THE FLUORIDES OF VANADIUM

by

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We accept this thesis as conforming to the required standard

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THE FLUORIDES OF VANADIUM

ABSTRACT

The density, surface tension and viscosity of liquid vanadium pentafluoride have been measured. The high value of the viscosity indicates that the liquid is probably associated in a somewhat similar manner to antimony pentafluoride, thus supporting recent evidence which has suggested that intermolecular association is also an important process in these associated fluorides.

The infrared spectrum of vanadium pentafluoride vapor has been measured in the region 250 to 3500 cm\(^{-1}\) and the results have been interpreted in terms of a monomeric trigonal bipyramid molecular structure in view of the normal vapor density.

Vanadium pentafluoride formed a 1:1 complex with selenium tetrafluoride. The apparently similar sulphur tetrafluoride complex was extremely unstable.

Vanadium tetrafluoride is best prepared by fluorinating vanadium tetrachloride with anhydrous hydrogen fluoride in trichlorofluoromethane solution. Vanadium tetrafluoride disproportionates readily at 100\(^\circ\) in vacuum into the trifluoride and the pentafluoride. Solid vanadium tetrafluoride also sublimes slowly at 100-120\(^\circ\) in vacuum.

The available structural information suggests that in vanadium tetrafluoride the vanadium atom is surrounded by six fluorine atoms to form an octahedral VF\(_6\) unit. Four fluorines are shared with adjacent vanadium atoms thus forming a polymeric fluorine bridge-bonded structure. The infrared spectrum of solid VF\(_4\) has been interpreted in terms of this model.

Bromine trifluoride and gaseous fluorine readily fluorinated vanadium tetrafluoride to the pentafluoride. In the presence of iodine pentafluoride, nitryl fluoride oxidised vanadium tetrafluoride and formed the nitryl salt NO\(_2\)VF\(_6\). Ammonia, pyridine and selenium tetrafluoride formed 1:1 complexes with VF\(_4\). Vanadium tetrafluoride did not react with sulphur tetrafluoride, sulphur trioxide or sulphur dioxide.

Potassium hexafluorovanadate (IV) was prepared from potassium fluoride and vanadium tetrafluoride in selenium tetrafluoride solution. The trigonal form was obtained with lattice constants of a = 5.68, c = 4.66 Å. Alkaline earth fluorides did not form hexafluorovanadate salts with vanadium tetrafluoride in iodine pentafluoride. KVF\(_5\) could not be prepared from equimolar proportions of potassium fluoride and vanadium tetrafluoride in iodine pentafluoride solution.

All of the tetravalent vanadium fluoride compounds which have been studied obeyed the Curie-Weiss law, with very high values of the Weiss Constant. Separation of antiferromagnetism and spin-orbit interaction is not possible as both effects are likely to arise from the proposed fluorine bridging.

The heat of hydrolysis of vanadium tetrafluoride in water has been found to be -27.5 kcal /mole, and this value was used in a Hess law calculation to obtain -332 kcal /mole for the heat of formation of vanadium tetrafluoride. Vanadium pentafluoride was hydrolysed under similar conditions in a dilute alkaline solution and the resultant heat of hydrolysis, -141 kcal /mole, was used to calculate the heat of formation of -352 kcal /mole for vanadium pentafluoride.

Lattice energies were estimated from a simple formula given by Kapustinskii and used in a Born-Haber cycle to calculate heats of formation. Using the calculated heat of formation of vanadium trifluoride and the experimental values for vanadium tetrafluoride and vanadium pentafluoride, the spontaneity of the disproportionation of vanadium tetrafluoride was confirmed.

The heat of hydrolysis of vanadium tetrachloride in water is -68.8 kcal /mole. With this value, the heat of formation of the aqueous vanadyl ion was calculated as -113 kcal /mole.
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The infrared spectrum of vanadium pentafluoride vapor has been measured in the region 250 to 3500 cm\(^{-1}\) and the results have been interpreted in terms of a monomeric trigonal bipyramid molecular structure in view of the normal vapor density.

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CHAPTER 1: INTRODUCTION

The development of fluorine chemistry was begun nearly eighty years ago by Moissan and continued by Ruff until the 1930's. These pioneer studies were not extended by other workers until recently when reliable supplies of elemental fluorine became available and vacuum techniques were developed to handle the more reactive fluorides.

The increased activity is shown by the preparation of many new compounds, the complete characterisation of many previously doubtful compounds and an ever-increasing amount of quantitative information on the properties of fluorine compounds. A striking example of the consequences of this re-awakened interest is the recent indication that osmium octafluoride, long regarded as the prime example of the ability of fluorine to bring out the highest valencies and coordination, is actually osmium hexafluoride(1).

Many of the recent advances have involved the use of properties of only recently available compounds. The use of bromine trifluoride as an oxidising and fluorinating agent or as an ionising solvent has resulted in the preparation of compounds such as auric fluoride, AuF$_3$(2) and many complex fluorosalts, such as the VF$_6^-$, NbF$_6^-$ salts; compounds which cannot otherwise be prepared because of their instability to heat and water. Selenium tetrafluoride acts as a mild reducing agent in addition to its solvent properties, thus lower valence fluorides such as PdF$_2$(3,4) can be prepared from the higher
fluorides. Sulphur tetrafluoride, now available commercially, is a good non-oxidative fluorinating agent for metallic oxides and sulphides and, in contrast to reagents such as selenium tetrafluoride and bromine trifluoride, has little tendency to solvate the products (eg. 5).

Most of the information obtained in the earlier studies was qualitative in nature, mainly because of the experimental difficulties arising from the etching properties of many volatile reactive fluorides. The use of inert fluorocarbon plastics, such as Teflon, or metals such as stainless steel, nickel or platinum can avoid such difficulties, however in most cases the convenience and economy of glass apparatus is desirable. Recently (6,7) it has been found that many reactive fluorides, which were previously reported to etch glass, can be readily handled in glass apparatus provided that all traces of moisture and hydrogen fluoride are excluded. Thus quantitative studies of the properties of volatile reactive fluorides are possible without the use of elaborate metal or plastic apparatus.

A considerable portion of the recent work has centered on the fluorides of the transition metals, the result of recent successes in the theoretical interpretation of the properties of transition metal compounds by means of the ligand field theory (10).

Almost all of the transition metals possess the ability to form compounds in which the outermost set of stable 'd' electron orbitals is only partially occupied. It is this
partial occupancy of the 'd' orbitals arising from the relatively unusual relations between the successive ionisation potentials of the 'd' electrons which causes the outstanding feature of transition metal chemistry, the variable valence of the metal. The partially occupied 'd' orbitals are also responsible for the magnetic and spectral properties of transition metal compounds, properties which were not successfully interpreted until the advent of the ligand field theory.

In the halogen group, fluorine tends to bring out the highest oxidation states possible, for example, vanadium forms a pentafluoride, but only a tetrachloride and molybdenum forms a hexafluoride but only a pentachloride. The unique properties of fluorine are largely responsible for this behaviour. It has the highest electronegativity and smallest size of the elements in the halogen series and the bond energy in the fluorine molecule is exceptionally low (11). The similarity of the properties of fluorine to those of oxygen often confers a greater resemblance of the properties of fluorides to oxides rather than to the other halides.

