

The blue chromium tetra-*t*-butoxide possesses a magnetic moment of 2.88 B.M. (17). The magnetic measurements on chromium dioxide were made by Bhatnagar (19) and a value of $\mu = 2.94$ and the Weiss Constant equal to 2° were found for this compound. However, the +4 oxidation state of chromium in chromium dioxide has recently been questioned by Russian workers (21). The complex Ba_2CrO_4 contains tetrapositive chromium and possesses a magnetic moment of 2.82 B.M. (74).

At the start of the present investigation, the magnetic moment of K_2CrF_6 only was known among the fluorine compounds containing tetrapositive chromium, and is 2.8 B.M. (74). In the present investigation, the magnetic moments of many compounds of tetrapositive chromium were measured, and in some cases measurements at low temperatures were also taken. The observed values are given below.

<u>Compound</u>	<u>μ_{294} (Curie Law)</u>	<u>θ</u>	<u>μ_{eff} (Curie-Weiss Law)</u>
CrF_4	2.74 B.M.	-70°	3.02 B.M.
KCrF_5	3.16 B.M.
$\text{KCrF}_5 \cdot 0.5\text{BrF}_3$	3.22 B.M.	-80°	3.67 B.M.
RbCrF_5	2.84 B.M. 3.17 B.M.	-32°	3.14 B.M.
CsCrF_5	3.09 B.M.
$\text{K}_2\text{CrF}_6 \cdot 0.5\text{BrF}_3$	3.06 B.M.	-105°	3.56 B.M.
$\text{Cs}_2\text{CrF}_6 \cdot 0.5\text{BrF}_3$	3.10 B.M.

5. Cr⁺⁵

The ground state of pentapositive chromium ion is $^2D_{3/2}$ and contains only one electron in the d shell, responsible for the magnetic moment. The expected magnetic moment in an octahedral environment--weak field or strong field--is 1.73 B.M.

Again, like tetrapositive chromium, this oxidation state is observed in oxyanions, in fluorides, and in oxyfluorides. In chromate (V), e.g. $Ba_3(CrO_4)_2$, the magnetic moment has been found to correspond to one unpaired electron (74). No magnetic measurements have been made on chromium pentafluoride. However, the compounds $KCrOF_4$ and $AgCrOF_4$ (72), Rb_2CrOCl_5 and Cs_2CrOCl_5 (71) have been observed to contain one unpaired electron.

In the present work, magnetic susceptibilities of oxyfluorides containing pentapositive chromium have been observed to correspond to one unpaired electron, as is shown in the table below.

<u>compound</u>	<u>μ_{294} (Curie Law)</u>
$CrOF_3 \cdot 0.25BrF_3$	2.02 B.M.
$CrOF_3 \cdot 0.25ClF_3$	1.83 B.M.
$CrOF_3 \cdot 0.25BrF_5$	1.85 B.M.
$KCrOF_4 \cdot 0.5BrF_3$	1.73 B.M.

The temperature dependence of the magnetic susceptibility of $KCrOF_4 \cdot 0.5BrF_3$ was measured, and the Weiss Constant was found to be +4°.

Magnetic measurements can be discussed under two headings:

- (i) paramagnetism and its temperature dependence
- (ii) paramagnetism and stereochemistry

PARAMAGNETISM AND ITS TEMPERATURE DEPENDENCE

Experimental observations show that all the chromium compounds are spin-free and obey the Curie-Weiss Law. The observed values of the Weiss Constant are fairly large in chromium tetrafluoride and in the complexes derived from it. It has usually been observed that the Weiss Constant is high in the case of fluorides.

The Weiss Constant, according to Van Vleck (68), is not an atomic property but can arise from interatomic forces and exchange effects. The magnitude of θ shows a marked dependence on the nature of the anion and on the ground state of the atom. As a result of his observations on iron and manganese salts, Van Vleck suggested that θ can arise from spin-orbit coupling which contributes to the angular momentum of the system and thus will be smallest for the S states. As it does not fall to zero at infinite dilution, the Weiss Constant is not wholly due to exchange effects--hence, exchange effects play only a subordinate role. The statement by Van Vleck that θ is due mainly to the influence of orbital angular momentum, and therefore should be high only for D or F states, does not seem to be always true; both low and high values of θ

have been observed for D or F states, as shown in the following table. Some examples of the compounds showing a wide range of θ values in the D and F states are given.

<u>ion</u>	<u>state</u>	<u>compound</u>	<u>θ</u>	<u>remark and reference</u>	
Cr ⁺³	F	CrCl ₃	32.5	low	(75)
		Cr ₂ O ₃	405	high	(19)
V ⁺²	F	VCl ₂	565	high	(76)
			700	high	(76)
Cr ⁺⁴	F	CrF ₄	70	high	present work
		KCrF ₅ ·0.5BrF ₃	80	high	present work
		K ₂ CrF ₆ ·0.5BrF ₃	105	high	present work
		RbCrF ₅	32	low	present work
Cr ⁺⁵	D	KCrOF ₄ ·0.5BrF ₃	+4	low	present work
V ⁺⁴	D	VF ₄	198	high	(31)
		VF ₄ ·SeF ₄	134	high	(31)
		K ₂ VF ₆	118 78	high high	(31, 77) (31, 77)

It is thus at present not possible to trace the real cause--exchange interaction or orbital interaction--of the high values of the Weiss Constant. Griffith (78) has shown that it is not possible to differentiate between the source of θ from the temperature studies of magnetic susceptibility, especially if the antiferromagnetic interactions are small or if the spin-orbit coupling occurs between the nearly degenerate levels, because both

antiferromagnetic interactions as well as spin-orbit interactions have similar effects on paramagnetism.

For chromium tetrafluoride, a polymerized structure similar to those for titanium tetrafluoride (29) and vanadium tetrafluoride (31), involving fluorine bridges, has been proposed. In such a structure, an antiferromagnetic exchange interaction is very easily possible and might lead to high values of the Weiss Constant. The fluorine bridges can also be considered to distort the regular octahedral symmetry of the CrF_6 basic octahedron and result in two types of fluorine bonds. This will cause a splitting of the low lying triplet (d_t) and a spin-orbit coupling can occur which may give rise to a high value of the Weiss Constant. Thus it is apparent that the presence of fluorine bridges can lead to high values of Θ ; whether this is achieved by exchange interactions or by spin-orbit interactions cannot be decided by the present theoretical approaches, in which in addition to other simplifying assumptions, Θ has been treated as independent of the applied field, which is especially not true at low temperatures.

If the existence of high Θ values is associated with bridge atoms, then there is no reason that they should be observed only in fluorides. Rather, other compounds which contain bridge atoms (halogen or other) should also exhibit high Θ values. For example, in the case of vanadium

dichloride, the high value of the Weiss constant, $\theta = 565^\circ$ or 700° , may be associated in part with the presence of chlorine bridges. Similarly, the observed values of the Weiss Constant for the complexes fit this pattern. The complexes of the type $ACrF_5$ possess high θ values (of the order of 100°) and this may be attributed, at least in part, to the presence of fluorine bridges in the structure.

Thus, to conclude, it can be said that even though it is not possible to separate the contributions of the two factors, viz. exchange forces and interatomic forces, the magnetic properties of chromium tetrafluoride and its complexes can be understood in the light of fluorine bridges.

PARAMAGNETISM AND STEREOCHEMISTRY

It has been mentioned earlier in this chapter that the moments of the first row transition metal ions are given by the spin-only formula. However, in practice it is found that deviations from this spin-only value do occur, and these are mostly towards higher values. The spin angular momentum of an electron is not affected by forces from other atoms, while on the other hand the interatomic forces are able to quench the orbital angular momentum.

The presence of electrically charged particles around a central metal ion gives rise to a ligand field which has two main effects:

- (i) It breaks up the coupling of L and S vectors to some degree, and the ion is no longer specified by a particular J value.
- (ii) It removes the degeneracy of $2L+1$ sublevels associated with the particular L value and splits them. The separations between these sublevels have an important effect on orbital contribution.

For an ion with narrow multiplet separation, i.e. $h\nu_{J_0-J_1} < kT$, the magnetic field reacts separately with S and L and $2S+1$ and $2L+1$ sublevels. It is this distribution over degenerate $2L+1$ sublevels that is responsible for the large orbital contribution in the formula

$$\mu = \sqrt{4S(S+1) + L(L+1)}$$

If the separation between the split sublevels is large as compared to kT , only the lowest (or lower) levels will be occupied. Furthermore, if this lowest level is a singlet, then the orbital contribution should be small.

Penney and Schlapp (79) have examined the effect of various kinds of crystalline fields on F and D states for transition metal ions. They found that the single energy level of an ion in the F state is split into three new levels when surrounded by a cubic field of an octahedron of six ligands. The separation between successive levels is of the order of 10^4 cm^{-1} . Usually the octahedron of ligands is slightly distorted; this may be regarded as

equivalent to imposing on the cubic field a small component of lower symmetry, e.g. tetragonal or rhombic. This will result in a further splitting of two adjacent energy levels into triplets, giving in all, seven levels for the F state. In this case the triplet is lowest and the singlet highest.

For an ion in a D state, the cubic field splits the orbital level into two levels, which are further split with a triplet and a doublet by a small rhombic component. This energy level diagram is known as a "Stark Pattern". If a triplet lies lowest there is large orbital contribution but a low lying doublet or singlet is "non-magnetic".

Until now only an octahedral arrangement has been considered. It will suffice to say here that in a tetrahedral environment the "Stark Pattern" will be inverted (69).

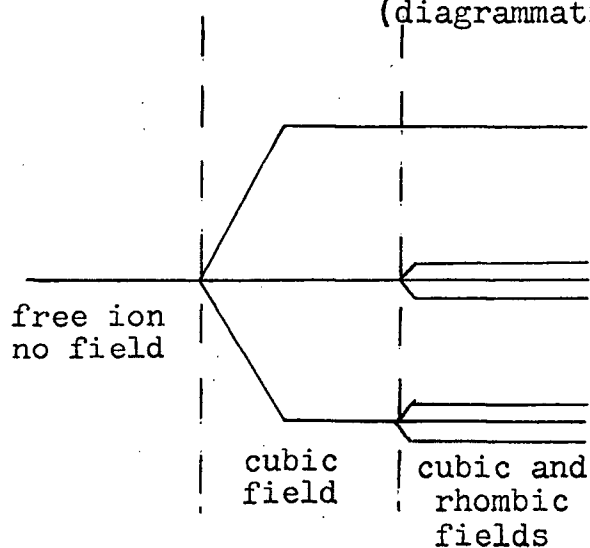
The "Stark Pattern" for Cr^{+4} and Cr^{+5} in octahedral and tetrahedral environments are given in Fig. no. I, (page 59). The remarkable difference between "Stark Patterns" of F and D states for tetrahedral and octahedral environments is that in the former, a singlet or doublet lies the lowest, and in the latter, a triplet lies lowest. For the tetrahedral case no orbital contribution is expected, as singlet and doublet are "non-magnetic", and a much closer approximation to the spin-only formula is to be expected. In the octahedral case a large orbital contribution is expected as the triplet lies the lowest.

In other words, if the observed values of the

Fig. I

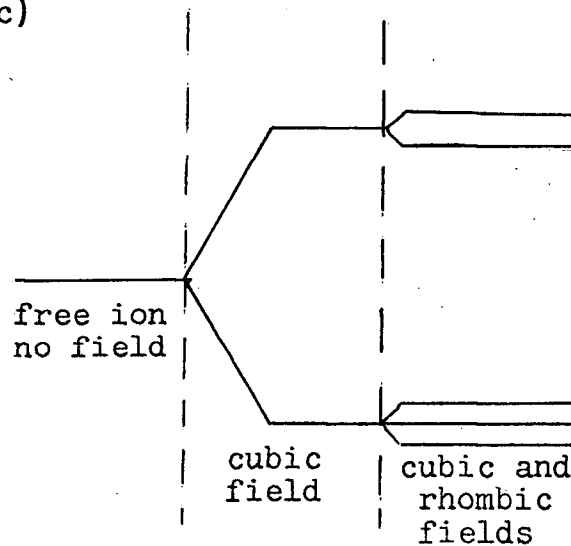
Stark Patterns for Cr^{+4} and Cr^{+5}
in octahedral and tetrahedral environment

(diagrammatic)



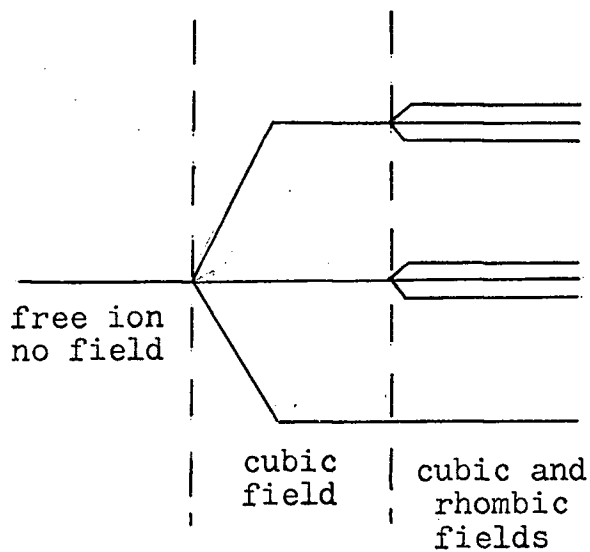
Cr^{+4} , F STATE

OCTAHEDRAL ENVIRONMENT



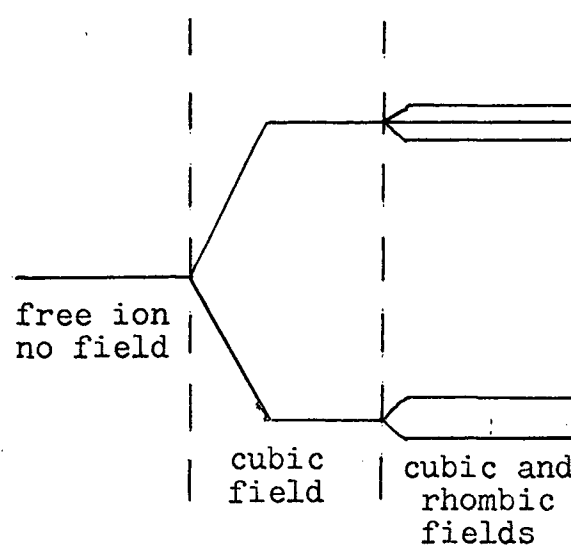
Cr^{+5} , D STATE

OCTAHEDRAL ENVIRONMENT



Cr^{+4} , F STATE

TETRAHEDRAL ENVIRONMENT



Cr^{+5} , D STATE

TETRAHEDRAL ENVIRONMENT

magnetic moment of ions in the F and D states are appreciably higher than the spin-only values, an octahedral arrangement around the ion may be suggested.

The observed value of μ_{eff} for chromium tetrafluoride (F state) is 3.02 B.M. and is higher than the spin-only value which is 2.83 B.M. for two unpaired electrons. There is a large orbital contribution suggesting an octahedral environment. Similarly, the values of the magnetic moments observed for complexes of the type ACrF_5 , containing tetrapositive chromium, are higher than the spin-only value. For example, KCrF_5 and CsCrF_5 have magnetic moments of 3.16 B.M. and 3.20 B.M. respectively, whereas the calculated spin-only value is 2.83 B.M. Again, an appreciable orbital contribution is indicated, suggesting that the central paramagnetic ion has attained hexacoordination.

An example of the D state is the tetrapositive vanadium ion, whose compound vanadium tetrafluoride and its complexes are well known. Its magnetic properties have been studied in detail (31) and the observed value of μ_{eff} is 2.17 B.M., and is higher than the calculated spin-only value of 1.73 B.M. This suggests an octahedral environment around the V^{+4} ion in vanadium tetrafluoride and also in complexes as K_2VF_6 and $\text{SeF}_4 \cdot \text{VF}_4$, which have values of 2.05 B.M. and 2.32 B.M. respectively for their magnetic moments. However, the observed value of μ_{eff}

for vanadium trifluoride (F state) is only 2.55 B.M. (72) and is noticeably lower than the spin-only value, but in the absence of data over a temperature range, no remarks can be made.

Hexacoordination of vanadium has already been suggested (31) in analogy with the structure of titanium tetrafluoride proposed at first by Hückel (29). Recent work on the heat capacity of titanium tetrafluoride (32) also supports this view.

Thus, the observed values of the magnetic moments of the fluorine compounds of tetrapositive chromium and vanadium show large orbital contribution which is in accord with hexacoordination of the central metal ion.

VII. REACTION OF CHROMIUM TRIOXIDE AND POTASSIUM DICHROMATE WITH HALOGEN FLUORIDES

Oxides react very differently with bromine trifluoride (80) and investigations of these reactions have resulted in the preparation and isolation of many new fluorides and oxyfluorides. Oxides can be divided into two classes, depending on whether or not they react with the fluoride.

- (i) oxides which do not react or which react very slowly: in this category are included BeO , MgO , ZnO , CdO , HgO , CaO , MnO_2 , Fe_2O_3 , etc.
- (ii) oxides which react with bromine trifluoride by exchanging oxygen with fluorine: these can be further divided into two groups--
 - (a) replacement of oxygen is complete, yielding a fully fluorinated product. Since bromine trifluoride is known to oxidize and fluorinate at the same time, the products contain the metal in the highest oxidation state. This category includes TiO_2 , As_2O_3 , Sb_2O_3 , and SeO_2 , which give TiF_4 , As_2F_5 , $\text{SbF}_5 \cdot \text{BrF}_3$, and SeF_6 respectively.
 - (b) replacement of oxygen is partial, and oxyfluorides result. For example, V_2O_5 reacts with bromine trifluoride to form VOF_3 .

The reactions of the oxides of the first series of transition metals show a gradual decrease in the tendency of

oxygen in the oxide to be replaced by fluorine. Thus, while titanium dioxide replaces all of its oxygen, vanadium pentoxide and chromium trioxide replace only two-thirds, and the oxides of the next two elements do not react. Why the replacement of oxygen by fluorine becomes more difficult as we proceed from titanium to manganese and iron cannot be explained at the present stage, as little is known about the structures and thermochemistry of oxyfluorides, and about the mechanism of reaction. However, the important point to note is that the reaction of CrO_3 and BrF_3 is the only one of its kind, as the product contains the metal atom in a lower oxidation state (+5) than in the starting material (+6).