Many transition metals form, in addition to the fluoride with the maximum oxidation state, a series of fluorides of lower oxidation states, the properties of which become increasingly salt-like as the valence of the metal decreases (10). Vanadium, for example, forms a volatile pentafluoride, an intermediate tetrafluoride and an involatile trifluoride. The present study is concerned with the properties of these three fluorides.
The preparation and some properties of the three simple fluorides of vanadium, the trifluoride, tetrafluoride and pentafluoride, were first reported by Ruff and Lickfett in 1911 (12). One interesting feature was the report that vanadium tetrafluoride disproportionates at 325° into the trifluoride and pentafluoride, and this is the method that they used to prepare vanadium pentafluoride. The lack of subsequent work on the vanadium fluorides lead to doubts as to the existence of vanadium tetrafluoride. In 1945 Simons and Powell (13), in a study of vanadium tetrachloride, stated that the existence of vanadium tetrachloride was surprising "in view of the existence of the tri- and pentafluorides and the non-existence of a tetrafluoride."

In spite of recent interest in vanadium trifluoride (14,21), vanadium pentafluoride (7,8,9,14) and complex fluorosalts of tetravalent vanadium (15,16,17) no study of the tetrafluoride has been reported since 1911. This is surprising in view of the fact that vanadium pentafluoride was first prepared by the disproportionation of the tetrafluoride (12), however recent work (7,14) has shown that the pentafluoride can be more conveniently prepared by the fluorination of vanadium metal at 350°, thus avoiding the laborious procedure of preparing the tetrafluoride.

Ruff and Lickfett (12) reported that vanadium pentafluoride was a volatile orange solid with a melting point "above 200°" and a boiling point of 111.2° C. As niobium pentafluoride and tantalum pentafluoride melt at
80° and 95° respectively and boil at 235° and 229° respectively (18), these values for vanadium pentafluoride were clearly unsatisfactory. Recent studies (7,9) have shown that vanadium pentafluoride is actually a white solid which melts at 19.5° to a straw-coloured liquid and boils at 48°, and thus the melting and boiling points of the group (V) transition metal pentafluorides increase with atomic size of the metal as is generally observed within a periodic group. The susceptibility of vanadium pentafluoride to hydrolysis may be responsible for the discrepancy as Ruff and Lickfett's measurements were probably done on the oxyfluoride, rather than the pentafluoride. For the same reason the value of 2.1766 g/cc. given by Ruff and Lickfett (12) for the density of the pentafluoride at 19° is probably unreliable.

As vanadium pentafluoride can be readily handled in all-glass apparatus when it is free of moisture (7), it has been possible to determine several of its physical properties. The vapour pressure of vanadium pentafluoride has been measured (7,9) and the heat of vapourisation calculated from the vapour pressure equation. The ratio of the heat of vapourisation to the temperature of vapourisation (the Trouton constant) is 33.1 cal/deg.mole, much higher than the normal value of 21 or 22. The specific conductivity of vanadium pentafluoride, 2.4 x 10^{-4} ohm^{-1} cm^{-1} (7), is between that of bromine trifluoride (8.0 x 10^{-3} ohm^{-1} cm^{-1} (19)) and iodine pentafluoride (5.4 x 10^{-6} ohm^{-1} cm^{-1} (19)).
High values of the Trouton constant are found in many other fluorides, particularly the halogen fluorides. A high Trouton constant is generally accompanied by relatively high melting and boiling points, appreciably large liquid ranges and fairly high specific conductivities. These properties are generally interpreted as indicative of intermolecular association or dissociation.

Considerable success has attended the interpretation of the properties of the halogen fluorides in terms of an acid-base solvent system (19) similar to the solvent systems formed by water and liquid ammonia, both of which have properties similar to the halogen fluorides. The electrical conductivity of bromine trifluoride, for example, is presumed to arise from the dissociation:

\[ 2\text{BrF}_3 \rightleftharpoons \text{BrF}_2^+ + \text{BrF}_4^- \]

forming the acidic (\(\text{BrF}_2^+\)) and basic (\(\text{BrF}_4^-\)) ions of the solvent system. The large specific conductivity of vanadium pentafluoride has been attributed to an analogous self-dissociation of vanadium pentafluoride to form an acid-base solvent system (7,8).

Recent studies of fluorine exchange in volatile fluorides, such as the halogen fluorides, by nuclear magnetic resonance (20) and radioactive \(^{18}\text{F}\) tracer (21) techniques have suggested that intermolecular association, rather than ionic dissociation, is responsible for the behaviour of these fluorides with high Trouton constants.
The relative importance of these two hypotheses is discussed more fully in Chapter 2.

In the present investigation, further physical properties of vanadium pentafluoride have been measured. In particular the density of the liquid has been measured because of recent indications (7,9) that the results of Ruff and Lickfett (12) on vanadium pentafluoride are not particularly reliable. The surface tension and viscosity have been measured to provide experimental data which are in some part indicative of molecular association within the liquid. The infrared spectrum of the vapour and some chemical properties of vanadium pentafluoride have also been investigated.

Vanadium trifluoride has been well characterised since the initial work of Ruff and Lickfett (12). The structure has been determined (22) and has proven to be a basic structural type for trifluorides (23). The structure is based on a bimolecular rhombohedral unit cell in which each vanadium is surrounded by an almost regular octahedron of fluorine atoms. The fluorines are shared by two vanadium atoms and hence act as bridging groups, so that the trifluoride can be regarded as highly associated. Vanadium trifluoride appears to be the lowest stable fluoride of vanadium, as attempts to prepare vanadium difluoride from the dichloride and hydrogen fluoride resulted in the formation of vanadium trifluoride (14).

Of the three fluorides of vanadium, the least known is the tetrafluoride, only the work of Ruff and Lickfett (12) has been reported. Therefore much of the present study is
concerned with establishing the existence of vanadium tetrafluoride and an investigation of its properties, in view of its intermediate position in the series of known vanadium fluorides.

Little is known about the thermodynamics of fluorides, particularly those of the transition metals. Most of the data available in the literature, until recently, has been calculated by statistical methods from the spectra of fluorides. The most extensive series of calculations is that on the hexafluorides of the group 6 elements, rhenium and uranium (24). Complete experimental thermochemical data is available only for simple fluorides such as the alkali metal and alkaline earth fluorides. Experimental thermochemical data is available for a few transition metal fluorides but in many cases the reliability is not exceptionally good because of the experimental difficulties associated with studies on fluorides. Indeed, reliable values for the dissociation energy of fluorine itself were determined not long ago (11).

The most straightforward method of measuring the heats of formation of metal fluorides, involving the measurement of the heat evolved on reacting fluorine with the metal in a calorimeter, was developed by von Wartenberg about twenty years ago (25). The values obtained are not considered to be very reliable because of the experimental difficulties encountered (26). Recently workers at the Argonne National Laboratory (26) have developed fluorine bomb calorimetry to a reliable method. This method has recently been used to measure the heats of formation of zirconium tetrafluoride (26)
and molybdenum hexafluoride (27).

Gross has refined the technique of measuring the heat of reaction of gaseous fluorine, near atmospheric pressure, with another element, without requiring elaborate bomb combustion apparatus. Using this method the heat of formation of titanium tetrafluoride (28) has been measured.

Most of the thermochemical data available until the advent of reliable fluorine combustion techniques had been obtained by indirect methods, measuring the heat of a reaction involving the fluoride, which can be combined with a series of known reactions, by means of Hess' law, to yield the required heat of formation. An example is the recent determination of the heat of formation of thorium tetrafluoride from the equilibrium constant of the reaction of the fluoride with silica (29). The difficulty encountered with this method is usually the choice of a suitable reaction.

The vigorous exothermic hydrolysis reactions exhibited by most fluorides have often been used to obtain heats of formation of the fluoride. Sufficient reliable data must be available to complete a Hess' law calculation, a requirement which may not easily be fulfilled. Woolf used the heat of hydrolysis to determine the heat of formation of iodine pentafluoride (30), and Meyers and Brady (31) have determined the heats of formation of molybdenum and tungsten hexafluorides and niobium pentafluoride from the measured heats of hydrolysis of these compounds.

The accuracy of this procedure is illustrated by a comparison of the two recently reported values for the heat
of formation of molybdenum hexafluoride. Meyers and Brady (31) obtained -388.6 kcal/mole for the heat of formation from the measured heat of hydrolysis and a Hess’ law calculation, while Settle et. al. (27) obtained -372.3 kcal./mole from the fluorine bomb combustion method. The difference is about 4%, not excessive when it is considered that the use of a Hess’ law calculation involves the heats of several reactions, all of varying reliability.

The final portion of the present investigation has been concerned with the thermochemical properties of the vanadium fluorides. The vigorous hydrolysis reactions of vanadium pentafluoride and vanadium tetrafluoride have been used to obtain heats of formation of these two compounds. Theoretical calculations of the heat of formation of trifluorides and tetrafluorides of the first period transition metals, based on lattice energies calculated from an approximate formula (32), have been made and the results are compared with available experimental data. An experimental value for the heat of formation of vanadium trifluoride was not determined in the same manner as for the tetrafluoride and pentafluoride because of the insolubility of vanadium trifluoride in water. Therefore the calculated value is used to evaluate the thermochemical properties of several reactions involving the simple fluorides of vanadium.
CHAPTER 2: ASSOCIATION AND DISSOCIATION IN FLUORIDES

The general theory of the structure of ionic solids is based on the assumptions (105) that the coordination number of the ions is as large as possible, subject to the restrictions imposed by the packing of ions (generally assumed to be spherical) about a central ion, and that the coordinated groups are arranged in a configuration which minimises the repulsions between them. In general the coordination about the central ion of a molecule will be higher than indicated by the stoichiometry of the molecule and the symmetry about the central ion will be quite high, eg. octahedral or cubic, even in low valence compounds.

As the arrangement of ions of one charge about those of another charge is stable only if the central ion is in contact with the surrounding ions and does not 'rattle', the packing in an ionic solid will be governed by the radius ratio rules (105). Thus in an ionic solid the coordination of a small metal atom depends on the ratio of its radius to that of the anion.

The preferred configuration of \( \text{AB}_4 \) and \( \text{AB}_6 \) groupings in solids will be tetrahedral and octahedral respectively as these configurations minimise the electrostatic repulsions between the B ions, maintaining at the same time equivalence between all A-B interactions (105).

It is interesting to consider the structure of an \( \text{AB}_5 \) complex in view of the general theory of ionic solids.
The only $\text{AB}_5$ configuration which maintains equivalence of all the A-B distances is the energetically unfavourable planar structure (105). Low electrostatic repulsion energies are also given by the trigonal bipyramid and square pyramidal structures and these are the most favourable $\text{AB}_5$ groupings. However, radius ratio requirements for both the square pyramidal and the trigonal bipyramid structures are identical to the octahedral requirements hence, if A is large enough to form an $\text{AB}_5$ group, octahedral $\text{AB}_6$ groups can also be formed. As the axial-equatorial B-B distances in the trigonal bipyramid or square pyramid structures are similar to those in the octahedral structure, conversion of an $\text{AB}_5$ to $\text{AB}_6$ group introduces no unfavourable interactions. The tendency to achieve maximum coordination of the central ion will be dominant and will make the six coordinate octahedron more favourable than either of the five coordinate structures, hence pentacoordination is not to be expected in ionic solids (105). In general this is found to be the case; tetrahedral and octahedral coordinations are found in solids in preference to pentacoordinate structures.

Rigorously these arguments apply only to monatomic ionic solids, however Orgel suggests (105) that these arguments can be qualitatively applied to the disposition of dipolar molecules and polyatomic anions about a central atom or ion. The occurrence of highly symmetric coordination structures in no way implies either covalent or ionic bonding in the
compounds. The stereochemical arrangements are simply those which achieve the maximum possible coordination about a central atom or ion, which is mostly governed by the relative sizes of the atoms or ions, with the minimum repulsions between the coordinating groups. The stereochemistry is not dependent on whether the coordinating groups are covalently bonded to the central atom, as is presumed in octahedrally coordinated \( \text{Co} (\text{NH}_3)_6^{3+} \) ions or ionically bonded as is presumed in the case of sodium chloride, where the sodium is octahedrally coordinated by chloride ions.

The small size of the fluoride ion (1.36Å compared to 1.81Å for a chloride ion (11)) ensures that maximum coordination will usually be achieved in solid fluorides. In general the maximum coordination will be much greater than that indicated by the molecular stoichiometry. A typical example is the structure of solid vanadium trifluoride (22) in which the vanadium atom is surrounded by six fluorine atoms, forming an octahedral \( \text{VF}_6 \) group. Each fluorine is shared between two vanadium atoms to maintain the stoichiometry while achieving six coordination about the vanadium. Many other examples of this type are known (23) where the fluorine acts as a bridge between the metal atoms, but the structure neither implies nor excludes covalent bridge bonding. Thus while the coordination state of a central atom of a molecule is quite easily established in solids, through complete structural analysis with such techniques as X-ray diffraction, this knowledge does not establish the nature of the bond formed
between the central atom and the coordinating ligands. Other evidence which will be discussed later suggests that an appreciable amount of covalent bridge bonding occurs in the solid fluorides, thus the high coordination about the metal atom may be interpreted in terms of a structural unit involving partly covalent bonds.

In the vapour state, the assumption of unimolecular species is usually valid. In contrast to the solid state, where ordering and intermolecular interaction is at a maximum, molecular interactions are minimised under the influence of increasing randomness. The coordination is generally identical to the stoichiometric coordination and coordination states not found in solids, such as pentacoordinate trigonal bipyramid structures, are frequently observed. The determination of the coordination is usually a more intuitive process, involving molecular spectra and electron diffraction techniques which nevertheless yield reliable results.

The problem of intermolecular interaction and coordination of molecules in the liquid state is more difficult. The intermediate degree of interaction found in liquids and the intermediate degree of randomisation of the structure precludes the use of X-ray diffraction techniques and yet it is not possible to assume as in gases, that there is little or no intermolecular interaction.

Some insight into the behaviour of liquids has been obtained from qualitative comparison of the properties of
liquids, nuclear resonance techniques and many other methods. The problem is often somewhat simplified by the quite reasonable assumption that the bonding in compounds varies continuously through the solid-liquid-gas phase changes, rather than discontinuously at each phase boundary. The validity of this assumption is quite dependent upon the nature of the compound and upon the particular phase change involved; nevertheless it often yields a useful insight into areas where data are severely lacking, and in particular into the problem of association in liquids as this assumption suggests that a compound which is associated in the solid state will be similarly associated in the liquid phase.