A. REACTIONS WITH CHROMIUM TRIOXIDE

The reaction of bromine trifluoride with chromium trioxide was investigated for the first time by Sharpe and Woolf (26). They observed that two-thirds of the oxygen was liberated and the product contained chromium in the +5 oxidation state. The removal of excess bromine trifluoride at a high temperature could not be achieved as it resulted in volatilization of the product, and thus pure CrOF_3 could not be isolated. During this investigation, reactions of chromium trioxide with bromine trifluoride, bromine pentafluoride, and chlorine trifluoride were carried out in an attempt to prepare CrOF_3 free of any solvate. Chromium trioxide reacted with all of these vigorously at room temperature and the product in each case contained

pentapositive chromium, as indicated by the magnetic measurements and supported by chemical analyses. The results of the reactions are given below.

reactants	product analysis		magnetic measurements		formula
	%F	%Cr	χ_M	μ_{294}	
			$\times 10^{-6}$	(B.M.)	
$\text{CrO}_3 + \text{BrF}_3$ (liq.)	obs. 44.5	33.4			
	calc. 44.81	32.71	1715	2.02	$\text{CrOF}_3 \cdot 0.25\text{BrF}_3$
$\text{CrO}_3 + \text{BrF}_5$ (liq.)	obs. 47.7	30.2			
	calc. 47.9	30.8	1443	1.85	$\text{CrOF}_3 \cdot 0.25\text{BrF}_5$
$\text{CrO}_3 + \text{ClF}_3$ (liq.)	obs. 48.00	34.2			
	calc. 48.11	35.13	1418	1.83	$\text{CrOF}_3 \cdot 0.25\text{ClF}_3$

Reactions of chromium trioxide with bromine pentafluoride and chlorine trifluoride were carried out to see if it is possible either to replace all of the oxygen in the molecule, or to obtain an oxyfluoride containing chromium in the +6 oxidation state, in view of the fact that both of these agents are considered to be stronger fluorinating agents than bromine trifluoride. Neither of these two reactions, carried out below a temperature of 50°C, gave the desired product. Therefore, it was decided to perform a reaction using a higher temperature, and with the fluorinating agent in the gaseous phase; chlorine trifluoride, being the more reactive of the two, was selected. A stream of chlorine trifluoride was passed over the heated oxide. The reaction product sublimed at the reaction temperature and a dull-red solid collected in the trap following the silica reaction tube. This appeared

completely different from the product obtained as a result of the reaction carried out using liquid chlorine trifluoride. This red product was paramagnetic, the magnetic moment corresponding to one unpaired electron, indicating that chromium was present in the +5 oxidation state. Chemical analysis showed the product to be identical with the liquid phase reaction product, $\text{CrOF}_3 \cdot 0.25\text{ClF}_3$. This indicated that the two compounds were identical chemically and differed only in state of aggregation or other physical properties. The one obtained in the vapour phase reaction was more compact, solid, and appeared crystalline, while the one obtained in the liquid phase reaction was less dense and appeared amorphous. In order to see if the dull-red compound obtained in the vapour phase reaction could be transformed into the liquid phase reaction product, a sample of the former was carefully heated in a silica tube. At a temperature of about 75°C the compound expanded considerably and occupied almost the whole of the tube; this final product was identical in appearance to the liquid phase reaction product. The composition of the compound was unchanged, as shown by analysis. Thus, the dull-red vapour phase product was converted, on heating, into the yellowish substance obtained with the liquid phase reaction, apparently a change only in the state of aggregation.

These oxyfluoride adducts are very reactive and

fume in air giving yellow fumes of chromyl fluoride. They are hydrolysed by water, yielding Cr^{+3} and CrO_4^{-2} ions in solution. The products are orange in colour and react with glass when stored for long periods, even under vacuum. However, they can be handled for short periods in glass vessels, and manipulated under dry-box conditions. The reaction with glass presumably is due to the halogen fluoride produced as a result of dissociation. Attempts were made to take X-ray photographs of these adducts but the capillaries containing the specimens exploded during exposure. Both silica and pyrex capillaries were used. The X-ray pattern of the dull-red product obtained from the vapour phase reaction was taken, but decomposition was seen to have occurred inside the capillary. It was therefore not possible to say whether the pattern was due to the original substance or to the decomposition product.

The fluorination of chromium trioxide with many different fluorinating agents can therefore be summarized as follows.

<u>fluorinating agent</u>	<u>product</u>	<u>% of displaced oxygen</u>	<u>reference</u>
SF_4	CrO_2F_2	33.3	(81)
IF_5	CrO_2F_2	33.3	(82)
SeF_4	CrO_2F_2	33.3	(83)
BrF_3	$\text{CrOF}_3 \cdot 0.25\text{BrF}_3$	66.6	present work
BrF_5	$\text{CrOF}_3 \cdot 0.25\text{BrF}_5$	66.6	present work
ClF_3	$\text{CrOF}_3 \cdot 0.25\text{ClF}_3$	66.6	present work

The percentage of displaced oxygen in these reactions falls in line with the general order of reactivity of these fluorinating agents. The weaker fluorinating agents displace only a third of the oxygen, while the stronger ones displace two-thirds.

Oxyfluorides of chromium

The possibility of the formation of oxyfluorides is apparent from the fact that the sizes of fluorine and oxygen are not very different and hence they can mutually replace each other in compounds without causing much structural change. Thus, some oxyfluorides of transition metals show a remarkable similarity in physical properties to binary fluorides of similar empirical composition (e.g. MoOF_4 has melting and boiling points similar to those of MoF_5), while others resemble oxides. Replacement of a fluorine atom by oxygen, however, will require a change in the oxidation number of the metal or a change in the coordination number if two fluorine atoms are replaced.

Knowing that the maximum oxidation number of chromium is +6 and that it shows lower oxidation states of +4 and +5, the following oxyfluorides, at least in theory, are possible.

<u>oxidation state</u>	<u>oxyfluorides</u>
Cr^{+6}	CrO_2F_2 , CrOF_4
Cr^{+5}	CrOF_3 , CrO_2F
Cr^{+4}	CrOF_2
Cr^{+3}	CrOF

The oxyfluoride CrO_2F_2 , chromyl fluoride, is well known and evidence for the existence of CrOF_3 was given by Sharpe and Woolf (26). In the present investigation, unsuccessful attempts were made to prepare pure CrOF_3 ; however, adducts of CrOF_3 were isolated.

The compound CrOF_4 was not formed in any reaction, and this is not easily understandable since the analogous compounds of molybdenum and tungsten (84,85) are well known. However, this parallels the fact that chromium hexafluoride is not known, although MoF_6 and WF_6 are well known compounds. Similarly, the compound CrOF_2 should be capable of isolation since the analogous compounds TiOF_2 (86), VOF_2 (87), and WOF_2 (88) are known. With further work, it is possible that the missing oxyfluorides will be prepared.

B. REACTION OF DICHROMATES WITH HALOGEN FLUORIDES

The reaction of potassium dichromate with bromine trifluoride has been previously studied by Sharpe and Woolf (26). They reported the formation of $\text{KCrOF}_4 \cdot 0.5\text{BrF}_3$, which on heating to 130--150°C lost the combined bromine trifluoride, yielding pure KCrOF_4 , containing pentapositive chromium. The oxidation state of chromium was confirmed by a magnetic moment measurement (72) which gave a value of 1.76 B.M.

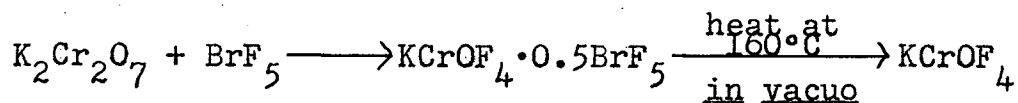
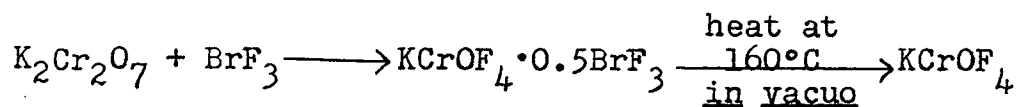
In the present work, the reaction of bromine trifluoride with potassium dichromate was repeated, and furthermore the reactions of bromine pentafluoride and chlorine trifluoride with potassium dichromate were

investigated. These latter reactions were studied in order to see if bromine pentafluoride and chlorine trifluoride, well known as fluorinating agents stronger than bromine trifluoride, could either replace all of the oxygen in the molecule or yield a product of type KCrOF_5 , containing chromium in the +6 oxidation state. However, it was found that in all cases the product of reaction was KCrOF_4 , containing chromium in the +5 oxidation state.

With bromine trifluoride, the product $\text{KCrOF}_4 \cdot 0.5\text{BrF}_3$ was obtained as reported by previous workers: it could be prepared free of bromine trifluoride when heated to 160°C in vacuo. X-ray photographs of both products, the adduct and the pure compound KCrOF_4 , were taken and were found to be identical, indicating that inclusion of bromine trifluoride in the lattice does not alter the crystal structure.

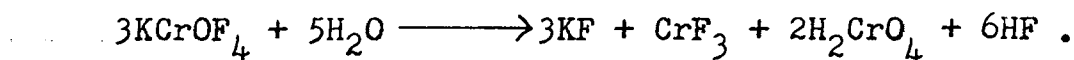
The reaction of bromine pentafluoride and potassium dichromate resulted in a product which gave an X-ray pattern different from that of $\text{KCrOF}_4 \cdot 0.5\text{BrF}_3$. Chemical analysis revealed that the product was a bromine pentafluoride adduct, and that chromium was in the +5 oxidation state since the compound was paramagnetic, the magnetic moment corresponding to one unpaired electron. The bromine pentafluoride contained in the complex could be very easily removed by heating the compound in vacuo at 160°C to yield pure KCrOF_4 , as shown both by chemical analysis and by the X-ray pattern, identical with that obtained from the product of reaction of

potassium dichromate with bromine trifluoride. The reactions of bromine fluorides with potassium dichromate can be formulated as the following:



A reaction of chlorine trifluoride with potassium dichromate at room temperature also gave a paramagnetic product whose X-ray pattern was like that of KCrOF_4 .

The compound KCrOF_4 is highly reactive. It decomposes in air and therefore needs to be handled in dry-box conditions. It dissolves in water giving chromic and chromate ions in solution, according to the equation



Magnetic susceptibility measurements were carried out at different temperatures down to 85°K. A plot of reciprocal molar susceptibility versus temperature gave a value of the Weiss Constant equal to +4°. Compared to those for binary fluorides and complex fluorides, the value of the Weiss Constant is remarkably low. Unfortunately, no binary fluoride of Cr^{+5} is known, and therefore no comparison can be made. However, the fluoride and complex fluorides of V^{+4} , isoelectronic with Cr^{+5} , are known to possess high values of the order of 150° (31). Whether or not the low

value of θ in KCrOF_4 is associated with the introduction of oxygen in the molecule cannot be decided at present.

It is furthermore remarkable to note that while the presence of bromine trifluoride in the lattice of KCrOF_4 does not affect the crystal structure of KCrOF_4 , this is not so with bromine pentafluoride, whose adduct possesses a structure different from that of KCrOF_4 . This difference produced by bromine pentafluoride is most probably due simply to its larger size as compared with bromine trifluoride.

VIII. THE ANALYTICAL DETERMINATION OF FLUORINE

The accurate determination of fluorine is still a major problem of analytical chemistry, and during recent years when fluorine has been put to manifold uses (from atomic research to fluoridation of water) a suitable, simple, and accurate method has become highly desirable. Indeed, during the past several years numerous modified or new methods have been described in the literature. In spite of this, few of the methods are as yet completely satisfactory. Excellent and detailed reviews on the analytical chemistry of fluorine have also appeared during the last few years (89,90).

All the methods for the determination of fluoride depend on the formation of either insoluble metal fluorides and fluorosilicates, or of stable, soluble, metal fluo-, borofluo-, or silico fluoride complexes. Since many other anions can show similar behaviour, most of the methods require separation of fluoride. The suitability of a certain method is determined by the amount of fluorine and by the nature of the cations present in the compound. If the fluorine in the sample is so contained that it is not easily amenable to precipitation (e.g. if it exists as complex ions) the fluoride is separated and then determined.

The methods for determining fluoride can be divided into two classes:

- (i) methods involving separation of fluoride. In this the procedure involves two steps--firstly, a separation of fluoride from cations, and secondly, determination of the amount of fluoride. In this class are included the pyrolytic method, the ion-exchange method, and the Winter-Willard method.
- (ii) methods applied directly to the fluorine-containing compound or to a solution of the compound. In this class are discussed the equivalent weight method and the Null-point potentiometric method.

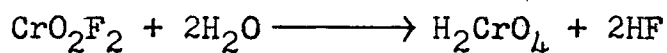
A. METHODS INVOLVING SEPARATION OF FLUORIDE

1. Pyrolytic method

In this method the sample containing fluorine is decomposed to liberate hydrofluoric acid which is condensed in water and then titrated with a standard alkali solution. Pyrolytic methods were first developed in work for the Atomic Energy Commission (91,92) and further studied at Oak Ridge National Laboratory (93). Two techniques using pyrolysis have been used. The first method (94,95) uses superheated steam while the second method involves using a stream of moist oxygen instead of steam (94,96). In the present work the samples were decomposed by steam, and details of the method are described in the experimental section.

Steam was passed over the sample of chromium

tetrafluoride contained in a heated platinum boat and the vapours of hydrofluoric acid and steam were condensed in water. It was observed that the condensate was colourless at first but that later the condensate was yellow. As the pyrohydrolysis was continued, the intensity of the yellow colour in the condensate increased. The yellow colour was due to chromate ions, as a precipitate of lead chromate was obtained when the solution was tested for chromate. This was presumably formed by the pyrohydrolysis of chromyl fluoride, produced by the reaction of chromium tetrafluoride and steam:



This indicated that it is not possible to separate fluorine from chromium by this method and that the condensate could not be used for titration with sodium hydroxide since it contained H_2CrO_4 . Pyrohydrolytic decomposition of chromium tetrafluoride was thus not suitable for analytical purposes.

2. Ion exchange method

The use of ion-exchange resins to separate ions from one another is well known and this has been used for the isolation of fluoride from other anions and cations. Two types of methods are possible, one using cation-exchange resins and the other using anion-exchange resins.

The use of an anion-exchange resin would involve adsorption of fluoride ions on the resin (97) followed by elution with a suitable solution such as sodium acetate (98)

or sodium hydroxide (99). In theory this method seems very suitable but in practice various complications are associated with it. For example, a solution of a fluoride of tetrapositive or pentapositive chromium will invariably contain terpositive and hexapositive chromium, the former as the anionic complex CrF_6^{-3} , in addition to simple fluoride ions. Naturally, the adsorption of chromate ions and the anionic complex is to be considered. Also, ions of the type $\text{CrF}_{6-x}(\text{OH})_x^{-3}$ will be present and their elution rates will cause complications. Taking into account the possible interference by chromate ions in the solutions containing chromate and fluoride ions, and by anionic complexes in solutions containing Cr^{+3} , no attempt was made to use anionic resins.

The use of cation-exchange resins would involve passing the solution through a column of cation-exchange resin in the hydrogen ion form. Cations will be adsorbed on the resin and the anions, (including fluoride), will pass into the effluent. The use of cation-exchange resins also suffers from the defect that anionic complexes of the type CrF_6^{-3} and $\text{CrF}_{6-x}(\text{OH})_x^{-3}$ will pass through if they are not decomposed by the resin. Separations with cation-exchange resins have been effected nicely for solutions which do not contain complex ions (100).

In the present work, an aqueous solution of chromium tetrafluoride was reduced with sulphur dioxide, excess of

which was removed by heating slowly. The solution was then passed through a column of cation-exchange resin (Dowex-50). The effluent appeared colourless and a dark-green chromium band was observed in the column. However, when the effluent was made alkaline and heated, a precipitate of chromic hydroxide formed.

This indicates that chromium forms stable anionic complexes with fluoride ions and hence a complete separation of chromium from fluoride ions was not possible under the conditions employed. However, it is possible that by a systematic study of the complexes, and by changing the experimental conditions, it might be possible to effect a separation of fluoride ions from chromium in this way.

3. Winter-Willard method

In 1933, Winter and Willard (101) discovered that fluoride could be separated from other elements by volatilization as hexafluosilicic acid, from perchloric or sulphuric acid. The method is applicable for all substances soluble in or decomposed by perchloric or sulphuric acid. The solution is maintained at 135°C in order to avoid excessive acid in the distillate.

Distillations using perchloric and sulphuric acids were performed during this investigation. When perchloric acid was used to decompose the fluorides of chromium, it was observed that the distillate always was yellowish in colour, due to chromium present in the hexapositive

oxidation state. A completely colourless distillate, free of hexapositive chromium, could not be obtained. When sulphuric acid was used, it was observed that by distilling 25 ml. of solution with 35 ml. of concentrated sulphuric acid at 135°C, the distillate always possessed a yellow colour. It was, however, noticed that the intensity of the yellow colour in the distillate depended on the amount of acid in the flask, and that the distillate was colourless when 25 ml. of concentrated sulphuric acid were heated with 25 ml. of just acidic solution of unknown. If the amount of sulphuric acid in the distillation flask was more than the "optimum" amount, 25 ml., the distillate was yellow. In a few determinations when the solution containing fluoride was acidic, a yellow colour in the distillate was again observed, even with 25 ml. of concentrated sulphuric acid. If the amount of the acid was less than 25 ml., the results were low, presumably because of incomplete decomposition of complex anions of chromium (CrF_6^{-3}). If the chromium in solution was present as chromate, the distillation with sulphuric acid again gave a distillate containing colour. This suggests that chromium should be present in the terpositive oxidation state if possible and that too much sulphuric acid should be avoided as an excess causes oxidation of chromic to chromate, causing the appearance of chromium in the distillate.

After separating fluorine as hexafluosilicic acid by volatilization, the determination of fluoride can be carried out by many methods. Those which have been largely used are listed below.

- (i) gravimetric methods (94): these include precipitation as calcium fluoride, as lithium fluoride, as triphenyl tin fluoride, and as lead chlorofluoride.
- (ii) volumetric methods (94): these involve the use of many different salt solutions as titrants, e.g. zirconium, aluminum, iron (III), cerium, and yttrium salt solutions. The most frequently used titrant is thorium nitrate.
- (iii) Null-point potentiometric method (102)--discussed later.

The difficulty in the detection of the end point in the volumetric method using thorium nitrate is well known and careful buffering of the solution is required. If some yellow colour due to CrO_4^{-2} ions is present, this will interfere with the detection of the end point. Precipitation as calcium fluoride gives a precipitate which is very gelatinous, filters with great difficulty, adsorbs other ions, and may become colloidal. It has also been shown that at 105°C calcium fluoride loses 0.5% of its weight through partial conversion to $\text{Ca}(\text{OH})\text{F}$, and at 400°C , 2.5% conversion to the oxide may occur and both of

these compounds retain about 1% HF adsorbed even at 1000°C (103). The conversion factor is not favourable for lithium fluoride. Precipitation as triphenyl tin fluoride is a very good method but requires carefully controlled conditions--the precipitation should be performed in 60--70% alcoholic solution. Moreover, the precipitant itself is not very soluble.

Precipitation as lead chlorofluoride is the most generally used method even though a rigid adherence to experimental procedure is required. The precipitate is granular, settles readily, and is very easy to filter. The conversion factor is favourable. Unfortunately, the composition of the precipitate varies from the stoichiometric ratio and the results can never be better than $\pm 0.5\%$ (104). However, the advantages of this method outweigh those of all others and therefore in this study the fluoride in the Winter-Willard distillate was always precipitated as lead chlorofluoride, which could be weighed as such or dissolved in dilute nitric acid and its chloride content determined by Volhard's method and from it, the fluoride calculated. Since there was a danger of the distillate being contaminated with sulphate and chromate ions, determination was completed volumetrically.

B. METHODS INVOLVING NO SEPARATION

1. Equivalent weight determination method

If an alkaline solution containing chromate and fluoride ions is passed through a cation exchanger, the

The solution containing free acids can be titrated and the normality of solution determined. Knowing the weight of substance taken, the equivalent weight can be calculated.

By knowing the percentage of chromium in the compound, its equivalent weight, and its magnetic moment, an unambiguous molecular formula can be assigned to the compound. As an example, three compounds, CrF_4 , CrF_5 , and CrOF_3 are considered below.

<u>compound</u>	<u>equiv. weight</u>	<u>% chromium</u>	<u>magnetic moment</u>
CrF_4	21.33	40.63	2.83 two unpaired electrons
CrF_5	21.00	35.38	1.73 one unpaired electron
CrOF_3	25.00	41.60	1.73 one unpaired electron

By determining the equivalent weight, it would therefore be easy to distinguish between CrF_5 and CrOF_3 , while the percentage of chromium determination and magnetic moment will distinguish between CrF_4 and CrF_5 , whose equivalent weights are very similar.

It is thus possible to avoid the direct determination of fluorine, which for fluorides of chromium can be extremely difficult for the reasons already described.

2. Null-point potentiometric method

This method, developed by O'Donnell and Stewart (102), is based on the complexing of Ce (IV) by fluoride ions. In

a solution containing both Ce (III) and Ce (IV) ions, addition of fluoride ions results in the lowering of the Ce (IV):Ce (III) ratio and thus in the lowering of the redox potential. In this method an unknown fluoride solution is added to one Ce (IV):Ce (III) half cell and standard fluoride solution is added to a similar half cell until the potential difference is zero. The fluoride ion concentration in both half cells is then the same and is calculated from the amount of standard fluoride solution added. The authors showed there is no interference by chloride, sulphate, and nitrate ions, but acetate, oxalate, phosphate, and molybdate ions caused interference. They did not investigate possible interference caused by cations, apart from observing that alkali or ammonium ions did not interfere; usually cations were removed before fluoride was determined.

In order to avoid the tedious and time-consuming step of separation of fluoride ions, it was decided to examine the effect of chromate and chromic ions on the applicability of this method. The following observations were made:

- (i) Using standard sodium fluoride solutions, the results were accurate and reproducible.
- (ii) Using sodium fluoride solution containing chromic ions, the results were low and the sensitivity of the potential changes towards the addition of

fluoride decreased considerably at the end point, and sensitivity to the addition of small amounts of water increased considerably. The results were not reproducible.

- (iii) Addition of potassium dichromate solution to one half cell and an equal volume of water to another half cell did not result in the development of potential difference. Furthermore, titrating with sodium fluoride and potassium dichromate solution, the results were not reproducible--perhaps some oxidation-reduction phenomena were taking place.

This method is based on the complexing of Ce (IV) species present in the solution and presupposes the availability of all of the fluoride ions for this purpose. Now, in solutions of alkali metal fluorides, it is quite reasonable to expect that all of the fluoride ions are available, but in solutions containing cations capable of forming complex ions with fluoride, the situation will be different. The availability of the fluoride ions will depend on the stability constant of various complex ions and other factors affecting the ionic equilibria. Another important factor which will affect the method considerably is the possibility of the occurrence of oxidation-reduction reactions in the half cell, especially when large concentrations of chromate ion are present and when the acidity

is very high.

Fluoride ions, the "universal addend" (105), are well known to form complex ions in aqueous solution with metallic ions. Indeed, the formation of stable fluoride complexes forms the basis of all colorimetric, fluorometric, potentiometric, and other methods for determination of fluoride. Naturally, the presence of any cation which can form complex ions with fluoride will interfere with the availability of fluoride ions for complexing Ce (IV) and the extent of interference will depend on the degree of dissociation of the complex. If it is completely or readily ionized, then there will be little or no interference, but in other cases, the stability constant of the complex will indicate the extent of interference. The interference by uranium ions in fluoride determination by the Null-point potentiometric method has been reported by the authors, who found that the results were very low, indicating that all fluoride ions were not available to complex Ce (IV). These authors also believe that the method is not suitable for solutions containing ferric ion.

In short, two equilibria need to be considered: the ionization of complex ions formed by cations other than cerium, and the complexing of Ce (IV) to lower the redox potential.

The first step is very important as on this depends the amount of fluoride available to the Ce (IV) ions. If

the stability constant of the complex is high, the equilibrium concentration of complex ion will be considerable, keeping some fluoride ions bound. The amount of fluoride ions to bind Ce (IV) will be less than in the absence of other complex cations, and consequently, the results will be low. In order to assess the value of this reasoning, it is appropriate to compare the stability constants of various complex ions.

Appropriate Logarithms of Formation Constants
for First Fluoride Complexes (94)

<u>ion</u>	<u>log of formation constant</u>	<u>ion</u>	<u>log K₁</u>
Mg ⁺²	1.5	Ti ⁺⁴	6.5
Ca ⁺²	1.5	Zr ⁺⁴	9.8
Zn ⁺²	1.0	UO ₂ ⁺²	4.5
Ag ⁺	0	Fe ⁺³	5.0
Cd ⁺²	0.5	Cr ⁺³	4.5
Ce ⁺³	4.0	Al ⁺³	6.0
VO ₂ ⁺	3.0		

A higher value of log K₁ means a higher equilibrium concentration of complex ions, i.e. low ionization.

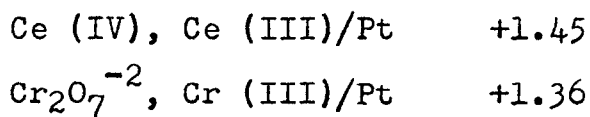
It is quite reasonable to expect that cations with a value of logarithm of formation constant higher than that of Ce (III) will interfere, e.g. Al⁺³, Fe⁺³, etc. The cations that will not interfere will be those having a value of log K₁ less than 3 or 2.5 .

The stability of CrF₆⁻³ ions has been mentioned by

Klemm and Huss (24) who observed that even concentrated sulphuric acid does not decompose the complex very easily. The value of log of formation constant is 4.5, which is higher than that for Ce (III) complex. It is therefore not surprising that the ionic equilibrium will be affected and low results will be obtained for the fluoride determination.

Another important point to consider is the role of pH and of concentration changes. In the original method, addition of unknown solution and of titrant is balanced by additions of equal amounts of distilled water. When the pH of the unknown solution is near seven, its addition will scarcely affect the pH, and this will be completely balanced by the addition of water to the other half cell. On the other hand, if the unknown solution is acidic or alkaline, then its addition to one half cell and addition of distilled water to another will not give comparable pH values. This imbalance of pH will disturb the various ionic equilibria which are sure to exist where complex-forming cations are present, and this will affect the potential changes. For example, using alkali fluoride solutions, it is observed that the determination is not very sensitive to the addition of small amounts of water--one millilitre or so--but when it contains cations (such as Cr (III)), the potential becomes very sensitive to water addition.

The other possibility is to oxidize chromic ions to chromate and then use this solution. If an alkaline solution is used, there is danger of precipitation of basic cerium salts (106). If an acidic solution is used oxidation-reduction reactions can occur. The oxidation potentials of Ce (IV) and Cr (VI) are very similar (107).



In small concentrations, dichromate ions should not cause any difficulty. In large concentrations, however, especially when fluoride ions are present in the solution (which will complex Ce (IV) and reduce its concentration and hence the potential) dichromate ions will interfere seriously and render the method unsuitable.

The foregoing review of various methods for the determination of fluorine indicates that to date the most widely applicable method is that of precipitating as lead chlorofluoride following the separation of combined fluorine by a Winter-Willard distillation. The present investigation demonstrates that the use of perchloric acid for Winter-Willard distillation should be avoided when the solution contains cations which can be oxidized or which form very stable fluoro-complexes. Sulphuric acid is more suitable than perchloric acid but there is danger of interference by the sulphate ion. The best procedure is to use sulphuric acid for distillation and precipitate

fluorine as lead chlorofluoride, and then complete the determination volumetrically.

The Null-point potentiometric method was not found directly applicable for the compounds encountered in the present research. Using this method after separating the combined fluorine by Winter-Willard distillation is rather tedious (and is of no advantage). Its application to the solution directly is determined by the ability of the cations to form fluoro-complexes. If the cations present in the solution do not form stable complexes, this method is applicable. On the other hand, if the cations present do form stable complexes, the Null-point potentiometric method will give very low results.

The equivalent weight determination method is very simple and requires no special equipment. This method is applicable to those cations which form stable complexes but which can be oxidized to oxyanions. The present investigation was concerned with fluorides of chromium, and because chromium could be oxidized to chromate, this method was particularly suitable. It gave good and reproducible results, and was therefore often used.

IX. TETRAFLUORIDES OF THE FIRST TRANSITION SERIES

The first transition series includes the metals from scandium to copper. The maximum oxidation states attained by these are (108):

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
3	4	5	6	7	6	4	2	2

The possibility of the formation of a tetrafluoride exists for the elements after scandium, and tetrafluorides of titanium, vanadium, chromium, and manganese are known. Iron does not show a +4 oxidation state, most probably because of the extra stability of ferric ion containing five electrons in the d orbital. The elements cobalt and nickel show +4 oxidation states in fluoro-complexes only.

Some guidance concerning the relative stabilities of oxidation states can be obtained by considering the values of the ionization potentials (109), which are given below.

	Ti	V	Cr	Mn	Fe	Co	Ni
4th <u>I.P.</u>	24	48	49.6				

It is observed that the value of the fourth ionization potential increases in the series, indicating the increasing difficulty of obtaining the elements in a +4 oxidation state. Strictly speaking, this problem of

the relative stabilities of oxidation states is very complex and is not amenable to a simple generalization. Recently Maksimova (110) has evaluated for the elements the function p , defined as

$$p = \frac{I_w}{\sum_{i=1}^w I_i}$$

This function represents the fraction of the energy expended in removal of the last electron to obtain the oxidation number w . According to the author, the question of the existence of various oxidation states can be solved on the basis of the values of p . This appears to be true in a qualitative way but the existence of a particular oxidation state is dependent very largely on the ligands. The values of p for the +4 oxidation state for the elements of the first transition series are given below.

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
p :	.482	.474	.479	.488	.493	.474	.476	.473

The general rule given by Maksimova is that the less the deviation from the value of p characteristic for the group, the greater the probability of the ion having the charge corresponding to that group. If for oxidation number +4, the value of p for titanium is taken to optimum, then it is seen that the deviation is maximum in the case of iron and

copper, and this is in accord with the fact that no tetrafluoride of these or complexes thereof are known. However, this would also predict the existence of nickel tetrafluoride and cobalt tetrafluoride, for which the deviation is less than or equal to that of vanadium tetrafluoride, but the spontaneous decomposition of vanadium tetrafluoride at room temperature is consistent with this, and might also predict instability for nickel tetrafluoride and cobalt tetrafluoride.

Of the known tetrafluorides of the first transition series, manganese tetrafluoride has been isolated only recently, and as yet not much is known about its chemical properties (30).

PREPARATION AND PHYSICAL PROPERTIES OF THE TETRAFLUORIDES

All the tetrafluorides are formed when the metal is fluorinated. Titanium tetrafluoride is a white solid and boils at 284°C (7). Vanadium tetrafluoride is a solid and sublimates at $100\text{--}120^{\circ}\text{C}$ (31) with disproportionation, while chromium tetrafluoride is also a solid and sublimates at 158°C in vacuo. Vanadium, chromium, and manganese in the +4 oxidation state possess one, two, and three unpaired electrons in the d orbitals and are therefore paramagnetic. The observed magnetic moments agree with this, and are given in the following.

	<u>$\mu_{\text{obs.}}$</u>	<u>$\mu_{\text{calc. (spin only)}}$</u>	<u>Weiss Const.</u>	<u>$\mu_{\text{obs.}} - \mu_{\text{calc.}}$</u>	<u>reference</u>
VF_4 :	2.17	1.73	198°	.44	(31)
CrF_4 :	3.02	2.83	70°	.19	present work
MnF_4 :	3.83	3.87	10°	.04	(30)

It is remarkable to note that the deviation from the spin-only values decreases from vanadium to manganese, indicating decreased orbital contribution to magnetic moment. The value of the Weiss Constant also falls in the series, and this may be due to the increased covalent character of the tetrafluoride.

To conclude, a comparison of the chemical properties of vanadium tetrafluoride and chromium tetrafluoride is given in Table 1 (page 93). Titanium tetrafluoride is omitted mainly because it contains no d electrons and the possibility of oxidation to a higher oxidation state does not exist. Manganese tetrafluoride is omitted because little has yet been reported about its chemical properties.

Table 1

A comparison of the chemical properties of
vanadium tetrafluoride and chromium tetrafluoride.

(a) with water	hydrolysed to $\text{VO}^{+2} + 4\text{F}^-$	hydrolysed to $\text{Cr}^{+3} + \text{CrO}_4^{-2} + 4\text{F}^-$
(b) with SO_2 and SO_3	no reaction	no reaction
(c) with NH_3 (liq.)	formed 1:1 adduct $\text{VF}_4 \cdot \text{NH}_3$	no reaction
(d) with BrF_3 (room temp.)	oxidation to VF_5	no reaction
(e) with BrF_3 (boiling)	oxidation to VF_5	yields green $\text{CrF}_3 \cdot 0.5\text{BrF}_3$
(f) with SeF_4 (room temp.)	formed 1:1 adduct $\text{SeF}_4 \cdot \text{VF}_4$	no reaction
(g) with SeF_4 (boiling)	formed 1:1 adduct $\text{SeF}_4 \cdot \text{VF}_4$	yields $\text{CrF}_3 \cdot \text{SeF}_4$ $\text{CrF}_2 \cdot \text{SeF}_4$
(h) with IF_5	no reaction	no reaction
(i) $\text{ACl} + \text{BrF}_3$	AVF_6	ACrF_5
(j) $2\text{ACl} + \text{BrF}_3$	A_2CrF_6

A = K, Rb, or Cs

E X P E R I M E N T A L

X. GENERAL TECHNIQUES

Progress in fluorine chemistry has been retarded because of the high reactivity of fluorine and many fluorides. Fluorine itself is the most powerful oxidizing agent known, while chlorine and bromine fluorides are almost as reactive as fluorine. Thus, extreme precautions must be taken in the storage of these compounds. For example, fluorine reacts very readily with organic materials such as vacuum grease and oil, and it is necessary to select materials for laboratory apparatus very carefully. We know now that a wide range of suitable materials is available, including most metals, ceramics, and siliceous bodies. The development of fluorocarbons and of fluorocarbon polymers has further extended the range of fluorine resistant materials.

The usual material for apparatus, glass, reacts with fluorine and many fluorides, producing hydrofluoric acid which not only contaminates the products but also in many cases masks the true chemical properties of the compounds being studied. It is true that metallic apparatus could be used, but the advantages of glass are well known and previous workers have shown that borosilicate or quartz glass can be used provided the apparatus has been baked dry on the exposed surface, preferably under vacuum. Also, in the use of reactive fluorides such as halogen fluorides, which have been widely used in this research,

care should be taken to use as little vacuum grease as possible, since this is readily attacked by these fluorides. In this study, therefore, most experiments were performed in all-glass vacuum systems using techniques described previously (111). The susceptibility of fluorides to hydrolysis also requires, in addition to rigorously dried apparatus, the use of reagents which are completely free of any traces of moisture. Before being reacted with fluorides, all the reagents used in this study were distilled from drying agents in all-glass apparatus.

A. PREPARATIVE TECHNIQUES

Preparative techniques in this work involved the use of fluorine, bromine trifluoride, bromine pentafluoride, and chlorine trifluoride as fluorinating agents and as solvents in complex-forming reactions.