The behaviour of volatile fluorides shows a marked dependence upon the general nature of the compound. The apparent reason for this behaviour is the possibility of intermolecular association in certain systems, in the solid, liquid and even gaseous phases. A comparison of simple properties of a large number of volatile fluorides such as melting and boiling points and Trouton constants, shown in table 1, leads to the conclusion that these fluorides can be roughly classified into two groups; associated and non-associated fluorides.
# Table 1

**The Physical Properties of the Volatile Fluorides**  
(Data are taken from Ref. 19 unless otherwise noted)

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td><strong>Non-associated fluorides</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiF$_4$</td>
<td>183</td>
<td>178(subl)</td>
<td>-</td>
<td>- (Ref 33)</td>
</tr>
<tr>
<td>GeF$_4$</td>
<td>158</td>
<td>136(subl)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PF$_5$</td>
<td>190</td>
<td>198</td>
<td>8</td>
<td>21 (Ref 34)</td>
</tr>
<tr>
<td>SF$_6$</td>
<td>223</td>
<td>209(subl)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SeF$_6$</td>
<td>238</td>
<td>227(subl)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TeF$_6$</td>
<td>235</td>
<td>234(subl)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MoF$_6$</td>
<td>290</td>
<td>308</td>
<td>18</td>
<td>21</td>
</tr>
<tr>
<td>WF$_6$</td>
<td>275</td>
<td>290</td>
<td>15</td>
<td>21</td>
</tr>
<tr>
<td>UF$_6$</td>
<td>337</td>
<td>330(subl)</td>
<td>-</td>
<td>20 (Ref 35)</td>
</tr>
<tr>
<td><strong>Associated Fluorides</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BrF$_3$</td>
<td>282</td>
<td>399</td>
<td>117</td>
<td>25.7</td>
</tr>
<tr>
<td>ClF$_3$</td>
<td>196</td>
<td>284</td>
<td>88</td>
<td>23.1</td>
</tr>
<tr>
<td>SF$_4$</td>
<td>152</td>
<td>233</td>
<td>81</td>
<td>27</td>
</tr>
<tr>
<td>SeF$_4$</td>
<td>264</td>
<td>381</td>
<td>117</td>
<td>30</td>
</tr>
<tr>
<td>AsF$_5$</td>
<td>193</td>
<td>220</td>
<td>27</td>
<td>24</td>
</tr>
<tr>
<td>SbF$_5$</td>
<td>282</td>
<td>416</td>
<td>134</td>
<td>26</td>
</tr>
<tr>
<td>BrF$_5$</td>
<td>213</td>
<td>314</td>
<td>101</td>
<td>23</td>
</tr>
<tr>
<td>IF$_5$</td>
<td>283</td>
<td>374</td>
<td>91</td>
<td>26</td>
</tr>
<tr>
<td>VF$_5$</td>
<td>293</td>
<td>321</td>
<td>29</td>
<td>33</td>
</tr>
<tr>
<td>NbF$_5$</td>
<td>353</td>
<td>508</td>
<td>155</td>
<td>25</td>
</tr>
<tr>
<td>TaF$_5$</td>
<td>368</td>
<td>503</td>
<td>133</td>
<td>26</td>
</tr>
</tbody>
</table>
The non-associated fluoride group, containing such fluorides as silicon tetrafluoride, sulphur hexafluoride and molybdenum hexafluoride show quite similar properties. The melting and boiling points are quite low and exhibit a fairly regular increase with molecular weight. The liquid range is very small, in many cases it is non-existant as the solid readily sublimes. The Trouton constant; the ratio of enthalpy of vapourisation to the boiling point, is generally close to the 'normal' value of 21 or 22, when it can be determined. Typically these properties reflect a very small degree of intermolecular association in the solid as well as the liquid. Silicon tetrafluoride is known to form cubic crystals of discrete tetrahedral molecular units in which the silicon atom maintains its tetrahedral coordination (36). The hexafluorides have been shown to possess regular octahedral structures (see 19) and probably crystallise as molecular crystals as well.

The 'non-associated' behaviour of the hexafluorides is easily understood, as the maximum valence and coordination has been attained. Silicon tetrafluoride and phosphorus pentfluoride, however, readily form the hexacoordinate ions SiF$_6^{-2}$ and PF$_6^{-}$ indicating that the maximum coordination of the central atom has not been attained, hence they should behave as associated fluorides. The reason that they do not may be that the energy of the vacant 'd' orbitals of the central atom, utilized in complex ion formation, may be too high in the neutral molecule to allow participation in the formation of neutral associated complexes.
The other group, encompassing a wide variety of fluorides of metals and non-metals alike such as bromine trifluoride, selenium tetrafluoride, antimony pentafluoride and vanadium pentafluoride all have properties (19) which are typical of intermolecular association. The melting and boiling points are greater than those of non-associated fluorides of comparable molecular weight. A large liquid range of approximately 100°C, and Trouton constants ranging from 23 to 33 are also observed. They all conduct electricity with varying ability (19) but at least as well as liquid ammonia or water (33) and in many cases the fluorides are better conductors. Abnormal behaviour is also observed in the vapour phase, for example chlorine trifluoride deviates from the perfect gas laws in a manner which suggests dimerisation (see 19). There is no evidence to indicate the behaviour of the solid associated fluorides, but it is reasonable to assume that if association occurs, it will be a maximum in the solid.

If the non-bonding electron pairs are assumed to fulfil the stereochemical function of a bonded atom (37) then most of the associated fluorides have an effective coordination number of five about the central atom. This assumption appears to be justified by the observed 'planar-T' structure of chlorine trifluoride (19) in which two lone pairs occupy planar sites in a trigonal bipyramid skeleton and the three fluorines occupy the two axial and one of the planar sites. Similarly the $C_{2v}$ structure of sulphur tetrafluoride (38,39) and selenium tetrafluoride (40) is also based on a trigonal
bipyramid with one planar site occupied by a non-bonding electron pair. Assuming that all the associated fluorides, except iodine and bromine pentafluorides, have a maximum coordination of six, these compounds are coordinatively unsaturated and hence can increase the coordination of the central atom through intermolecular association. Iodine and bromine pentafluorides can probably associate to hepta-coordinate structures, because of their larger size, and hence also tend to achieve maximum coordination.

The marked change from associated behaviour to non-associated behaviour on converting sulphur and selenium tetrafluorides to the hexafluorides supports the proposal that the behaviour of the 'associated' fluorides is due to a tendency to increase the coordination of the central atom as much as possible.

It is interesting to notice that 'associated' fluorides are mainly formed by the halogens and the transition metals, elements which likely have unoccupied 'd' orbitals of sufficiently low energy to be involved in bridge bond formation. Low lying 'd' orbitals are probably available in antimony, because of its large size, and tetravalent sulphur and selenium because their maximum valence has not been satisfied.

Before considering the nature of the associated species it is necessary to consider an alternative explanation for the properties of the 'associated' fluorides. It was proposed that the high specific conductivities exhibited by most of these
fluorides was due to a self-dissociation of the type (see Ref 19):

\[ 2MF_n \rightleftharpoons MF_{n-1}^+ + MF_{n+1}^- \]

to form an acid-base solvent system. Acids in the system are compounds which contain the \( MF_{n-1}^+ \) ion and bases are those compounds which contain the \( MF_{n+1}^- \) ion. To establish the existence of such a solvent system it is necessary to isolate both acid and base compounds, show a partial ionic character in these compounds and to perform neutralisation reactions between the acid and base to yield a salt and solvent. These conditions have been completely fulfilled for only the bromine trifluoride solvent system (19) although most of the other 'associated' fluorides satisfy at least one and frequently more of the above conditions (19).