1. Fluorine

Fluorine was obtained from a 6 lb. cylinder which was clamped in a vertical position and well shielded with bricks on two sides and with fume-hood walls on the other two sides. The cylinder valve was opened by a key having a handle 4 ft. long. Two Hoke stainless steel needle valves in series were used to reduce the pressure of the fluorine gas, which was 400 lbs./in.² in the cylinder. The high pressure side was made from half-inch stainless steel tubing and was connected to the cylinder by a compression fitting, a Teflon gasket being employed. A stainless steel

Bourdon type pressure gauge was screwed and silver-soldered into this part of the system. The low pressure side of the system was constructed from quarter-inch copper tubing, with the exception of the sodium fluoride chamber (to remove hydrogen fluoride), which was of half-inch diameter. All valves on the low pressure side of the system were brass bellows-sealed needle valves. Also on the low pressure side, a safety blowout valve was provided in which excess pressure of fluorine was reduced by bubbling through a fluorocarbon oil (Hooker Chemicals F S-5). This could also be used, before carrying out any reaction, to give a rough estimate of the fluorine flow-rate.

2. Bromine trifluoride

Bromine trifluoride was taken from a cylinder provided by Matheson Co., Inc. A train of four traps was connected to the valve on the cylinder of bromine trifluoride by Teflon tubing. The traps were provided with break-seals and with constrictions in their side arms, by means of which they could be sealed off. The traps were dried under vacuum by flaming and the three traps following the cylinder were cooled by liquid nitrogen baths and the valve of the cylinder was opened; bromine trifluoride condensed in the trap closest to the cylinder. When a sufficient quantity of bromine trifluoride had distilled, the system was sealed off from the cylinder. The bromine trifluoride in the first trap was separated into three portions by distilling into other traps. All the traps

were sealed off and kept at -78°C until required.

The bromine trifluoride obtained from the cylinder contained bromine pentafluoride as an impurity. Because in some reactions it was desirable to use bromine trifluoride free of pentafluoride, the trifluoride was prepared in the laboratory by direct fluorination of bromine. Bromine dried over phosphorus pentoxide was taken in a glass reaction vessel and nitrogen-diluted fluorine was bubbled through it at a slow rate. The reaction vessel was connected to a train of traps provided with break-seals and was surrounded by a beaker containing carbon tetrachloride, which was kept cool by dropping some liquid nitrogen onto its surface from time to time. The fluorination of bromine proceeded very smoothly, as could be seen by the gradual disappearance of the bromine colour. After two to three hours, the bromine in the vessel had changed to a clear yellow liquid. The reaction vessel was then sealed off from the fluorine supply and flushed with nitrogen. The bromine trifluoride was distilled into a storage trap provided with a break-seal.

3. Bromine pentafluoride

Bromine pentafluoride was taken from a cylinder supplied by Matheson Co., Inc., and was condensed into traps in the same manner as bromine trifluoride.

4. Chlorine trifluoride

Chlorine trifluoride was supplied by Matheson Co., Inc., and was similarly taken into traps.

B. APPARATUS FOR REACTIONS WITH BROMINE TRIFLUORIDE, CHLORINE TRIFLUORIDE, BROMINE PENTAFLUORIDE, AND SELENIUM TETRAFLUORIDE.

The reaction vessel was made of silica tube of 12 mm. diameter closed at one end and connected to a 6 cm. length of silica tube of 10 mm. diameter. The 10 mm. tube was joined to an extended B-10 ground silica cone. The extended cone was used to prevent any reaction of the fluorinating agent with grease. Before each use the reaction vessel was cleaned with chromic acid and dried.

In summary then, to minimize as far as possible the contact of grease with reactive fluorides, the following modifications were found useful.

- (i) use of extended cones
- (ii) use of sockets with inlet tubes

C. REACTION WITH HALOGEN FLUORIDES

This involved condensation of halogen fluoride onto reactants in the reaction vessel and then heating the contents of the vessel to the desired temperature under atmospheric pressure. After the completion of the reaction, excess halogen fluoride was distilled away. Removal of the excess of halogen fluoride was accomplished by distillation in vacuo, at first at room temperature and then at higher temperatures. Bromine pentafluoride could be distilled off much more easily than bromine trifluoride, which required heating to a temperature of 160°C for complete removal. Chlorine trifluoride was very easily distilled.

A typical example of a preparation involving a halogen fluoride is the preparation of potassium pentafluoro-chromium (IV), KCrF_5 , and is described below.

Apparatus was set up as shown in Fig. no. II (page 101) and was thoroughly dried and evacuated. It was disconnected from the vacuum line and then air was allowed to enter very slowly while trap J was surrounded by a CO_2 --alcohol mixture to condense any moisture.

The silica vessel containing weighed quantities of chromium tetrafluoride and potassium chloride (1:1 molar ratio) was attached to the system by means of a B-10 joint and the system was evacuated again. The break-seal of trap B containing bromine trifluoride, which was surrounded by the CO_2 --alcohol bath, was broken magnetically and any more volatile impurities were pumped off. Stopcock T was closed, the silica reaction vessel was surrounded by a liquid nitrogen dewar, and the CO_2 --alcohol bath surrounding trap B was removed. As trap B warmed up, bromine trifluoride was condensed into the reaction vessel. Bromine trifluoride in trap B melted, and then the trap was turned around through an angle of 180° very cautiously, causing the liquid bromine trifluoride to run down into the reaction vessel. After the transfer of bromine trifluoride, trap B was sealed off and removed. The system was disconnected from the vacuum line and traps L, K, and J were surrounded by CO_2 --alcohol baths. The tap T was opened very slowly to let in air. The

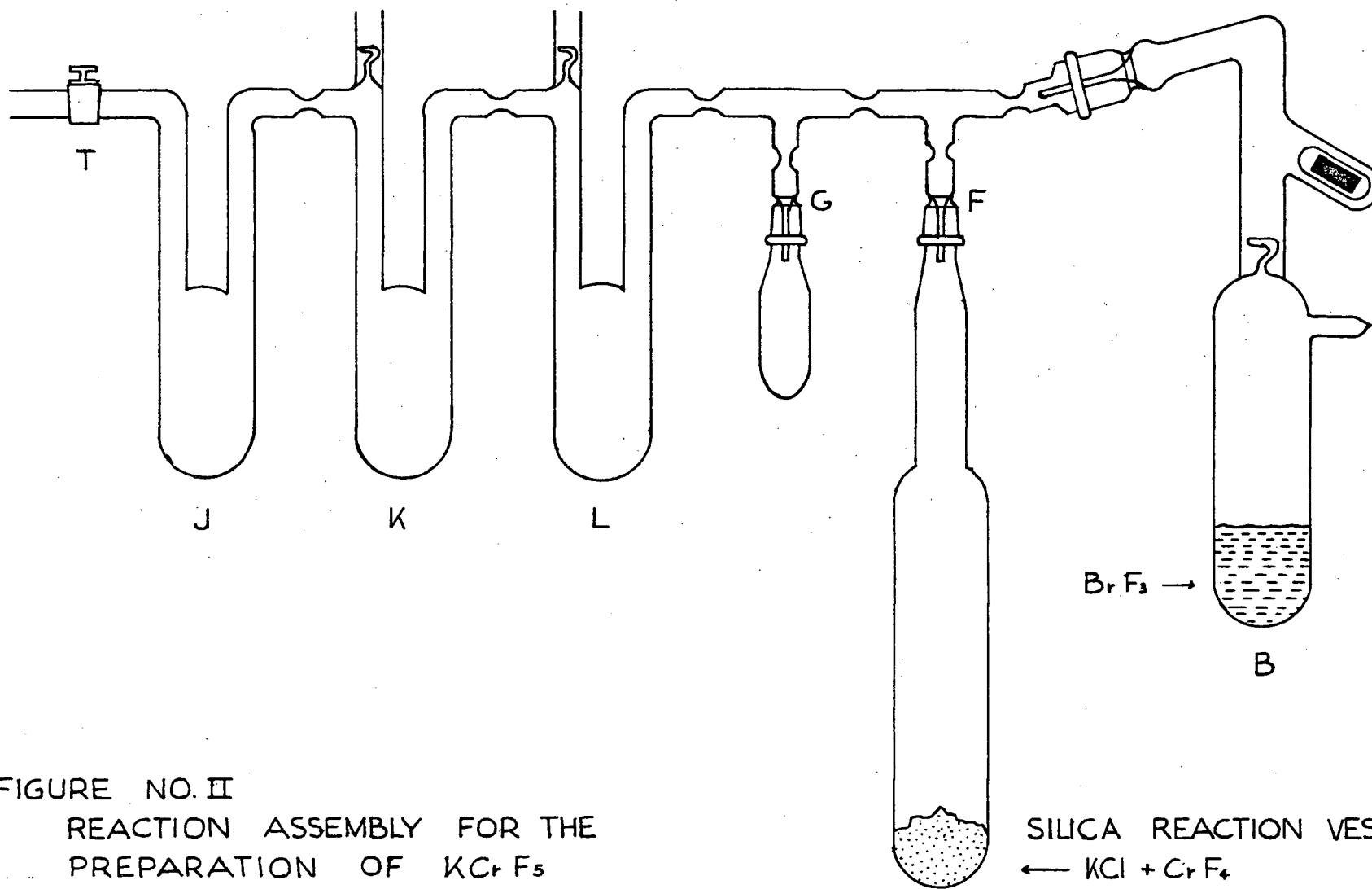


FIGURE NO. II
REACTION ASSEMBLY FOR THE
PREPARATION OF KCrF_5

cooling of traps L, K, and J prevented the entry of moisture. The liquid nitrogen bath surrounding the reaction vessel was removed and the silica vessel was allowed to warm to room temperature. At this stage the silica vessel was transferred from F to G, and F was closed by a cone.

The silica reaction vessel was heated by means of a small flame for ten to fifteen minutes and when the reaction was complete, the vessel was surrounded by a CO_2 --alcohol bath and tap T was closed. The tube V was connected to the vacuum line. The trap L was surrounded by a liquid nitrogen dewar and vacuum was applied very slowly by opening carefully the tap T. The CO_2 --alcohol bath surrounding the reaction vessel was removed and excess bromine trifluoride was distilled off very slowly. Particular care was needed while distilling off excess bromine trifluoride, as a quick distillation rate results in spurting, and the recording of weights becomes meaningless. When no more bromine trifluoride was distilling over at room temperature, the reaction vessel was surrounded by boiling water. An oil bath maintained at a temperature of 160°C was used to obtain a product free of bromine trifluoride. In order to ensure complete removal of bromine trifluoride, the substance had sometimes to be heated for twenty-four hours. After complete removal of bromine trifluoride, the reaction vessel was sealed off and kept in the dry-box.

XI. ANALYTICAL TECHNIQUES

The required analytical techniques involved quantitative determinations of chromium, fluorine, bromine, and chlorine. During all analytical work, an automatic Sartorius analytical balance was used. The chemicals used were of AnalaR or C.P. grades and standard analytical techniques were followed throughout (107).

A. CHROMIUM

Chromium was determined volumetrically by oxidation of the salt to chromate with hydrogen peroxide in alkaline solution. The excess peroxide was decomposed by boiling the alkaline solution. The solution was acidified and its dichromate content determined by the addition of an excess of standard ferrous ammonium sulphate solution and titration of the excess of the latter with standard decinormal potassium dichromate.

Procedure.--A ground glass stoppered conical flask containing 25 ml. distilled water and 5 gm. sodium hydroxide was taken. Powdered sample (0.3--0.5 gm.) was accurately weighed into a small glass tube and the tube was dropped into the conical flask which was very quickly stoppered. Vapours of chromyl fluoride were formed in many cases, which took some time to dissolve. Hydrogen peroxide (10--15 ml.) was added and the solution turned clear. When all of the Cr (III) had been oxidized, the solution was heated for an hour to decompose the excess

peroxide. The solution, when cool, was acidified with 9 N sulphuric acid and transferred to a 100 ml. volumetric flask. For each determination 10 ml. of this solution were used.

To 10 ml. of this solution in a 250 ml. conical flask were added 20 ml. of standard ferrous ammonium sulphate solution, 100 ml. of 2 N sulphuric acid, and 0.5 ml. of N-phenylanthranilic acid. This was titrated with standard potassium dichromate. The volume of ferrous salt solution consumed by dichromate in the original solution was calculated, and from this the percentage of chromium in the sample was found.

B. BROMINE AND CHLORINE

Halide ion was determined by precipitation as silver halide by adding an excess of standard silver nitrate solution, and then titrating the excess silver nitrate with standard potassium thiocyanate (107).

C. FLUORINE

The determination of fluorine was greatly complicated by the formation of very stable chromium complex ions CrF_6^{-3} . Various analytical methods were tried and their values assessed. These methods have been reviewed in an earlier chapter.

1. Methods involving separation

Pyrohydrolysis.--In this method the fluorine is liberated as hydrogen fluoride which is determined titrimetric-

ally with sodium hydroxide, using phenolphthalein as an indicator. Two techniques using pyrolysis have been described in the literature--the first uses steam to decompose fluoride at an elevated temperature, and the second method involves using a stream of moist oxygen.

In the present work steam was used to decompose the sample. The apparatus consisted essentially of a silica tube of 2 cm. diameter and 40 cm. length, having a 35/20 B.S. silica socket at one end and a B-10 ground silica cone at the other. The pyrex steam condenser was attached to the silica tube by way of a B-10 ground silica cone. The steam preheater and steam trap made of quarter-inch internal diameter copper tubing were attached to the other end of the silica tube by means of a brass ball machined to fit the 35/20 B.S. silica socket. The brass ball and the B-10 silica cone were provided with inset tubes to prevent seepage at the joints. The sample was heated by means of an electric furnace. Steam was generated in a 1 l. flask with three necks--one taking the air inlet bubbler, another the moist air/steam outlet, and the third a thermometer.

To carry out a fluorine determination a platinum boat was weighed to a constant weight after heating it to 300°C in a stream of steam and then in a stream of hydrogen. The sample was transferred to the platinum boat in the dry-box, and the boat was re-weighed and transferred quickly into the silica tube. The hydrolysis was carried out by

first passing moist air over the sample, then slowly raising the temperature of the water in the bubbler together with the temperature of the furnace, until eventually the steam was passing over the sample at 300°C. At first a colourless distillate collected, but later a yellow "chromium" colour was seen in the distillate, and as the pyrohydrolysis was continued, the intensity of the yellow colour also increased. The distillate naturally could not be used for estimations of hydrofluoric acid owing to the impurity of chromic acid. Decomposition of the sample by pyrohydrolysis was thus found to be inapplicable to fluorides of chromium.

Ion exchange.--The use of ion-exchange resins to separate cations from anions is well known. It was desired to see if this method could be used to separate chromium from fluorine by running the solution down a column containing cation-exchange resin.

The resin (Dowex-50) was stirred with portions of water until a clear liquid was obtained on decanting from the resin. The resin was then transferred in a water slurry to an ion-exchange column, before backwashing and re-settling repeatedly with water to form a resin bed through which the solution flowed in an even non-channelling stream. The column was then eluted with concentrated hydrochloric acid to convert the resin into the hydrogen form and to remove other cations, particularly ferric ions, originally sorbed onto the resin. Elution was then continued with dilute

hydrochloric acid and finally with water until the effluent was free from chloride ions.

In order to carry out a separation, a solution was prepared by dissolving 1.05 gm of chromium tetrafluoride, oxidizing it to chromate with hydrogen peroxide, and then diluting the solution to 250 ml. An aliquot portion (25 ml.) of this solution was heated with concentrated hydrochloric acid and alcohol to reduce chromate to the chromic state. The solution was then diluted and passed through the ion-exchange column. The eluant appeared colourless and a dark green band was seen in the column. Concentration of eluant, after making it alkaline, gave a precipitate of chromic hydroxide, indicating that some chromium had passed as an anion complex. Thus it was not possible under these experimental conditions to separate chromic from fluoride ions by passing the solution through the column.

Winter-Willard method (101).---Winter and Willard found that fluoride may be volatilized as fluosilicic acid from a perchloric or sulphuric acid solution in the presence of quartz, glass, or porous plate with steam vapour as the carrier gas. In this work sulphuric acid was used to decompose fluoride, as perchloric acid was not found suitable.

A sample of the compound was accurately weighed and dissolved in a sodium hydroxide solution contained in a

beaker. The solution was acidified until clear and then transferred to a 250 ml. flask. Of this solution 50 ml. were taken into a 250 ml. distilling flask equipped with a thermometer, a dropping funnel, and a condenser. Concentrated sulphuric acid (25 ml.) was added through the dropping funnel and mixed with the solution, the solution was brought to a boil, and the liquid in the flask was maintained at 135--140°C by adding water slowly from the dropping funnel. The distillate was collected in a beaker containing 25 ml. of dilute sodium hydroxide solution. Approximately 300 ml. of distillate was collected over a period of two hours. The estimation of fluorine in the distillate could be completed in two ways, gravimetrically and volumetrically.

(i) gravimetrically

The Winter-Willard distillate was acidified with nitric acid, using bromophenol blue as an indicator. The solution was then made alkaline by careful addition of sodium hydroxide, acidified with hydrochloric acid, and 1 ml. hydrochloric acid added in excess. The solution was heated to 80°C and 5 gm. of lead nitrate were added with constant stirring. The solution was heated to boiling, and when the lead nitrate had dissolved, 5 gm. of sodium acetate were added, resulting in the precipitation of lead chlorofluoride. The white crystalline precipitate was digested on a water bath for an hour and left overnight. The precipitate was

filtered off on a sintered-glass crucible (weighed to a constant weight), washed once with cold water, five times with a saturated solution of lead chlorofluoride, and finally with water once more. The crucible was dried to a constant weight at 134--140°C and the percentage of fluorine calculated.

(ii) volumetrically

The fluoride in the distillate was precipitated as lead chlorofluoride as described above in the procedure for gravimetric determination, and instead of filtering through a sintered glass crucible, the precipitate was filtered on a No. 42 Whatman filter paper and washed as above. The filter paper with the precipitate was transferred to the beaker in which the precipitation had been carried out, and stirred to a pulp in 100 ml. 5% nitric acid. The beaker was heated on a steam bath and an excess of standard silver nitrate solution was added and the determination of chlorine was carried out by the Volhard method (107). The percentage of fluorine was thus calculated.

In the present work, it was observed that the distillate always contained sulphate ions and the precipitate of lead chlorofluoride contained the impurity of lead sulphate. The determinations of fluorine, therefore, were always completed by the volumetric method.