The proposal that the behaviour of 'associated' fluorides is due to self-dissociation does not invalidate the suggestion that unsaturated coordination of the molecular fluoride is the basic factor responsible for the behaviour of the 'associated' fluorides although it suggests that the behaviour of these fluorides may be better described in terms of unstable coordination of the molecular fluoride. Consider, for example, the dissociation of bromine trifluoride into acidic and basic ions:

\[ 2\text{BrF}_3 \rightleftharpoons \text{BrF}_2^+ + \text{BrF}_4^- \]

Assuming as before that the two non-bonding pairs on the bromine atom are stereochemically active, the result of this
dissociation is the conversion of two pentacoordinate molecules into one tetrahedral \((\text{BrF}_2^+)\) ion and one octahedral \((\text{BrF}_4^-)\) ion. The coordination states formed in the ions, tetrahedral and octahedral, are frequently observed and may be regarded as being \textit{stable}. The pentacoordination of the neutral molecule, on the other hand, is rarely observed in condensed systems and may be regarded as being \textit{unstable}. Thus the effect of the dissociation is to convert two species of unstable coordination into two species with stable coordination.

However, there is no inherent reason for a pentacoordinate molecule to be \textit{unstable} relative to tetra- and hexacoordinate molecules. A more likely explanation is that a pentacoordinate molecule is unsaturated, that is the central atom can accommodate another ligand without overcrowding the molecule. Where orbitals of sufficiently low energy are available to participate in bonding another ligand, association to create a higher coordination state occurs, whereas if the requisite orbitals have excessively high energies no association occurs.

Other properties of the associated fluorides are not fully explained by ionic dissociation. If the associated fluorides are partially dissociated according to the previously outlined ionic dissociation mechanism, exchange of fluorine atoms between central atoms will occur. The \(^{19}\text{F}\) nuclear magnetic resonance spectra of liquid associated fluorides do indeed show this behaviour \((20,41)\). In general broad
nuclear resonance absorption peaks are observed at normal temperatures, but on cooling the sample, the multiplet structure arising from non-equivalent fluorine environments on the central nucleus can be resolved. This behaviour is consistent with rapid fluorine exchange between non-equivalent fluorine atoms. The rate of exchange, measured as the lifetime of a fluorine atom in a given environment, can be estimated from the splitting of the broad resonance upon resolution. Muettertties and Phillips (20) concluded from their exchange measurements that the rate of fluorine exchange in the halogen fluorides decreases in the order $\text{BrF}_3 > \text{ClF}_3 > \text{IF}_5 > \text{BrF}_5$. However the specific conductivity decreases in the order $\text{BrF}_3 > \text{IF}_5 > \text{BrF}_5 > \text{ClF}_3$. Much better agreement would be expected if ionic dissociation were responsible for fluorine exchange.

A similar fluorine exchange behaviour has also been observed in sulphur tetrafluoride (39,41) and selenium tetrafluoride (41). Muettertties and Phillips have shown (41) that the exchange in sulphur tetrafluoride was independent of the wall area of the sample container and that the exchange reaction was at least second order. Also a free radical dissociation mechanism of the type:

$$\text{SF}_4 \rightleftharpoons \text{SF}_3^+ + \text{F}^-$$

was rigorously excluded because the solvents used to dilute the sulphur tetrafluoride were not fluorinated (41).

In the earlier paper (20) Muettertties and Phillips suggested that as the rate of fluorine exchange did not follow the specific conductivity the exchange was due to an
associative mechanism involving fluorine bridge dimers. This is consistent with the second order rate law (41) suggested for exchange in sulphur tetrafluoride and with the observation that a radical dissociation mechanism is not permissible.

Rogers and Katz (21) observed rapid $^{18}\text{F}$ exchange between tagged hydrogen fluoride or chlorine trifluoride and several halogen fluorides and antimony pentafluoride both in the liquid and gaseous phases. While liquid exchange reactions are compatible with the ionic dissociation, it is unlikely that the vapour phase exchange, which was shown to be homogeneous, occurs through an ionic dissociation mechanism. Rogers and Katz (21) concluded from these studies that ionic dissociation is not responsible for the exchange, but rather that exchange arises from the formation of a fluorine-bridge bonded associated dimeric species such as was proposed to explain the association of chlorine trifluoride in the gas phase (see 19), for example, an exchange of the type:

\[
\begin{align*}
&\text{F} \quad \text{F} \\
&\text{Cl} \quad \text{Cl} \\
&\text{F} \quad \text{F}
\end{align*}
\]

\[
\begin{align*}
&\text{F} \quad \text{F} \\
&\text{Cl} \quad \text{Cl} \\
&\text{F} \quad \text{F}
\end{align*}
\]

Association by fluorine bridging and ionic dissociation are not mutually exclusive processes because association to dimers is probably a preliminary step in the ionisation process. Homogeneous dissociation of the dimer into two molecular species leads to exchange if the bridge bonds become equivalent in the dimer and therefore undistinguishable when broken during dissociation. Heterogeneous dissociation of the dimer so that
the two bridge bonds accompany one central atom will lead to
the formation of the ions \( MF_{n-1}^+ \) and \( MF_{n+1}^- \). The extent of
dissociation into ions will therefore depend on the ability
of the liquid fluoride to stabilise its ions, thus the magni-
tude of the ionic dissociation constant (represented by the
specific conductivity) will parallel the dielectric constant
of the solvent. A complete comparison is not possible because
of inadequate data, however the available data given in
Table 2 do show a correspondence between specific conducti-
vity and dielectric constant.

<table>
<thead>
<tr>
<th>SPECIFIC CONDUCTIVITY &amp; DIELECTRIC CONSTANT OF HALOGEN FLUORIDES</th>
</tr>
</thead>
<tbody>
<tr>
<td>IF(_5)</td>
</tr>
<tr>
<td>Specific conductivity (10^6 k_{sp})</td>
</tr>
<tr>
<td>Dielectric constant of liquid</td>
</tr>
</tbody>
</table>

The similarity in the properties of the associated
fluorides suggests that a similar type of intermolecular
bonding will be found in halogen fluorides and associated
metal fluorides. In the halogen fluorides, dimerisation
could involve the non-bonding electron pairs in a classical
donor-acceptor bond between the central atoms, however it is
then difficult to explain association in the metal fluorides
which have no electrons available for the formation of a
metal to metal bond. The non-classical fluorine bridge bond proposed by Muetterties and Phillips (20) provides a bonding mechanism which can be applied to both the halogen fluorides and the associated metal fluorides. According to this proposal, association involves the donation of electrons from the fluorine atom into vacant orbitals of the central atom in another molecule. Back donation from the second molecule to the first by a similar mechanism prevents the accumulation of excessive electron density on one molecule of the associated complex. Since fluorine is not regarded as a good electron donor, the bridge bond may involve a formal charge transfer from fluorine atoms of one molecule to the fluorine atoms of a second molecule, rather like the charge transfer interactions proposed by Burbank and Bensey (42) to account for the different bond lengths in chlorine trifluoride. As before, a second charge transfer bond is formed by a similar mechanism to prevent accumulation of electronic charge on any one molecule of the associated complex. The two alternatives, which are essentially equivalent, are illustrated below for the chlorine trifluoride dimer:

In either case the configuration about each chlorine atom can be regarded as octahedral with the non-bonding electron pairs occupying the two axial positions of each octahedral
unit. A similar argument applies to the formation of 
associated polymers, which in some cases may be preferable 
to dimers.