2. Methods involving no separation

Equivalent weight determination.--A neutral or alkaline

solution containing chromate and fluoride anions was passed through a cation-exchange resin column. This resulted in the generation of free acids-- H_2CrO_4 and HF. The eluant was titrated with standard alkali and the equivalent weight of the compound was determined. From a knowledge of the chromium percentage, equivalent weight, and the oxidation state of chromium in the compound, it was possible to decide the molecular formula of the compound. The ion-exchange column used has been described earlier in this chapter.

Before carrying out the determinations with unknowns, it was deemed necessary to check the validity of this method, to see whether chromate ions and fluoride ions could be determined both separately and when present together. For this purpose, a standard sodium fluoride solution and a standard potassium dichromate solution and then a mixture of the two were passed in turn through the resin column, and the resulting acid solutions were titrated with standard alkali. The end points were determined graphically and the results of a typical series are given below.

10.00 ml. of NaF solution after elution required
7.50 ml. NaOH

10.00 ml. of $\text{K}_2\text{Cr}_2\text{O}_7$ solution after elution required
3.40 ml. NaOH

10.00 ml. NaF + 10.00 ml. $\text{K}_2\text{Cr}_2\text{O}_7$ after elution required
10.85 ml. NaOH

It is observed that the titre value for the mixture is equal

to the sum of the values for individual solutions, suggesting that this method is applicable and that the two ions do not interfere.

A solution of chromium tetrafluoride was prepared as follows: chromium tetrafluoride (0.4536 gm.) was weighed accurately into a beaker containing 5 gm. of sodium hydroxide dissolved in 25 ml. of distilled water. Hydrogen peroxide was added to oxidize the chromic ion to chromate. After the oxidation was complete, the excess hydrogen peroxide was removed by boiling the alkaline solution carefully. The peroxide-free yellow solution was transferred to a 100 ml. volumetric flask and 10 ml. of this solution were taken for each determination. The solution (10 ml.) was diluted with 20 ml. of water and passed through the ion-exchange column and the eluant was titrated with standard sodium hydroxide. A value of 21.84 was obtained for the equivalent weight (calc. for CrF_4 : 21.33).

Null-point potentiometric method (102).--Two 250 ml. beakers were used as half cells and were connected by an agar-potassium chloride salt bridge. Two clean platinum wire electrodes were dipping into the half cells and were connected to a potentiometer. The beakers were provided with stirring rods. A solution 0.005 M with respect to Ce (IV) and Ce (III) was prepared, and 50 ml. of this solution were pipetted out in each half cell. The e.m.f. of the cell was checked to be zero. Two standard solutions--

one of sodium fluoride (11.120 gm/l.) and one of potassium dichromate (10.810 gm/l.)--were prepared to study the effect of chromate and chromic ions on the accuracy of the method.

(i) Standard sodium fluoride solution (5 ml.) was added to one of the half cells and 5.00 ml. of distilled water to the other to account for the volume changes. The potential difference was read and brought to zero by careful addition of standard sodium fluoride solution to the other half cell. This required 5.00 ml. of standard sodium fluoride solution.

(ii) Two half cells were set up and the potential difference checked to be zero. To one half cell 5 ml. of chromic sulphate solution (0.5%) were added and the potential difference was again found to be zero.

(iii) Another set of half cells was set up and the potential difference was zero. Standard potassium dichromate solution (5 ml., 10 ml., and 15 ml.) was added successively to one half cell and an equal amount of water was added to the other. There was no change in the potential difference between the two half cells.

(iv) A solution containing both fluoride ions and chromic ions was prepared. Standard potassium dichromate (10.810 gm/l; 50 ml.) was taken in a beaker, reduced with sulphur dioxide, and boiled to remove excess sulphur dioxide and to reduce the volume. To this, 50 ml. of

standard sodium fluoride solution (11.28 gm/l.) was added and the mixture was transferred to a volumetric flask. This was solution A.

In another volumetric flask 50 ml. of sodium fluoride solution (11.28 gm/l.) were diluted to 100 ml. and used as a titre. The fluoride concentration in both solution A and the titre was the same.

Solution A (10 ml.) was added to one half cell and titrated. This required 9.00 ml. of titre to bring the potential back to zero. In another run 8.95 ml. of titre were required. This was approximately 10% less than the amount theoretically required and the results were not reproducible. It was also noticed that near the endpoint the sensitivity decreased considerably, and the potential was very sensitive to changes in the water concentration.

A solution of chromium tetrafluoride was prepared by dissolving 0.4218 gm. of chromium tetrafluoride in water (25 ml.) and sulphuric acid (1 ml.) in a beaker. The solution was transferred to a 100 ml. volumetric flask and 10.00 ml of this solution were used for each determination. Two determinations were carried out and gave the results 37.75% fluorine, and 71.27% fluorine (CrF_4 requires 59.37% fluorine).

Due to serious errors in the results and a lack of reproducibility, this method was not useful for determination of fluorine in chromium tetrafluoride.

XII. MAGNETIC MEASUREMENTS AND X-RAY INVESTIGATIONS

A. MAGNETIC MEASUREMENTS

Magnetic susceptibilities were measured at room temperature and at lower temperatures utilizing a Gouy balance. The apparatus has earlier been described (112) in detail.

The magnetic balance consisted of a semi-micro balance standing on a slate-topped table, the slate top being mounted on an anti-vibration mounting. The magnet used was a Varian 4 in. electromagnet (Model V 4084) with 2 in. tapered pole faces. The pole gap was set at one inch and with a current of 2 amp. per winding section; a field of approximately 15 kilogauss was obtained. The current and hence the field was maintained constant by a current regulator.

1. Room temperature measurement

The compound, contained in a tube sealed under vacuum, was taken into the dry-box. The container was opened and the compound powdered in a dry agate mortar and then transferred to a trap having a side tube of a size suitable for the sample holder, a glass top, and a B-14 cone and socket. This trap had been baked dry before use. The trap containing the sample was evacuated and then disconnected from the vacuum line by closing the glass top. The compound was tipped into the side tube, an appropriate length of which was then sealed off

carefully. The specimen was fitted into the brass holder and suspended from the balance into the pole gap. The weight of the sample was recorded at first without any magnetic field and then in the field. The specimen tube was removed and taken into the dry-box and emptied into another container. The specimen tube was washed with water, dried, and suspended in the magnetic field. The weights in the field and without any field were recorded. The tube was then filled to the same length as the unknown sample with standard HgCo(SCN)_4 (113). A great deal of care was taken to ensure similar packing in both cases. The specimen tube, now containing the standard, was suspended in the pole gap and the change in weight on application of the field recorded. From a knowledge of the weights and changes in weights of unknown and standard, the magnetic moment of the sample could be calculated by the formula

$$\mu = 2.839 \sqrt{\frac{\Delta w(x)}{w(x)} \times \frac{\Delta w(s)}{w(s)} \times \chi_{g(s)} \times M(x) \times T}$$

where $\Delta w(x)$ = change in the weight of unknown

$\Delta w(s)$ = change in the weight of standard

$w(x)$ = weight of the unknown

$w(s)$ = weight of the standard

$\chi_{g(s)}$ = Gram Susceptibility of the standard
 $= 16.44 \times 10^{-6}$ c.g.s. units

$M(x)$ = molecular weight of the unknown

2. Low temperature measurement

The equipment used was a modified form of that used by Figgis and Nyholm (114). Low temperatures were produced by using liquid nitrogen, and the apparatus could be set at any desired temperature in the range of 90--298°K. Measurements were made as already described, and at each temperature fifteen to twenty minutes were allowed to stabilize the circuit and the temperature. From the measurement with the standard, HgCo(SCN)_4 , at room temperature, a tube constant C was calculated and this constant was used to calculate the susceptibility at various temperatures. The molar susceptibility (χ_M) could be obtained and then the reciprocal of molar susceptibility was plotted against absolute temperature to obtain the Weiss Constant.

As an example, measurements on chromium tetrafluoride and the resulting calculations are shown in Table 2, page 117. The plot of the value of $\frac{1}{\chi_M}$ versus T, which gave a value of $\theta = -70^\circ\text{K}$, is shown in Fig. no.III (page 118).

B. X-RAY INVESTIGATIONS

X-ray powder photographs were taken on a General Electric unit with a camera of 14.4 cm. diameter, using $\text{Cu-K}\alpha$ radiation. The samples were sealed in 0.5 mm., thin-walled X-ray capillaries (Pantak Ltd.) in a dry-box to protect them from atmospheric moisture. In general, the diffraction patterns obtained possessed dark background

Table 2

Magnetic susceptibility measurements of
chromium tetrafluoride.

weight of chromium tetrafluoride	1.6425 gm.
weight of standard	1.2480 gm.
room temperature	21°C (294°K)
change in weight (Δw) for standard	0.0200 gm.
change in weight (Δw) for empty tube	0.0007 gm.
χ_g for standard	16.4×10^{-6}

$$C = \frac{16.44 \times 1.248 \times 10^{-6}}{.0207} = 991 \times 10^{-6}$$

$$C' = \frac{991 \times 10^{-6}}{1.6425} = 603.6 \times 10^{-6}$$

<u>Temp. (K)</u>	<u>Δw</u>	<u>$\chi_g, -6$</u> <u>$\times 10^{-6}$</u>	<u>$\chi_M, -6$</u> <u>$\times 10^{-6}$</u>	<u>$\frac{1}{\chi_M}$</u> <u>$\times 10^2$</u>	<u>μ (Curie</u> <u>Law)</u> <u>(B.M.)</u>	<u>μ_{eff} (Curie-</u> <u>Weiss Law)</u> <u>(B.M.)</u>
294°	.0405	24.46	3127	3.20	2.74	3.02
245	.0484	29.20	3746	2.68	2.72	3.06
220	.0517	31.20	3994	2.51	2.66	3.04
198	.0546	32.92	4217	2.37	2.60	3.02
170	.0645	38.93	4983	2.10	2.61	3.12
148	.0687	41.47	5319	1.89	2.52	3.04
123	.0757	45.69	5849	1.70	2.41	3.02

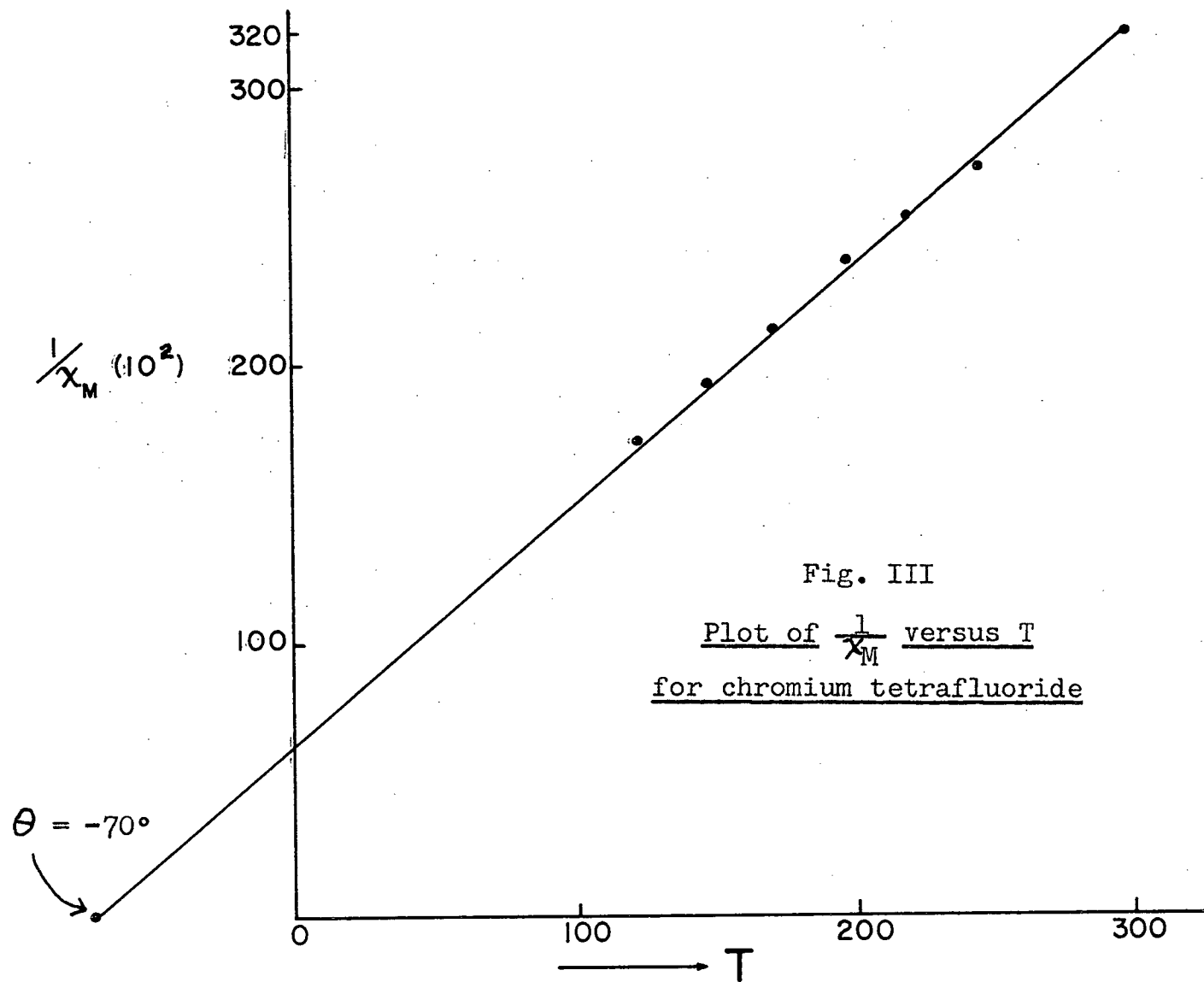


Fig. III
Plot of $\frac{1}{X_M}$ versus T
for chromium tetrafluoride

and showed no lines at high angles. Consequently, no intensity measurements were possible and therefore no detailed structure determinations were made.

XIII. PREPARATION AND REACTIONS OF CHROMIUM TETRAFLUORIDE

A. PREPARATION OF CHROMIUM TETRAFLUORIDE

Chromium tetrafluoride was prepared by the fluorination of powdered chromium metal at 300--350°C (22). Fluorination was carried out in a nickel reactor tube 12 in. long and 1 in. in diameter. One end of the nickel tube was flanged so that the nickel boat containing the powdered metal to be fluorinated could be introduced. This end could be sealed by bolting a nickel plate, with a 1/4 in. exit tube silver-soldered to it, to the flange compressing a lead washer to make a gas-tight seal. The 1/4 in. exit tube in the faceplate was connected to the train of traps by a brass compression fitting. The other end of the nickel tube was silver-soldered to a 4 in. length of 1/4 in. nickel tubing which could be connected to the fluorine supply line with a 1/4 in. compression fitting.

The first two of the train of four traps following the reactor were each equipped with capillary constrictions and break-seals. The other two traps were used to prevent any back diffusion of moisture into the apparatus.

To prepare chromium tetrafluoride, about 8--10 gm. of powdered chromium metal were weighed out into the nickel boat (6 in. x 3/4 in.) which was then placed into the nickel reactor tube. The flange was bolted into place and then the nickel reactor tube was placed in a tube furnace. The reactor tube was connected to the fluorine-nitrogen

supply on one end and to the train of traps on the other.

Before fluorinating, it was absolutely necessary to dry the apparatus as well as possible. This was achieved by pumping on it while the furnace was adjusted to a temperature of 200°C. The glass traps were occasionally heated by means of a Bunsen flame, with the vacuum still applied. Then nitrogen gas was let into the reactor tube very slowly and the system was disconnected from the vacuum line. Nitrogen gas was then passed through the system for two hours while the chromium was maintained at a temperature of 350°C. When the apparatus was dry and filled with nitrogen, the glass traps were cooled by dry ice--alcohol baths. Fluorine gas diluted with nitrogen was then passed over the heated metal and the reaction commenced. Dense yellow vapours condensed in the first cold trap and as the fluorination was continued, a thin red layer was observed to deposit on the inside of the glass tube connecting the traps with the reactor tube and also the amount of yellow condensate in the trap increased.

After twenty minutes the fluorine supply was stopped and the system was flushed with nitrogen gas, while the furnace was switched off. When fluorine had been completely displaced by nitrogen and the reactor tube was at room temperature, the system was connected to a vacuum line and the traps were sealed off from the nickel tube. Nitrogen gas was let in the nickel tube and the faceplate

was removed. A dark glassy solid was noticed to have been deposited in the exit tube of the faceplate and also on the inside of the tube adjacent to the flange, i.e. the region of the tube just outside the furnace. This was chromium tetrafluoride, and was scraped off from the tube under a fast flow of nitrogen, and was taken into a weighing tube which was then placed in a desiccator. In every preparation 2--4 gm. of product were obtained.

The boat inside the reactor was found to contain some unreacted metal covered by a green substance which was later shown to be chromium trifluoride.

In one fluorination reaction a silica reaction tube was used instead of a nickel reactor tube, in order to observe the fluorination more closely. The silica tube was 10 in. long and $3/4$ in. in diameter, and was connected to a train of traps on one side and to the fluorine supply on the other by means of a B-14 standard ground glass joint. A small nickel boat containing chromium metal was placed in the tube. This tube was surrounded by a mantle heater. After the apparatus had been dried, the tube was heated to a temperature of 350°C and fluorine gas diluted with nitrogen was passed through. Chromium metal in the nickel tube began to glow and bright blue vapours were seen in the hot zone of the tube. These vapours were carried with the stream of fluorine-nitrogen gas mixture and condensed in the cooler part to a dark green solid, later shown by

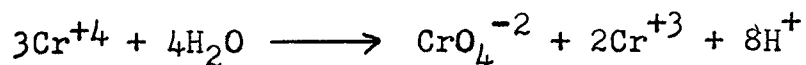
analysis to be chromium tetrafluoride. The amount of heat produced during the reaction was so considerable that the silica tube melted at the hottest point and a hole was blown in the tube, indicating that silica could not be used for carrying out the fluorination.

Analysis.--Chemical analyses for chromium and fluorine were carried out as described in an earlier chapter. Found: Cr, 40.52, 40.00; F, 59.63. Calc. for CrF_4 : Cr, 40.63; F, 59.37%.

B. REACTIONS OF CHROMIUM TETRAFLUORIDE

1. Reaction with water

Chromium tetrafluoride was weighed into a beaker containing 50 ml. distilled water. It reacted vigorously with water and a solution containing chromate and chromic ions was produced. It was acidified to dissolve the small amount of chromic hydroxide, and made up to 100 ml. Of this solution 10.00 ml. were used for the determination of hexapositive chromium. In another 10.00 ml., total chromium was determined after oxidation of Cr^{+3} to Cr^{+6} . The ratio of $\text{Cr}^{+6}:\text{Cr}^{+3}$ was 1:2, indicating a hydrolysis of the type



2. Fluorination of chromium tetrafluoride

Fluorination was carried out in a silica tube similar to the one used for the fluorination of chromium. A small nickel boat was dried and a small amount of

powdered chromium tetrafluoride was transferred into it in the dry-box. The boat was placed in the silica tube and fluorination was carried out at a temperature of 100--150°C. Higher temperatures resulted in reaction with the silica tube and decomposition of chromium tetrafluoride. Signs of any extensive reaction were not observed. However, because of some traces of oxygen in the fluorine and some derived from the reaction with the silica tube, small amounts of chromyl fluoride were formed and collected in the cold trap. The yellow chromyl fluoride formed a layer on the inside of the connecting glass tubes. Because of the messy nature of the reaction, it was stopped and the product in the boat, on analysis, was found to be chromium tetrafluoride. (Found: Cr, 39.95, 40.26. Calc. for CrF_4 : Cr, 40.63%.)

3. Reaction with liquid ammonia

Gaseous ammonia (Matheson Co., Inc.) was carefully dried by condensing it on to metallic sodium in an all-glass distillation system which had been baked dry. An excess was then distilled from sodium on to chromium tetrafluoride and allowed to melt. There were no signs of reaction and the residue after the removal of ammonia was found to be chromium tetrafluoride. (Found: Cr, 39.8. Calc. for CrF_4 : Cr, 40.6%.)

4. Reaction with sulphur dioxide

Sulphur dioxide from a cylinder was passed through two tubes containing phosphorus pentoxide and was

condensed at -184°C in a glass trap fitted with a break-seal and a capillary constriction. The trap was evacuated and sealed at the constriction when sufficient sulphur dioxide had collected. The reaction of sulphur dioxide with chromium tetrafluoride was performed in the usual all-glass system which had previously been baked dry. The trap containing sulphur dioxide was attached to the apparatus. Then the silica reaction vessel containing chromium tetrafluoride was attached to the reaction assembly by means of a B-10 joint. The system was evacuated and sulphur dioxide distilled in vacuo on to chromium tetrafluoride contained in the reaction vessel, and the trap originally containing sulphur dioxide was sealed off. The reaction vessel was then allowed to warm to room temperature. After two hours sulphur dioxide was distilled off and the residue was found to be chromium tetrafluoride. (Found: Cr, 39.89. Calc. for CrF_4 : Cr, 40.63%.)

5. Reaction with sulphur trioxide

Pure dry Δ -sulphur trioxide was obtained by distilling a mixture of fuming sulphuric acid and phosphorus pentoxide at 100°C . The sulphur trioxide was distilled in vacuo into a second trap provided with a break-seal, which was then sealed off and attached to an all-glass reaction assembly, and the reaction was carried out as with sulphur dioxide. There were no visible signs of reaction; the product after removal of sulphur trioxide had the same

weight as the starting material, and was shown by chemical analysis to be chromium tetrafluoride. (Found: Cr, 39.96. Calc. for CrF_4 : Cr, 40.63%.)

6. Reaction with selenium tetrafluoride

Selenium tetrafluoride was prepared by fluorination of selenium (115) and was stored in a trap provided with a break-seal. An all-glass apparatus was set up as for reaction with bromine trifluoride. Reaction with selenium tetrafluoride was carried out at room temperature and also at the boiling point of selenium tetrafluoride.

(i) at room temperature

Powdered chromium tetrafluoride (0.2230 gm.) was taken in a silica reaction vessel and an excess of selenium tetrafluoride distilled on to it from a trap which was sealed off after the distillation was complete. Air was let into the system through traps cooled by a CO_2 --alcohol mixture to ensure removal of water from the air. The silica reaction vessel was allowed to warm to room temperature. There were no visible signs of reaction. The powdered chromium tetrafluoride was allowed to remain in contact with the liquid selenium tetrafluoride for fifteen minutes, after which all the traps were cooled to -78°C and connected to the vacuum line. The dewar surrounding the silica reaction vessel was removed and selenium tetrafluoride was allowed to distil over into the adjacent cooled trap. The reaction vessel was heated to 90°C to

remove all of the selenium tetrafluoride. Distillation in vacuo was continued until there was no selenium tetrafluoride distilling and the reaction vessel was then sealed off. There were no visible signs of reaction and the weight of the starting material had not changed. On analysis the residue was found to be chromium tetrafluoride. (Found: Cr, 40.55. Calc. for CrF_4 : Cr, 40.63%.)

(ii) at the boiling point of selenium tetrafluoride, 106°C

An apparatus similar to that used in the preceding experiment was set up and powdered chromium tetrafluoride was taken into the silica reaction vessel. Selenium tetrafluoride from a trap was distilled on to it and the reaction was carried out in exactly the same way as in the previous experiment, except that the reaction vessel was heated carefully so that the selenium tetrafluoride refluxed. Reaction between chromium tetrafluoride and selenium tetrafluoride occurred on heating, and the reaction vessel was heated for fifteen minutes, after which it was allowed to cool to room temperature. Excess selenium tetrafluoride was removed by distilling it under vacuum at room temperature and when no more was distilling the reaction vessel was sealed off. The silica reaction vessel was seen to contain a non-homogeneous product consisting of at least two phases. The vessel was again connected to a train of cooled traps with break-seals by means of a B-10 joint and vacuum was applied. The reaction vessel was surrounded by

a beaker containing boiling water in order to remove selenium tetrafluoride completely. It was unexpectedly observed that a buff-coloured portion of the solid product was swept through into the cold trap. The reaction vessel was maintained at the temperature of boiling water until the transfer of the buff-coloured product was complete. It was also noticed that the reaction vessel then contained only one type of product, needle-like crystals of a pink colour. At this stage the reaction vessel and also the trap containing the light buff-coloured compound were both sealed off and the contents of each examined separately.

Pink product.--The substance gave a positive qualitative test for selenium, suggesting that it was a selenium tetrafluoride adduct. Chromium and fluorine analyses gave the formula $\text{CrF}_2 \cdot \text{SeF}_4$. (Found: Cr, 22.00; F, 47.50. Calc. for $\text{CrF}_2 \cdot \text{SeF}_4$: Cr, 21.24; F, 46.75%.)

The magnetic susceptibility was measured at room temperature and gave a value of 5.34 B.M. for the magnetic moment.

$$\text{Magnetic susceptibility} = 11900 \times 10^{-6} \text{ c.g.s. units}$$

The X-ray powder pattern of the compound gave a complex diagram and no attempt was made to index it.

Buff-coloured product.--The trap containing the buff-coloured product was opened in the dry-box and the contents were examined by X-ray, magnetic, and analytical methods. It was a very light compound. Chemical analysis showed

that it contained selenium and was therefore probably a selenium tetrafluoride adduct. Chromium and fluorine determinations gave the formula $\text{CrF}_3 \cdot \text{SeF}_4$. (Found: Cr, 19.7; F, 50.00. Calc. for $\text{CrF}_3 \cdot \text{SeF}_4$: Cr, 19.7; F, 50.40%.)

Magnetic measurements were difficult, presumably because of the very low density of the solid, and also because it could not be packed very tightly. Therefore, no importance can be attached to this measurement.

7. Reaction with iodine pentafluoride

In an all-glass well dried reaction assembly similar to the one used for reaction with bromine trifluoride, iodine pentafluoride was condensed on to a weighed quantity of chromium tetrafluoride taken in a silica reaction vessel. The reaction vessel was then allowed to warm to room temperature and chromium tetrafluoride was kept in contact with liquid iodine pentafluoride for fifteen minutes. There were no signs of reaction. Iodine pentafluoride was removed at 100°C. There was no significant change in the weight and the residue, on analysis, was found to be chromium tetrafluoride. (Found: Cr, 39.98, 40.34. Calc. for CrF_4 : Cr, 40.63%.)

A similar experiment was carried out; iodine pentafluoride was condensed on to chromium tetrafluoride contained in the silica reaction vessel. The reaction was carried out at the boiling point of iodine pentafluoride,

100.94°C. The reactants were heated together for fifteen minutes but no signs of reaction were observed. Excess iodine pentafluoride was then removed. A temperature of 100°C was used to obtain a product free of iodine pentafluoride. When distillation of iodine pentafluoride was complete, the reaction vessel was sealed off. There was no change in the weight of chromium tetrafluoride, and chemical analysis showed that it was unchanged chromium tetrafluoride. (Found: Cr, 38.5. Calc. for CrF_4 : Cr, 40.63%.) The percentage of chromium was low because of some adsorbed iodine pentafluoride.

8. Reaction with bromine trifluoride

(i) at room temperature

A weighed sample of powdered chromium tetrafluoride was taken in a silica reaction vessel and attached to an all-glass reaction assembly to which a trap containing bromine trifluoride had also been attached. Bromine trifluoride was condensed on to the reactant in the reaction vessel. The trap originally containing bromine trifluoride was sealed off and the reaction was carried out at atmospheric pressure and at room temperature, as described earlier. Excess bromine trifluoride was removed, a temperature of 100°C being used to remove the final traces. The residue in the reaction vessel appeared identical to the starting material and by chemical analysis was found to be unchanged chromium tetrafluoride. (Found: Cr, 40.55.

Calc. for CrF_4 : Cr, 40.63%.)

(ii) at the boiling point of bromine trifluoride, 127°C

The usual all-glass reaction assembly was assembled and baked dry. To it, a trap containing bromine trifluoride was attached by means of a B-14 joint. The silica reaction vessel containing a weighed amount of chromium tetrafluoride was attached by means of a B-10 joint. The bromine trifluoride was condensed in the reaction vessel and the trap originally containing bromine trifluoride was sealed off. The reaction assembly was opened to the air, care being taken to avoid entry of moisture. The reaction vessel was warmed to room temperature and heated slowly with a low Bunsen flame until the bromine trifluoride was boiling; the reaction vessel was maintained at this temperature for twenty minutes. A greenish powder was seen to form. Excess bromine trifluoride was removed by distillation under vacuum at 120°C , and when distillation was complete, the reaction vessel was sealed off and taken to the dry-box. Samples were taken for chemical analysis and for X-ray and magnetic measurements.

Qualitative chemical analysis showed the presence of bromine and hence probably the product was a bromine trifluoride adduct. Quantitative analysis showed it to be $\text{CrF}_3 \cdot 0.5\text{BrF}_3$. (Found: Cr, 30.00; equiv. wt. 25.5. Calc. for $\text{CrF}_3 \cdot 0.5\text{BrF}_3$: Cr, 29.4%; equiv. wt. 25.4.)

Magnetic susceptibility measurements were carried

out at room temperature (294°K) and the following values were obtained.

$$\chi_M = 6583 \times 10^{-6} \text{ c.g.s. units, } \mu_{294} = 3.96 \text{ B.M.}$$

The value of the magnetic moment corresponds to three unpaired electrons, indicating that chromium is in an oxidation state of +3.

9. Reaction with bromine pentafluoride

A weighed sample of chromium tetrafluoride was taken in the silica reaction vessel and attached by means of a B-10 joint to the usual type of reaction assembly with a trap containing bromine pentafluoride. After evacuating the apparatus, bromine pentafluoride was condensed into the reaction vessel and the reaction was carried out at room temperature in the usual way. After the tetrafluoride had stood in contact with liquid bromine pentafluoride for fifteen minutes, the reaction assembly was connected to the vacuum line and bromine pentafluoride was removed by distillation into a trap cooled by liquid nitrogen. When all the bromine pentafluoride had been removed, first at room temperature and then at 100°C, the reaction vessel was sealed off and the contents analysed. Chromium determination showed the product to be unchanged chromium tetrafluoride. (Found: Cr, 39.52. Calc. for CrF_4 : Cr, 40.63%.)

In another experiment the reaction was performed similarly, with the exception that the reaction vessel was heated very slowly with a low Bunsen flame. On heating the

reaction vessel, bromine pentafluoride boiled off in a short time. The residue was found to be chromium tetrafluoride.

(Found: Cr, 39.80. Calc. for CrF_4 : Cr, 40.63%.)

10. Reaction with a mixture of bromine trifluoride and bromine pentafluoride

A weighed sample of chromium tetrafluoride was refluxed with a mixture of bromine trifluoride and bromine pentafluoride. The reaction mixture was observed to be deep-red in colour. After the removal of the volatile bromine fluorides at 100°C , a reddish residue was left in the reaction vessel, which was then sealed off from the reaction assembly and taken into the dry-box. Samples of the residue were taken for chemical analysis and magnetic measurements.

Chemical analysis indicated the presence of bromine, and a quantitative determination of chromium showed the compound to be $\text{CrOF}_3 \cdot 0.25 \text{ BrF}_3$. (Found: Cr, 33.8, 32.9. Calc. for $\text{CrOF}_3 \cdot 0.25 \text{ BrF}_3$: Cr, 32.71%.)

Magnetic susceptibility measurements were carried out at room temperature (294°K) and the following values were obtained.

$$\chi_M = 1710 \times 10^{-6} \text{ c.g.s. units, } \mu_{294} = 2.01 \text{ B.M.}$$

XIV. COMPLEXES DERIVED FROM CHROMIUM TETRAFLUORIDE

A. POTASSIUM PENTAFLUOROCHROMIUM (IV)

Preparation.--Potassium pentafluorochromium (IV) was prepared by heating together a mixture of chromium tetrafluoride and potassium chloride in a 1:1 molar ratio. Potassium chloride rather than potassium bromide was used because when the latter is employed bromine collects in the glass connecting tubes. Potassium chloride used was of AnalaR grade and was well dried before use.

The preparation was carried out as described in the general experimental technique. Two preparations were carried out, one in which bromine trifluoride was distilled off at 100°C, and another in which it was removed at 160°C.

(i) preparation I

After heating together the mixture of chromium tetrafluoride, potassium chloride, and bromine trifluoride, the reaction vessel was allowed to cool to room temperature and then excess bromine trifluoride was removed by distilling in vacuo, at first at room temperature, and then at 100°C. When distillation was complete, the reaction vessel was sealed off and taken to the dry-box. Samples were taken for chemical, magnetic, and X-ray analyses.

Analysis.--Qualitative tests showed the presence of bromine, indicating that even at 100°C all bromine trifluoride had not been removed, and that possibly a bromine trifluoride adduct had been formed. Quantitative analysis

gave the formula $\text{KCrF}_5 \cdot 0.5\text{BrF}_3$ for the compound. (Found: Cr, 20.00; F, 49.10. Calc. for $\text{KCrF}_5 \cdot 0.5\text{BrF}_3$: Cr, 20.43, F, 48.50%.)

Magnetic measurement.—The magnetic susceptibility was measured at room temperature and gave a value of 3.22 B.M. for its magnetic moment, indicating the presence of two unpaired electrons, i.e. chromium (IV). With another sample the measurement of magnetic susceptibility was carried out over a temperature range, down to -175°C . The values obtained are given below, in Table 3.

Table 3

Magnetic susceptibility measurements of $\text{KCrF}_5 \cdot 0.5\text{BrF}_3$

<u>Temp (K)</u>	<u>$\chi_M, \times 10^{-6}$</u>	<u>μ (Curie Law) (B.M.)</u>	<u>μ (Curie-Weiss Law) (B.M.)</u>
98°	8830	2.65	3.56
123	8063	2.82	3.63
148	7182	2.92	3.63
171	6485	2.99	3.62
198	5847	3.05	3.62
226	5474	3.18	3.67
253	5040	3.19	3.67
294	4485	3.22	3.67

The plot of $\frac{1}{\chi_M}$ versus T gave a value of

$$\theta = -80^\circ$$

Crystal structure.--The X-ray powder pattern was indexed on a tetragonal lattice with

$$a = 9.168 \text{ \AA}$$

$$c = 13.49 \text{ \AA}$$

The values of the observed and calculated $\sin^2\theta$ values are given in Table 4 (page 137).

(ii) preparation II

Another reaction using chromium tetrafluoride, potassium chloride, and bromine trifluoride was carried out in exactly the same way, except that the temperature at which bromine trifluoride was distilled off was 160°C . This was done in order to get a product free of bromine trifluoride. In this experiment, chromium tetrafluoride (0.6112 gm.) and potassium chloride (0.3582 gm.) were heated together in bromine trifluoride. The weight of the product was 0.9750 gm.

Distillation of bromine trifluoride was carried on for twenty-four hours, after which the reaction vessel was sealed and taken to the dry-box.

Analysis.--Qualitative analysis showed no precipitate of silver bromide on addition of silver nitrate to a solution of the compound. Quantitative analysis showed that the compound was KCrF_5 . (Found: Cr, 26.00; F, 49.50. Calc. for KCrF_5 : Cr, 27.94; F, 51.07%.)