Muetterties and Phillips (20), in proposing fluorine 
bridging in halogen fluorides by donation of electrons from 
the fluorine atoms into the vacant $d^1$ orbitals of the central 
halogen atom, suggested that the stability of these fluorine 
bridge bonds involving $d^1$ orbitals would increase with the 
atomic number and size of the central halogen atom. They 
also suggested that fluorine bridge bonds between $XF_3$ mole-
cules would be more stable than those formed between $XF_5$ 
molecules, presumably because of the increased stability of 
the $d^1$ orbital bridge bond accompanying the greater size of 
a trivalent $X$ ion relative to a pentavalent $X$ ion. Thus 
the stability of dimers should decrease in the order (20) 
$BrF_3 > ClF_3 > IF_5 > BrF_5$, that is the same as the order of 
decreasing fluorine exchange which was observed with $^{19}F$
nuclear magnetic resonance measurements (20). While 
Muetterties and Phillips have not made entirely clear the 
reasons for this order of stability, especially the conclusion 
that dimer stability is greater in trifluorides than penta-
fluorides, their proposal of a $d^1$ orbital bond can be 
extended successfully to other systems. The increase in the 
stability of a $d^1$ orbital bond would be expected to increase 
with the increasing size and atomic number in the series 
phosphorus, arsenic and antimony, leading to bridge bond 
stability which decreases in the order: $SbF_5 > AsF_5 > PF_5$. 
The behaviour of antimony pentafluoride suggests that it is highly associated, while arsenic pentafluoride appears to be a borderline case of association and phosphorus pentafluoride is best classed as non-associated, in agreement with predictions based on Muettterties and Phillips proposal.

Further evidence for fluorine bridge bonding in associated fluorides has been obtained from the nuclear magnetic resonance spectrum of antimony pentafluoride (43) which suggests that a polymer of octahedral SbF₆ units is formed by sharing fluorines with adjacent octahedra at right angles to each other. This structure is consistent with the extremely high viscosity of antimony pentafluoride (44). The molecular complexity of (SbF₅)₃ at 150° and (SbF₅)₂ at 250° in the vapour state (45) suggests that the polymeric structure is partially preserved upon vapourisation. The low conductivity of antimony pentafluoride (19) is also not surprising in view of the polymeric structure of the liquid.

The extent of intermolecular association in a liquid will likely be reflected by properties such as surface tension and viscosity which are largely dependent on the size and shape of the molecules in the liquid. Visual observation of the mobility of liquid fluorides is often sufficient to indicate qualitatively that associated fluorides have a higher viscosity than non-associated fluorides, however quantitative data is necessary to evaluate the relative degree of association. The available surface tension and viscosity data for associated fluorides are shown with their specific
The similarity in the behaviour of the surface tension and viscosity of the associated fluorides is quite evident. The values of all these properties decrease in the order: $\text{SbF}_5 \rightarrow \text{BrF}_3 \rightarrow \text{IF}_5 \rightarrow \text{BrF}_5 \rightarrow \text{ClF}_3$. Agreement between the values of the surface tension and the viscosity is to be expected, as these two properties probably arise from intermolecular association. The order of decreasing molecular association indicated by the viscosity and surface tension for the interhalogens is not the order of decreasing Trouton constants.
Likewise the nuclear magnetic resonance study (20) indicated that molecular association decreased in the order:

BrF$_3$ $>$ ClF$_3$ $>$ IF$_5$ $>$ BrF$_5$, an entirely different order to that indicated by the viscosity and surface tension of the halogen fluorides.

The disagreement between the relative extent of association, as indicated by viscosity or surface tension, and that indicated by the Trouton constant is not serious as the Trouton constant is only approximate in any case. The reason for the disagreement between the relative extent of association indicated by nuclear magnetic resonance measurements and by the surface tension or viscosity is not readily apparent but it probably arises because measurements on microscopic systems (e.g., nuclear magnetic resonance) are not directly comparable with measurements such as surface tension or viscosity on macroscopic systems because somewhat different processes are being observed.

The specific conductivity of the halogen fluorides also decreases in the same order as the viscosity or surface tension decrease which is somewhat surprising. A property indicative of molecular dissociation, such as specific conductivity, would not be expected to behave similarly to properties indicative of molecular association. Considering also that ionic mobility will likely decrease with increasing viscosity, a decrease in specific conductivity with increasing viscosity would be expected; just the opposite is observed.
The parallel behaviour of associative properties and specific conductivity suggests that association to dimers is a necessary preliminary step to ionic dissociation, hence the greatest specific conductivity will be found in the most highly associated system. This will only be true if the molecules associate into easily ionized species, that is into dimers and not polymers because polymeric structures will not be as likely to form high concentrations of mobile ions.

The low viscosity of the halogen fluorides relative to, say, antimony pentafluoride, suggests that the halogen fluorides tend to associate into dimers rather than polymers. Hence the specific conductivity will follow the trend of intermolecular association indicated by viscosity and surface tension. The parallel behaviour of conductivity and association, indicated by viscosity does not extend to antimony pentafluoride because of the tendency of antimony pentafluoride to form polymers rather than dimers. This does not necessarily imply that the fluorine bridge bonds are different in the associated molecules, but only a difference in the structure of the resultant associated fluoride.

The properties of 'associated' fluorides are therefore probably due to the tendency of these fluorides to form dimeric or polymeric associated structures, by means of fluorine-bridge bonds, to achieve a more stable coordination about the central atom. Ionic dissociation, while it accounts for the solvent properties of these fluorides, is of secondary importance, especially in highly associated, polymeric structures such
as antimony pentafluoride. The fluorine bridge association proposed for these liquid fluorides appears to be similar to the bridging often found in solid fluorides, however in a liquid such association implies the formation of a bond. The proposal that the association involves bond formation by donation of electrons from the fluorine atom into the vacant \( 'd' \) orbitals of the central atom is supported by the agreement between predicted \( 'd' \) orbital bond stability and the observed stability of association in a series of related molecules.
(1) Physical Properties of Vanadium Pentafluoride

The high specific conductivity and Trouton constant of vanadium pentafluoride (7) suggested that vanadium pentafluoride ionizes according to the equation:

$$2VF_5 \rightleftharpoons VF_4^+ + VF_6^-$$

thus forming an acid-base solvent system. The existence of salts containing the $VF_6^-$ ion (14) and the occurrence of reactions which are best explained as neutralisation reactions (8) support this proposal.

Vanadium pentafluoride was therefore considered to resemble niobium and tantalum pentafluorides (49) and the halogen fluorides (19), which have similar specific conductivities and Trouton constants. Considerable success attended the interpretation of the properties of bromine trifluoride in terms of acid-base solvent behaviour (19) however it has not been possible to rigorously establish acid-base solvent behaviour for the other halogen fluorides or the group five fluorides (19).