Magnetic measurement.--The magnetic susceptibility

Table 4

Calculated and observed $\sin^2\theta$ values for $\text{KCrF}_5 \cdot 0.5\text{BrF}_3$

<u>hkl</u>	<u>$\sin^2\theta$ obs.</u>	<u>$\sin^2\theta$ calc.</u>	<u>intensity obs.</u>
112	.0603	.0599	w.
212	.1079	.1067	v.w.
004	.1144	.1152	m.
220	.1234	.1246	v.v.w.
300	.1405	.1402	m.
310	.1598	.1558	v.v.w.
302	.1684	.1690	w.
204	.1750	.1775	v.w.
313	.2194	.2206	v.v.w.
224	.2395	.2398	v.w.
314	.2725	.2710	w.
225	.3004	.3046	m.
332	.3101	.3092	m.
324	.3174	.3177	w.
206	.3264	.3216	v.v.w.
334	.3970	.3956	v.v.w.
522	.4811	.4806	v.v.w.
514	.5209	.5202	v.v.w.
128	.5384	.5387	v.w.
426	.5719	.5702	v.v.w.
540	.6361	.6387	v.v.w.
604	.6743	.6760	v.v.w.
630	.7000	.7011	v.v.w.
00;10	.7202	.7202	v.v.w.
517	.7555	.7578	v.v.w.
550	.7773	.7770	v.v.w.
702	.7933	.7922	v.v.w.
447	.8514	.8513	v.v.w.
643	.8717	.8747	v.v.w.

lattice: tetragonal

$$a = 9.168 \text{ \AA}$$

$$c = 13.49 \text{ \AA}$$

measurement gave a value of

$$\chi_M = 4193 \times 10^{-6}; \quad \mu_{294} = 3.16 \text{ B.M.}$$

Crystal structure.--The X-ray powder pattern was indexed on a hexagonal unit cell with

$$a = 8.739 \text{ \AA}$$

$$c = 5.226 \text{ \AA}$$

The calculated and observed $\sin^2\theta$ values are given in Table 5 (page 139).

B. RUBIDIUM PENTAFLUOROCHROMIUM (IV)

Preparation.--Chromium tetrafluoride (0.7324 gm.) was taken in the silica reaction vessel, and to it well dried rubidium chloride (0.69 gm.) was added. The silica reaction vessel was then attached to a reaction assembly and bromine trifluoride condensed on it. The reaction was carried out as for preparation II of the potassium analogue; excess bromine trifluoride was removed at a temperature of 160°C. The product weighed 1.3841 gm. (Calc. for RbCrF_5 : 1.32 gm.)

Analysis.--Qualitative tests indicated that no bromine was present, suggesting that the compound was not a bromine trifluoride adduct, and quantitative analysis gave the formula RbCrF_5 . (Found: Cr, 21.5; F, 40.7. Calc. for RbCrF_5 : Cr, 22.4; F, 40.7%.)

Magnetic measurement.--The magnetic susceptibility measurement at room temperature (21°C) gave a value of

Table 5

Calculated and observed $\sin^2\theta$ values for KCrF_5

<u>hkl</u>	<u>$\sin^2\theta$ obs.</u>	<u>$\sin^2\theta$ calc.</u>	<u>intensity obs.</u>
110	.0314	.0310	w.
111	.0518	.0527	w.
210	.0726	.0724	v.w.
220	.1244	.1242	m.w.
212	.1584	.1592	w.
003	.1960	.1953	v.w.
320	.1960	.1966	v.w.
203	.2322	.2367	v.v.w.
303	.2887	.2884	v.v.w.

lattice: hexagonal

$$a = 8.739 \text{ \AA}$$

$$c = 5.226 \text{ \AA}$$

magnetic moment $\mu_{294} = 3.17$ B.M., corresponding to two unpaired electrons. The magnetic susceptibility measurements were then taken on another sample over the temperature range -194°C to -23°C . The values computed are given below in Table 6.

Table 6

Magnetic susceptibility measurements of RbCrF_5

<u>Temp (K)</u>	<u>$\chi_M \times 10^{-6}$</u>	<u>μ (Curie Law) (B.M.)</u>	<u>μ (Curie-Weiss Law) (B.M.)</u>
73°	9550	2.36	2.84
118	7245	2.62	2.96
157	5935	2.76	3.01
188	5234	2.80	3.04
197	4841	2.82	2.99
202	4754	2.78	2.99
246	4228	2.88	3.08
265	3987	2.84	3.09
294	3918	2.84	3.14

The plot of $\frac{1}{\chi_M}$ versus T gave a value of

$$\theta = -32^{\circ}$$

Crystal structure.--The X-ray powder photograph of RbCrF_5 was indexed on the basis of an hexagonal lattice with

$$a = 6.985 \text{ \AA}$$

$$c = 12.119 \text{ \AA}$$

The calculated and observed $\sin^2 \theta$ values are given in Table 7 (page 142).

C. CESIUM PENTAFLUOROCHROMIUM (IV)

Preparation.--Chromium tetrafluoride (0.4597 gm.) was transferred to the silica reaction vessel in the dry-box and to this, 0.7604 gm. of previously dried cesium bromide were added. The silica reaction vessel was attached to the reaction assembly and bromine trifluoride condensed in it. The reactants were heated together and the reaction was completed as in the case of KCrF_5 (preparation II); distillation of excess bromine trifluoride was carried out at 160°C . When distillation was complete, the reaction vessel was weighed and taken to the dry-box for analysis and characterization. The weight of the product was 1.073 gm. (calc. for CsCrF_5 : 1.004 gm.).

Analysis.--A qualitative test showed the absence of bromine. Quantitative analysis gave the formula CsCrF_5 . (Found: Cr, 18.00; F, 32.8. Calc. for CsCrF_5 : Cr, 18.55; F, 33.95%.)

Magnetic measurement.--The magnetic susceptibility was measured at room temperature and the results are as follows:

$$\chi_M = 4044 \times 10^{-6} \text{ c.g.s. units}$$

$$\mu_{294} = 3.09 \text{ B.M.}$$

Crystal structure.--The X-ray pattern was indexed on a cubic lattice with $a = 8.107 \text{ \AA}$. The indices of all but one

Table 7

Calculated and observed $\sin^2\theta$ values for RbCrF_5

<u>hkl</u>	<u>$\sin^2\theta$ obs.</u>	<u>$\sin^2\theta$ calc.</u>	<u>intensity obs.</u>
110	.0485	.0486	m.
111	.0680	.0688	m.
203	.1013	.1007	w.
202	.0806	.0807	w.
105	.1157	.1157	m.
213	.1484	.1491	w.
303	.1833	.1817	w.
313	.2159	.2147	w.
108	.2696	.2709	w.
315	.3136	.3121	v.v.w.
405	.3580	.3587	v.v.w.
502	.4290	.4229	v.v.w.

lattice: hexagonal

$$a = 6.985 \text{ \AA}$$

$$c = 12.119 \text{ \AA}$$

arc on the pattern were either odd or even as for a face-centred lattice. The values of the observed and calculated $\sin^2\theta$ are given in Table 8, below.

Table 8
Calculated and observed $\sin^2\theta$ values for CsCrF_5

<u>hkl</u>	<u>$\sin^2\theta$ obs.</u>	<u>$\sin^2\theta$ calc.</u>	<u>intensity obs.</u>
200	.0366	.0361	m.
220	.0722	.0722	m.
311	.0987	.0993	m.
222	.1079	.1083	v.w.
320	.1169	.1173	v.w.
420	.1782	.1806	v.w.
422	.2136	.2167	v.v.w.
511) 333)	.2406	.2438	v.v.w.

lattice: cubic

$$a = 8.107 \text{ \AA}$$

D. REACTION OF CHROMIUM TETRAFLUORIDE AND SODIUM FLUORIDE (1:1) IN BROMINE TRIFLUORIDE

Chromium tetrafluoride and re-crystallized sodium fluoride in a 1:1 molar ratio were heated together in bromine trifluoride in a silica reaction vessel. Upon distilling off excess bromine trifluoride, two solid phases were clearly discernible in the reaction vessel. There were no signs of the formation of the complex NaCrF_5 .

E. REACTION OF CHROMIUM TETRAFLUORIDE AND SILVER CARBONATE
(1:1) IN BROMINE TRIFLUORIDE

Chromium tetrafluoride and well dried silver carbonate in a 1:1 molar ratio were taken into the silica reaction vessel, which was then attached to a reaction assembly and bromine trifluoride was condensed on the reactants. The reaction was carried out in the usual way and excess bromine trifluoride was removed at 160°C. A blackish residue was left in the reaction vessel, and was presumably impure.

The X-ray powder pattern of the compound was different from those of silver carbonate and silver fluoride, and was complex. No attempt was made to index it.

F. REACTION OF CHROMIUM TETRAFLUORIDE AND BARIUM FLUORIDE
(1:1) IN BROMINE TRIFLUORIDE

Chromium tetrafluoride and barium fluoride in a 1:1 molar ratio were taken into the reaction vessel, which was attached to the reaction assembly, and bromine trifluoride was condensed in it. The reaction was carried out by heating the silica reaction vessel for fifteen to twenty minutes, after which excess bromine trifluoride was distilled off. Two phases were discernible in the reaction vessel, indicating that no complex formation had occurred.

G. PREPARATION AND CRYSTAL STRUCTURE OF POTASSIUM PENTA-
FLUOROMANGANITE (IV)

Potassium pentafluoromanganite (IV) was prepared

by the method of Sharpe and Woolf (26). Potassium permanganate and bromine trifluoride were heated together in a silica reaction vessel and excess bromine trifluoride was removed at 160°C over a forty-eight hour period. An X-ray picture of the product was taken in order to compare it with those of the complexes of chromium of the type ACrF_5 .

The X-ray powder pattern was indexed on a hexagonal lattice with

$$a = 11.445 \text{ \AA}$$

$$c = 8.208 \text{ \AA}$$

The calculated and observed $\sin^2\theta$ values are given in Table 9 (page 146).

H. POTASSIUM HEXAFLUOROCHROMIUM (IV)

Preparation.--Chromium tetrafluoride (0.6100 gm.) was weighed into the silica reaction vessel and to this, 0.7022 gm. of potassium chloride, previously dried, were added. The vessel was attached to a reaction assembly of the type used for preparation of KCrF_5 , by means of a B-10 joint. Bromine trifluoride was then condensed on to the reaction mixture and the reaction was completed by heating the reactants for ten minutes. Excess bromine trifluoride was removed first at room temperature and then at 100°C. When the distillation of bromine trifluoride at this temperature was complete, the reaction vessel was

Table 9

Calculated and observed $\sin^2\theta$ values for KMnF_5

<u>hkl</u>	<u>$\sin^2\theta$ obs.</u>	<u>$\sin^2\theta$ calc.</u>	<u>intensity obs.</u>
110	.0184	.1809	m.
111	.0271	.0268	s.
102	.0414	.0408	m.
202	.0591	.0589	v.s.
220	.0719	.0723	m.
221	.0816	.0811	m.w.
302	.0894	.0891	v.w.
222	.1073	.1072	w.
321	.1227	.1233	w.
004	.1408	.1392	w.
500	.1509	.1507	m.w.
333	.1621	.1628	m.
214	.1813	.1814	w.
323	.1904	.1928	v.v.w.
413	.2010	.2049	m.
512	.2202	.2217	m.w.
520	.2352	.2352	v.w.
440	.2840	.2894	v.v.w.
442	.3258	.3242	v.v.w.
540	.3660	.3678	v.v.w.

lattice: hexagonal

$$a = 11.445 \text{ \AA}$$

$$c = 8.255 \text{ \AA}$$

sealed off and taken into the dry-box. Samples were taken for chemical, magnetic, and X-ray analyses.

Analysis.--Qualitative analysis showed the presence of bromine, indicating that the product was probably a bromine trifluoride adduct. Chromium and fluorine analyses showed that the compound was $K_2CrF_6 \cdot 0.5BrF_3$. (Found: Cr, 16.30; F, 46.93. Calc. for $K_2CrF_6 \cdot 0.5BrF_3$: Cr, 16.62; F, 45.56%.)

Magnetic measurement.--Magnetic susceptibility measurements at room temperature gave a value of magnetic moment $\mu_{294} = 3.30$ B.M.

Another sample was prepared and magnetic susceptibility measurements at different temperatures were carried out. The results are given in Table 10, below.

Table 10

<u>Magnetic susceptibility measurements of $K_2CrF_6 \cdot 0.5BrF_3$</u>			
<u>Temp (K)</u>	<u>$\chi_M, \times 10^{-6}$</u>	<u>μ (Curie Law) (B.M.)</u>	<u>μ (Curie-Weiss Law) (B.M.)</u>
123°	6699	2.58	3.51
143	6209	2.67	3.52
173	5542	2.78	3.52
199	5045	2.84	3.51
223	4789	2.93	3.55
248	4498	2.99	3.57
294	3954	3.06	3.56

The plot of $\frac{1}{\chi_M}$ versus T gave a value of

$$\theta = -105^\circ$$

Crystal structure.--The X-ray pattern of the compound was indexed on a tetragonal unit cell, with the following lattice constants:

$$a = 4.339 \text{ \AA}$$

$$c = 5.500 \text{ \AA}$$

The values of the calculated and observed $\sin^2\theta$ are given in Table 11, below.

Table 11

Calculated and observed $\sin^2\theta$ values for $\text{K}_2\text{CrF}_6 \cdot 0.5\text{BrF}_3$

<u>hkl</u>	<u>$\sin^2\theta$ obs.</u>	<u>$\sin^2\theta$ calc.</u>	<u>intensity obs.</u>
100	.0315	.0315	m.
101	.0509	.0511	s.
110	.0629	.0633	m.
111	.0833	.0826	w.
200	.1255	.1260	w.
112	.1404	.1414	m.
002	.1760	.1764	m.
202	.2047	.2044	v.w.
212	.2347	.2359	w.
203	.3007	.3024	v.w.
310	.3151	.3150	v.w.
222	.3292	.3304	v.w.

Effect of heat on the structure of $\text{K}_2\text{CrF}_6 \cdot 0.5\text{BrF}_3$.--A few samples of the tetragonal compound were sealed in

pyrex glass tubes in vacuo. The glass tubes were heated in an oven at different temperatures for varying lengths of time in order to remove the bromine trifluoride present. Vapours of bromine--bromine trifluoride were observed in every tube in the oven. The tubes were cooled slowly after the samples had been heated for the desired length of time, taken into the dry-box, and samples for X-ray examination were prepared. The results are given below.

<u>Temp. (C)</u>	<u>Time (hrs.)</u>	<u>Remarks</u>	<u>X-ray pattern</u>
120°	240	slight reaction with glass	sharp
170	70	reaction with glass	not sharp
250	24	reaction with glass	not good
360	5	slight reaction with glass	good

All these pictures showed common lines, indicating the presence of the same phase in all samples. These lines were due to a phase different from the compound $K_2CrF_6 \cdot 0.5BrF_3$. The X-ray pictures on measurement gave a set of $\sin^2\theta$ values which were indexed on a cubic lattice with $a = 8.104 \text{ \AA}$. The calculated and observed values of $\sin^2\theta$ are given in Table 12 (page 150). The photographs also showed very faint lines due to some other phase, probably an impurity.

I. CESIUM HEXAFLUROCHROMIUM (IV)

Preparation.--Chromium tetrafluoride (0.4918 gm.) and well dried cesium chloride (1.264 gm.) in a 1:2 molar ratio

Table 12

Calculated and observed $\sin^2\theta$ values for K_2CrF_6

<u>hkl</u>	<u>$\sin^2\theta$ obs.</u>	<u>$\sin^2\theta$ calc.</u>	<u>intensity obs.</u>
111	.0272	.0270	s.
220	.0724	.0722	m.s.
222	.1083	.1082	s.
400	.1442	.1443	s.
311	.1724	.1714	v.w.
422	.2159	.2164	w.
511) 333)	.2431	.2435	m.w.
440	.2877	.2886	m.
531	.3152	.3157	v.w.
620	.3590	.3608	w.
622	.3965	.3968	v.w.
444	.4318	.4329	v.w.
551) 711)	.4562	.4600	v.v.w.
642	.5007	.5051	v.v.w.
733	.6097	.6043	v.v.w.

lattice: cubic

$$a = 8.104 \text{ \AA}$$

were weighed into the silica reaction vessel which had been previously baked dry to a constant weight. The reaction vessel was attached to the reaction assembly and evacuated. The break-seal of the trap containing bromine trifluoride was broken magnetically and bromine trifluoride condensed on to the reaction mixture in the silica vessel. When all bromine trifluoride had distilled off, the trap originally containing it was sealed off. The reaction was performed by opening the reaction assembly to the air and heating the reaction vessel with a small flame. When the reaction was complete, excess bromine trifluoride was distilled under vacuum first at room temperature and then at 100°C. When distillation was complete, the reaction vessel was sealed off and taken into the dry-box.

Analysis.--Qualitative analysis showed the presence of bromine; hence, the product was probably a bromine trifluoride adduct. Chemical determinations of chromium and fluorine gave the formula $\text{Cs}_2\text{CrF}_6 \cdot 0.5\text{BrF}_3$ for the compound. (Found: Cr, 10.65; F, 28.10. Calc. for $\text{Cs}_2\text{CrF}_6 \cdot 0.5\text{BrF}_3$: Cr, 10.40; F, 28.50%.)

Magnetic measurement.--The magnetic susceptibility was measured at room temperature and the results are as follows:

$$\chi_M = 4144 \times 10^{-6} \text{ c.g.s. units}$$

$$\mu_{294} = 3.14 \text{ B.M.}$$

Crystal structure.--The X-ray pattern was indexed on a cubic lattice with $a = 8.9156 \text{ \AA}$. In Table 13 (page 152) the

Table 13

Calculated and observed $\sin^2\theta$ values for $\text{Cs}_2\text{CrF}_6 \cdot 0.5\text{BrF}_3$

<u>hkl</u>	<u>$\sin^2\theta$ obs.</u>	<u>$\sin^2\theta$ calc.</u>	<u>intensity obs.</u>
111	.0234	.0224	v.w.
200	.0310	.0298	v.w.
211	.0486	.0448	m.
220	.0606	.0597	m.s.
310	.0756	.0747	v.w.
222	.0903	.0896	m.s.
400	.1205	.1195	m.
420	.1506	.1494	m.
422	.1793	.1793	m.
440	.2392	.2390	m.w.
600)			
442)	.2688	.2689	v.w.
620	.2974	.2988	v.v.w.
622	.3270	.3287	v.v.w.
444	.3564	.3585	v.v.w.
711	.3827	.3809	v.v.w.
642	.4154	.4183	v.v.w.

lattice: cubic

$$a = 8.9156 \text{ \AA}$$

calculated and observed $\sin^2\theta$ values are given. The indices of all the reflections observed are either even or odd, indicating that the lattice is face-centred.

Effect of heat on $\text{Cs}_2\text{CrF}_6 \cdot 0.5\text{BrF}_3$.---The complex (0.6204 gm.) was weighed into a small silica tube joined to a B-10 cone. This was fixed on to an assembly of three traps by means of a B-10 socket. The system was evacuated and the two traps next to the silica tube were surrounded with a CO_2 --alcohol bath. The silica tube was surrounded by an oil bath which was then heated to 110°C . The temperature was slowly raised to 135°C and the silica tube kept at this temperature until bromine trifluoride no longer distilled off (seventy-two hours). The silica tube was cooled to room temperature and the weight recorded. The tube was then taken into the dry-box and its contents were analysed.

Qualitative tests showed an absence of bromine. Chromium determination showed that the compound was Cs_2CrF_6 . (Found: Cr, 12.2. Calc. for Cs_2CrF_6 : Cr, 12.04%.)

The X-ray powder pattern of the specimen was similar to that for $\text{Cs}_2\text{CrF}_6 \cdot 0.5\text{BrF}_3$.

XV. REACTIONS OF CHROMIUM TRIOXIDE AND POTASSIUM DICHROMATE

A. REACTIONS OF CHROMIUM TRIOXIDE1. Reaction with bromine trifluoride at room temperature

The reaction of chromium trioxide with bromine trifluoride was carried out in the usual apparatus, utilizing the silica reaction vessel. A weighed quantity of chromium trioxide, previously dried at 120°C, was taken in the reaction vessel and the vessel attached to the system, which was then evacuated. Chromium trioxide was kept at a temperature of 60--70°C while evacuation was being carried out and the system baked. Bromine trifluoride from a trap was condensed on to the chromium trioxide in the silica reaction vessel. When all the bromine trifluoride had been transferred, the trap originally containing bromine trifluoride was sealed off. The system was then disconnected from the vacuum line and opened to the air, care being taken to avoid the entry of moisture. The reactants were allowed to warm to room temperature. A liquid phase and a garnet-red solid phase were observed. There was effervescence which decreased with time, and the garnet-red phase dissolved. After twenty to twenty-five minutes, the effervescence had nearly ceased and a deep-red coloured precipitate was observed. Excess bromine trifluoride was removed at first at room temperature and then at 100°C by distillation in vacuo, and when distillation was complete the reaction vessel was sealed and its contents examined.

Analysis.--Chemical analysis indicated the presence of bromine, and quantitative determination of chromium and fluorine showed the product to be $\text{CrOF}_3 \cdot 0.25\text{BrF}_3$.

(Found: Cr, 33.4; F, 44.5. Calc. for $\text{CrOF}_3 \cdot 0.25\text{BrF}_3$: Cr, 32.71; F, 44.81%.)

Magnetic measurements.--Magnetic susceptibility measurements at room temperature confirmed that the oxidation state of chromium in this compound was +5. The measurements gave the following values, corresponding to one unpaired electron.

$$\chi_M = 1715 \times 10^{-6} \text{ c.g.s. units; } \mu_{294} = 2.02 \text{ B.M.}$$

Crystal structure.--An X-ray diffraction photograph of the powder showed no lines.

2. Reaction with bromine trifluoride at 126°C

In a second experiment, a sample of dry chromium trioxide was taken in the silica reaction vessel and bromine trifluoride was condensed on to it. The reaction was carried out at atmospheric pressure. When the reaction was complete, as indicated by the cessation of effervescence, excess bromine trifluoride was distilled off in vacuo, at first at room temperature and later at 120°C. The reaction vessel was surrounded by an oil bath at 120°C and left overnight to obtain a product free of bromine trifluoride. After a period of twenty-four hours, the reaction vessel was sealed off and taken into the dry-box.

The product of the reaction was a light-green substance, resembling a chromic compound. It was examined by chemical analysis, and magnetic measurements and an X-ray photograph were taken.

Analysis.--Quantitative analysis showed that the compound was $\text{CrF}_3 \cdot \text{BrF}_3$. (Found: Cr, 21.6; F, 46.5, 48.5. Calc. for $\text{CrF}_3 \cdot \text{BrF}_3$: Cr, 21.14; F, 47.17%.)

Magnetic measurement.--Magnetic susceptibility measurements were carried out at room temperature and the following values obtained:

$$\chi_M = 5682 \times 10^{-6} \text{ c.g.s. units; } \mu_{294} = 3.67 \text{ B.M.}$$

The value of the magnetic moment indicates that chromium is present in the +3 oxidation state.

Crystal structure.--An X-ray diffraction photograph of the product showed only one broad diffraction line.

3. Reaction with bromine pentafluoride

Dry chromium trioxide was transferred to the silica reaction vessel which was then attached to the usual type of reaction assembly by means of a B-10 joint. The reaction assembly, to which a trap containing bromine pentafluoride had already been attached, was being evacuated, during which time it was also heated. Meanwhile the sealed trap of bromine pentafluoride was kept surrounded by a dewar containing liquid nitrogen. When the apparatus was dry, the break-seal of the bromine pentafluoride trap was broken magnetically, the dewar surrounding the trap was removed,

and bromine pentafluoride condensed into the reaction vessel, which was cooled in liquid nitrogen. After distillation of bromine pentafluoride was complete, the reaction assembly was disconnected from the vacuum line and dry air was let in slowly. The reaction was carried out by letting the reaction vessel warm to room temperature at atmospheric pressure. Although the reaction occurred at room temperature, the vessel was heated slightly (to 40.5°C) to ensure completion of the reaction. After fifteen minutes, the reaction assembly was connected to the vacuum line and excess bromine pentafluoride was removed by distillation in vacuo. After ten hours of distillation at 80°C, a reddish powdery mass was left in the silica reaction vessel. The reaction vessel was then sealed off from the system and taken into the dry-box, where on opening the reaction vessel, it was observed that the product of this reaction was more reactive than was the product obtained from the reaction of chromium trioxide with bromine trifluoride; it fumed in the dry-box giving yellow vapours of chromyl fluoride, and reacted much more rapidly with glass. A sample of the product was taken in an X-ray capillary and an X-ray picture was taken.

Analysis.--A sample (0.2909 gm.) was taken in a small weighed tube for chemical analysis. The tube was dropped into an alkaline (sodium hydroxide) solution contained in a 250 ml. conical flask with a ground glass stopper. There

was vigorous reaction, with the evolution of yellow fumes, and the flask was agitated until these fumes dissolved. Qualitative tests indicated the presence of bromine, and quantitative analysis showed that the compound was $\text{CrOF}_3 \cdot 0.25\text{BrF}_5$. (Found: Cr, 30.2; F, 47.7, 48.5; Br, 13.3. Calc. for $\text{CrOF}_3 \cdot 0.25\text{BrF}_5$: Cr, 30.6; F, 47.9; Br, 11.9%.)

Magnetic measurement.--The magnetic susceptibility measurement was carried out at room temperature (21°C) and the following values obtained:

$$\chi_M = 1443 \times 10^{-6} \text{ c.g.s. units; } \mu_{294} = 1.85 \text{ B.M.}$$

Crystal structure.--An X-ray photograph was taken but showed no diffraction lines; the sample decomposed during exposure.

4. Reactions with chlorine trifluoride

(i) liquid phase reaction

Chlorine trifluoride was condensed in a silica reaction vessel containing a sample (0.4358 gm.) of well dried chromium trioxide. The reaction, carried out at room temperature, occurred smoothly; during it the chlorine trifluoride was boiling. When the reaction was complete, as indicated by the cessation of effervescence, unreacted chlorine trifluoride was distilled in vacuo at room temperature. During the last stages of distillation, the silica reaction vessel was heated to 50°C, and was sealed off when distillation was complete. A light, orange-red powder was observed in the silica vessel, which was taken

into the dry-box and opened; this product also fumed in the dry-box.

Analysis.--Qualitative analysis showed the presence of chlorine, indicating that the product was probably a chlorine trifluoride adduct. Quantitative determinations of chromium and fluorine showed the product to be $\text{CrOF}_3 \cdot 0.25\text{ClF}_3$. (Found: Cr, 34.20; F, 48.0, 47.5. Calc. for $\text{CrOF}_3 \cdot 0.25\text{ClF}_3$: Cr, 35.1; F, 48.1%.)

Magnetic measurement.--The magnetic susceptibility was measured at room temperature and the following values obtained:

$$\chi_M = 1418 \times 10^{-6} \text{ c.g.s. units; } \mu_{294} = 1.83 \text{ B.M.}$$

Crystal structure.--No X-ray diffraction lines were observed in the photograph; the sample decomposed during exposure.

(ii) vapour phase reaction

Since the previous reaction did not permit the use of high temperatures--the boiling point of chlorine trifluoride is 12.1°C --it was decided to carry out a similar reaction, this time by passing the vapours of chlorine trifluoride over heated chromium trioxide. This reaction was performed in a silica reaction tube.

A silica reaction tube having a B-14 socket at one end and a pyrex-silica graded seal at the other, was connected to a train of traps by means of the graded seal.

Each trap was provided with a break-seal. The last trap was connected to a vacuum line with a stop-cock in the line. On the other side, the silica tube was attached to a trap by means of a B-14 joint, which in turn was connected to a cylinder of chlorine trifluoride by means of Teflon tubing. The silica reaction tube was surrounded by a mantle heater.

A small nickel boat containing chromium trioxide was placed inside the silica reaction tube and the assembly was evacuated. During evacuation, carried out for twelve hours, the silica tube was heated to 120°C. The assembly was occasionally heated by a Bunsen flame in order to bake it dry. After the apparatus was dry, the trap following the chlorine trifluoride cylinder was cooled with liquid nitrogen, and a suitable amount of chlorine trifluoride condensed into it from the cylinder. While this trap was cooled, vacuum was applied to remove the more volatile impurities. The stop-cock between the traps and the vacuum line was closed, and the traps following the silica reaction vessel were cooled, while the dewar of liquid nitrogen surrounding the trap containing chlorine trifluoride was removed. Chlorine trifluoride was distilled through the silica tube and condensed in the cooled trap following it. During its passage through the tube, chlorine trifluoride reacted with the hot chromium trioxide. A dull-red solid, the reaction product, condensed in the cold

trap. During this reaction, chlorine trifluoride was passed back and forth until all the chromium trioxide had disappeared, and then the train of traps was sealed off from the silica tube. Vacuum was applied and a more volatile gas was observed to escape, indicating the liberation of oxygen during the reaction. The chlorine trifluoride which had condensed in the trap along with the reaction product was separated from it by letting the trap warm to room temperature and keeping the other traps cooled in liquid nitrogen. This caused condensation of chlorine trifluoride in the cold traps, leaving behind the dull-red solid in the first trap. When no more chlorine trifluoride was distilling into the cold traps, the trap containing the product of reaction was sealed off and transferred into the dry-box.

Analysis.--Qualitative analysis indicated the presence of chlorine, and chromium and fluorine determinations gave the composition $\text{CrOF}_3 \cdot 0.25\text{ClF}_3$. (Found: Cr, 34.24, 34.5; F, 49.5, 50.0. Calc. for $\text{CrOF}_3 \cdot 0.25\text{ClF}_3$: Cr, 35.1; F, 48.1%.)

Magnetic measurement.--Magnetic susceptibility was measured at room temperature and the following values obtained:

$$\chi_M = 1308 \times 10^{-6} \text{ c.g.s. units; } \mu_{294} = 1.76 \text{ B.M.}$$

Crystal structure.--An X-ray picture of the sample was taken, but the capillary exploded during exposure.

Effect of heat on the vapour phase reaction product.--

The dull-red solid obtained from the vapour phase reaction was taken in a silica tube and attached to a train of traps by means of a B-10 joint. The system was connected to the vacuum line by means of a glass stop-cock. The two traps following the silica tube were cooled in liquid nitrogen, and the silica tube containing the dull-red product was immersed in an oil bath. The stop-cock was closed and the oil bath heated gradually. At a temperature of 75°C, the compound in the silica tube began to expand, and when the silica tube was maintained at this temperature for a few minutes, a considerable increase in volume occurred; the final product was identical in appearance to that obtained in the liquid phase reaction. However, the composition was unchanged, as shown by chromium analysis.

B. REACTIONS OF POTASSIUM DICHROMATE

1. Reaction with bromine trifluoride

This reaction was carried out in a silica reaction vessel attached to the usual reaction assembly. A sample of previously dried potassium dichromate was taken into the silica reaction vessel and bromine trifluoride condensed on it from a trap, which was sealed off after the bromine trifluoride had distilled off. The apparatus was opened to the air with due precaution, and a reaction occurred at

room temperature as indicated by the effervescence at the surface. When the reaction was complete, excess bromine trifluoride was distilled off in vacuo. A temperature of 100°C was used to remove bromine trifluoride. After distillation was complete, the silica vessel was sealed off and a sample of the product was taken out in the dry-box and analysed.

Analysis.--Qualitative tests indicated the presence of bromine, and chromium analysis gave the formula $\text{KCrOF}_4 \cdot 0.5\text{BrF}_3$. (Found: Cr, 19.88. Calc. for $\text{KCrOF}_4 \cdot 0.5\text{BrF}_3$: Cr, 20.66%.)

Magnetic measurement.--The magnetic susceptibility, measured at room temperature, confirmed that chromium was in the +5 oxidation state. Susceptibility measurements were then carried out over a temperature range of 85--294°K and the results are given in Table 14, below.

Table 14
Magnetic susceptibility measurements of $\text{KCrOF}_4 \cdot 0.5\text{BrF}_3$

Temp (K)	$\chi_M, \times 10^{-6}$	μ (Curie Law) (B.M.)
85°	3617	1.58
116	2776	1.61
191	1773	1.65
217	1575	1.66
239	1426	1.66
294	1265	1.73

A plot of $\frac{1}{\chi_M}$ versus T gave a value of $\theta = +4^\circ$.

Crystal structure.--A sample of the compound as prepared was examined by X-rays. The powder pattern was sharp and was indexed on the basis of an orthorhombic lattice, with

$$a = 13.24 \text{ \AA}$$

$$b = 10.31 \text{ \AA}$$

$$c = 8.317 \text{ \AA}$$

Another sample of the complex $\text{KCrOF}_4 \cdot 0.5\text{BrF}_3$ was taken in a silica tube and heated in vacuo to a temperature of 160°C . This removed the bromine trifluoride and pure KCrOF_4 was obtained, as indicated by a negative response to a test for bromide ions and by chromium analysis. An X-ray picture of this sample was taken and was found to be identical to the one obtained from the bromine trifluoride adduct.

2. Reaction with bromine pentafluoride

Dry potassium dichromate (1.6764 gm.) was weighed into the silica reaction vessel which was then joined to a reaction assembly by means of a B-10 joint. The reaction assembly had a sealed trap containing bromine pentafluoride cooled in liquid nitrogen. The apparatus was evacuated and dried, and then the break-seal of the bromine pentafluoride trap was broken and bromine pentafluoride was distilled into the silica vessel which was cooled in liquid nitrogen. The reaction assembly was opened to the air and the reaction

vessel allowed to warm to room temperature when the reaction occurred. When the reaction had taken place, the assembly was connected to the vacuum line and excess bromine pentafluoride was distilled off from the reaction vessel into a trap cooled in liquid nitrogen. The reaction vessel was heated to a temperature of 100°C to drive off all bromine pentafluoride, and when distillation at this temperature was complete, the reaction vessel was sealed off and its contents were examined.

Analysis.--Qualitative analysis showed the presence of bromine, indicating the compound was an adduct, and quantitative analysis gave the formula $\text{KCrOF}_4 \cdot 0.5\text{BrF}_5$. (Found: Cr, 19.00; F, 44.5. Calc. for $\text{KCrOF}_4 \cdot 0.5\text{BrF}_5$: Cr, 19.20; F, 45.64%.)

Magnetic measurement.--Magnetic susceptibility measurements were carried out at room temperature with the following results:

$$\chi_M = 1237 \times 10^{-6} \text{ c.g.s. units; } \mu_{294} = 1.75 \text{ B.M.}$$

Crystal structure.--A sample of the compound as prepared was taken into a capillary tube and an X-ray picture was taken. The powder pattern was different from the one obtained for $\text{KCrOF}_4 \cdot 0.5\text{BrF}_3$. It was, however, complex, and no attempt was made to index it.

Another sample of the compound $\text{KCrOF}_4 \cdot 0.5\text{BrF}_5$ was taken in a small silica tube with a B-10 cone, by means of which it was attached to a train of traps. The traps were

cooled by liquid nitrogen and connected to the vacuum line. The silica tube was then sealed off and taken into the dry-box where it was opened and its contents examined with X-rays. The powder pattern of this substance was identical with that of KCrOF_4 , indicating the decomposition of the solvate $\text{KCrOF}_4 \cdot 0.5\text{BrF}_5$ into KCrOF_4 .

3. Reaction with chlorine trifluoride

The reaction of potassium dichromate with chlorine trifluoride occurred smoothly and the product obtained gave a diffraction pattern characteristic of KCrOF_4 .

C. REACTION OF CALCIUM CHROMATE WITH BROMINE PENTAFLUORIDE

A sample of calcium chromate which had been thoroughly dried was taken into a dry silica reaction tube, which was then joined to a reaction assembly by means of a B-10 joint. Bromine pentafluoride from a trap was condensed in the silica reaction vessel containing calcium chromate. The reaction was carried out at room temperature and at atmospheric pressure. Bromine pentafluoride reacted with it smoothly with an evolution of gases. When the effervescence ceased, indicating the completion of the reaction, the excess of pentafluoride was distilled off in vacuo. The product was heated to 160°C by means of an oil bath in order to drive off all bromine pentafluoride. When bromine pentafluoride no longer distilled off, the silica vessel was sealed off and taken to the dry-box. The product was a lilac coloured powder.

Analysis.--Preliminary analysis showed it was not a bromine pentafluoride adduct, and quantitative chemical analysis indicated that the compound corresponded to the composition CaCrOF_5 . (Found: Cr, 24.44, 25.00. Calc. for CaCrOF_5 : Cr, 25.6%.)

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