Recent studies of fluorine exchange in the halogen fluorides by nuclear magnetic resonance (20) or the use of a radioactive fluorine tracer (21), as discussed in the previous chapter, indicated that the important process was intermolecular association rather than ionic dissociation (19). Further support of this proposal is given by the nuclear
magnetic resonance spectrum of antimony pentafluoride which indicates that the molecules associate through fluorine bridge bond formation to form polymeric chains in the liquid.

The extent of intermolecular association in a liquid appears to be reflected by properties such as surface tension and viscosity as mentioned earlier. Qualitatively vanadium pentafluoride appears to be a highly viscous liquid, suggesting that the liquid is highly associated.

In an attempt to quantitatively establish the extent of intermolecular association in liquid vanadium pentafluoride the density, viscosity and surface tension have been determined in the present investigation.

The density \((\rho)\) of vanadium pentafluoride is a linear function of temperature over most of the liquid range \((19.5^\circ\text{C} \text{ to } 48^\circ\text{C})\) of the compound. Between \(20^\circ\text{C}\) and \(40^\circ\text{C}\) the density is given by the expression:

\[
\rho = 2.483 - 0.00349(t-25^\circ) \text{ g./cc.}
\]

The density of solid vanadium pentafluoride is probably considerably greater than the density of the liquid, since on freezing the pentafluoride in the dilatometer a very marked contraction occurred. The value of 2.1766 g./cc. for the density of solid vanadium pentafluoride at 19°C is probably wrong, just as the values of Ruff and Lickfett (12) for the melting and boiling points of vanadium pentafluoride were wrong (7). These erroneous results are probably due to extensive hydrolysis of Ruff and Lickfett's samples of the
pentafluoride to the oxytrifluoride (7).

The value of 2.483 g./cc. for the density of vanadium pentafluoride at 25° is within the expected range as it is consistent with the densities (19) of antimony pentafluoride (2.99 g./cc.), bromine trifluoride (2.80 g./cc.), bromine pentafluoride (2.46 g./cc.) and iodine pentafluoride (3.19 g./cc.).

The average coefficient of cubical expansion of vanadium pentafluoride, determined in the same experiments as the density, is 1.26 x 10^{-3} cc/deg.

The viscosity of vanadium pentafluoride was measured in an Ostwald type viscometer modified, as described in the experimental section, to prevent hydrolysis of the fluoride by atmospheric moisture. The viscosity varies linearly with temperature although a few points deviated considerably from the straight line as shown in Figure 1a. The viscosity (\( \eta \)) of vanadium pentafluoride, between 25° and 35° is given by the equation:

\[
\eta = 125 - 7.2(t-25°) \pm 20\% \text{ centipoise.}
\]

Unfortunately the value is not exceptionally accurate because of rather large errors in the measurement arising from decomposition of the vanadium pentafluoride and the necessarily small capacity of the viscometer. It is apparent, however, that the viscosity is considerably higher than that of most liquid fluorides, which is about 1-2 centipoises. (Table 3). Only antimony pentafluoride, with a viscosity of 460 centipoise (44), has a higher viscosity and it has been
FIG. I to follow p. 34

PROPERTIES OF LIQUID VANADIUM PENTAFLUORIDE

(a) VISCOSITY

(b) SURFACE TENSION

\[ \text{VISCOITY (CENITPOISE)} \]

\[ \text{SURFACE TENSION (DYNES/CM)} \]

\[ \text{TEMPERATURE (DEGREES C.)} \]

\[ \text{\( \square \) = average of several determinations} \]
shown (43) that antimony pentafluoride is associated into fluorine bridged polymers. The high viscosity of vanadium pentafluoride indicates considerable polymeric association in the liquid, probably of a similar type to that in antimony pentafluoride.

The surface tension of vanadium pentafluoride, measured by two capillary rise techniques, was an approximately linear function of the temperature as shown in Figure 1b, although some of the values do not coincide with the straight line. The rather high limits of error arise from the tendency of the liquid to form bubbles in the capillaries. The surface tension ($\gamma$) of vanadium pentafluoride from $25^\circ$ to $35^\circ$ is given by the equation:

$$\gamma = 18.2 - 0.142(t-25^\circ) + 0.2 \text{ dynes/cm}^2.$$  

The standard deviation of $\pm 0.2$ (or about 1% error) for measurements in two types of capillary rise apparatus suggests that the results are probably reasonably reliable.

The value of 18.2 dynes/cm$^2$ for the surface tension of vanadium pentafluoride is lower than the values for all of the associated fluorides (Table 3). This low surface tension for such a viscous liquid is surprising because in the associated fluorides the viscosity and surface tension decrease in the same order: $\text{SbF}_5 > \text{BrF}_3 > \text{IF}_5 > \text{BrF}_5 > \text{ClF}_3$. While the viscosity of vanadium pentafluoride falls between those of antimony pentafluoride and bromine trifluoride the surface tension is less than that of chlorine trifluoride. The high viscosity of
the liquid may have led to a false result for the surface tension, since it was found that reliable values for the surface tension of antimony pentafluoride could not be obtained from capillary rise methods, and it was necessary to use the maximum bubble pressure method (45). If this is the case for vanadium pentafluoride it is difficult to understand why two determinations of the surface tension in two types of apparatus, although both are measuring capillary rise, should agree so well with each other.

The change of the molar surface energy (\(\Gamma\)), given by the equation:

\[ \Gamma = \gamma \left( \frac{Mv}{2} \right)^{2/3} \]

where \(\gamma\) is the surface tension, \(M\) is the molecular weight and \(v\) is the specific volume, with temperature is supposed to be indicative of molecular association (20). For non-associated liquids the slope of the molar surface energy versus temperature curve (\(d\Gamma/dt\)) is a universal constant (the Eötvos coefficient) with a value of -2.1 (50). Using the data given in Table 18, the slope of the molar surface energy versus temperature graph for vanadium pentafluoride is -1.9. The degree of molecular association estimated from the ratio of Eötvos coefficients (50) is not much greater than unity. However, the surface tension and the molar surface energy, which is derived from the surface tension, are not reliable indicators of molecular association. Many associated as well as non-associated liquids obey the Eötvos law (50) and attempts
to calculate the degree of molecular association for liquids with slopes less than the Eötvos coefficient have not been very successful (50).

The viscosity is a more reliable indication of association, and the high viscosity of vanadium pentafluoride means that the liquid is probably highly associated in spite of the low surface tension and normal Eötvos coefficient. The similarity of the viscosity of vanadium pentafluoride to that of antimony pentafluoride, both of which are much greater than that of the halogen fluorides, suggests that both pentafluorides are associated into chain polymers in contrast to the dimeric associated species which probably form in the halogen fluorides.

(ii) Chemical Properties of Vanadium Pentafluoride

Chemical interactions between two fluorides which exhibit acid-base solvent properties sometimes result in the formation of solid complexes containing one ion from each solvent system. Bromine trifluoride (l4) or antimony pentafluoride (7) are readily miscible with vanadium pentafluoride and form solutions from which the component fluorides can not be separated by distillation. Salt formation is not observed.

Selenium tetrafluoride however forms a reactive solid 1:1 complex with vanadium pentafluoride. The most likely formulation of this $\text{VF}_5 \cdot \text{SeF}_4$ complex is as the salt $\text{SeF}_3^+\text{VF}_6^-$, which combines the most stable ion of the selenium tetrafluoride solvent system (4) with the most stable ion of the vanadium
pentafluoride solvent system (7,8,14).

Sulphur tetrafluoride appears to form a solid complex with vanadium pentafluoride which is stable only at low temperatures. The analysis indicates an approximate composition VF$_5$·0.5 SF$_4$. This may be due to partial decomposition of a 1:1 complex or the true formula of the adduct. On the basis of present information it is not possible to decide between the two alternatives. It is interesting to note that the reaction of niobium pentoxide with sulphur tetrafluoride (5) yielded a product of the composition NbF$_5$·0.54 SF$_4$ which again may be a partially decomposed 1:1 SF$_4$ complex with niobium pentafluoride or the true formula of the adduct.

The formation of a stable complex of vanadium pentafluoride with selenium tetrafluoride whereas bromine trifluoride, antimony pentafluoride and sulphur tetrafluoride form unstable solids or no solid complexes at all probably reflects the greater stability of the SeF$_3^+$ cation relative to the SF$_3^+$ and BrF$_2^+$ cations. The instability of the VF$_4^+$ cation is probably responsible for the lack of a solid complex between antimony pentafluoride and vanadium pentafluoride, as antimony pentafluoride is well known to form complexes containing the SbF$_6^-$ ion (19).
(1) Preparation and Physical Properties of Vanadium Tetrafluoride

At the start of this investigation, vanadium tetrafluoride was prepared by fluorinating vanadium tetrachloride with liquid anhydrous hydrogen fluoride at -78°, exactly according to the method of Ruff and Lickfett (12). The vanadium tetrafluoride obtained was usually contaminated with appreciable amounts of a brown, granular impurity and the magnetic moment indicated that appreciable amounts of trivalent vanadium were present. At -78° vanadium tetrachloride is solid, and the impurities probably resulted from incomplete reaction between solid vanadium tetrachloride and liquid hydrogen fluoride due to the formation of a solid film of insoluble tetrafluoride on the surface of the tetrachloride. Localised reduction to form lower fluorides may also be due to the presence of solid tetrachloride. Increasing the reaction temperature to -25°, the melting point of the tetrachloride, provides a liquid-liquid reaction system but sacrifices the control over the reaction rate which is achieved at -78°, and would probably lead to greater reduction to the trifluoride. The addition of an inert solvent such as trichlorofluoromethane (mp. -112°) provided a reaction mixture which remained liquid at -78° and could be continuously stirred throughout the reaction. With these improvements, a product with a high degree of purity was consistently obtained.
Vanadium tetrafluoride may also be prepared from the metal and gaseous fluorine. At high temperatures, eg. 350° to 370°, the pentafluoride is obtained almost exclusively, but if the fluorine supply is not sufficient for complete conversion to the pentafluoride, a brown liquid is formed which leaves a small amount of a light brown residue of vanadium tetrafluoride when the volatile pentafluoride is removed. At lower temperatures, in the neighbourhood of 200°, all three known fluorides of vanadium, the trifluoride, tetrafluoride and pentafluoride are obtained although the principal product is still the pentafluoride. The different volatilities of the three fluorides provide complete separation of the fluorides during the preparation, and reasonably pure vanadium tetrafluoride can be isolated. For convenience, greatest yield and highest purity, however, the fluorination of vanadium tetrachloride with hydrogen fluoride in a solvent is the preferred preparative method for vanadium tetrafluoride.

Pure vanadium tetrafluoride, prepared from vanadium tetrachloride and hydrogen fluoride is a brilliant, lime-green powder which on exposure to moisture hydrolyses on the surface to a brown powder and eventually to a blue paste. The product obtained on fluorination of vanadium metal is a slightly darker green, and hydrolyses in much the same manner as the powder form but with somewhat reduced rate presumably because of its greater compactness. The brown colour of Ruff and Lickfett's (12) preparation was probably due to slight hydrolysis during the preparation.
Vanadium tetrafluoride dissolved vigorously in water forming a bright blue solution which is characteristic of the VO\(^{+2}\) ion. Vanadium tetrafluoride was completely insoluble in a variety of organic and inorganic solvents and Lewis base solvents reacted with vanadium tetrafluoride to form dark, gummy residues.

Vanadium tetrafluoride is thermally unstable. At 100-120°C in vacuum, the disproportionation into vanadium trifluoride and pentafluoride, first reported by Ruff and Lickfett (12), proceeded quite rapidly. The rate of disproportionation increases with temperature, however a high temperature (e.g., Ruff and Lickfett's report (12) of 325°C as the disproportionation temperature) is not necessary to induce disproportionation. Samples of vanadium tetrafluoride stored four to six days at room temperature, sealed in dry glass tubes, at atmospheric pressure, contained about 5% vanadium trifluoride plus a gas, which is presumably silicon tetrafluoride arising from the reaction of vanadium pentafluoride with the glass. At -78°C, vanadium tetrafluoride could be stored at least two weeks without excessive decomposition to the tri- and pentafluorides.

The disproportionation of vanadium tetrafluoride into the tri- and pentafluorides is apparently irreversible and is analogous to the disproportionation of vanadium trichloride into the di- and tetrachlorides. Vanadium tetrafluoride is one of the few simple fluorides which spontaneously dispropor-
tionates into higher and lower fluorides, although many higher fluorides are known to lose fluorine under the influence of heat or light to achieve a lower oxidation state (23). The thermochemistry of this disproportionation will be discussed in Chapter 7. The spontaneous disproportionation of the tetrafluoride means that all work must be done with freshly prepared tetrafluoride as there is no method available for separating the tri- and tetrafluorides.

Coincident with the disproportionation, vanadium tetrafluoride was found to sublime at 100-120° in vacuum, depositing, in the cold portion of the pyrolysis tube, a dark green solid resembling the product obtained on fluorination of vanadium metal at 200°. The volatility of vanadium tetrafluoride is then between that of vanadium trifluoride, which does not sublime up to red heat (51) and vanadium pentafluoride, which sublimes quite readily at room temperatures and boils at 48° (7). Vanadium tetrafluoride resembles titanium and chromium tetrafluorides which sublime in vacuum between 100° and 250° (51,52) but differs from the tetrafluorides of zirconium and hafnium, which sublime only at red heat (51).

Two determinations of the density of vanadium tetrafluoride under carbon tetrachloride gave an average value of 3.15±0.15 g./cc. which is slightly higher than Ruff and Lickfett's value of 2.975 g./cc. (12), however their value was determined under toluene, which appears to react with vanadium
tetrafluoride. A determination of the density of the present sample of vanadium tetrafluoride under toluene yielded a value of 2.2 g./cc. and the solid changed from a bright green to a dark brown colour when in contact with the toluene.

Vanadium tetrafluoride appears to have a crystal structure unlike that of any of the known tetrafluoride structures. The best agreement with the powder photograph was obtained with a hexagonal unit cell of dimensions $a=5.37$, $c=5.16$ Å, containing two formula units. The X-ray density of 3.28 g./cc. agrees satisfactorily with the average pyknometric density of 3.15 g./cc. Unfortunately a complete structural assignment is not possible because of the uniformly poor quality of the diffraction diagrams. Powder photographs of vanadium tetrafluoride from many sources, for example preparations from (a) vanadium tetrachloride and hydrogen fluoride, (b) vanadium metal and fluorine, both the solid isolated from low temperature fluorination and residues remaining on removal of vanadium pentafluoride from the volatile products of the high temperature fluorination, and (c) sublimed vanadium tetrafluoride, showed exactly the same pattern. The powder pattern showed a number of diffuse lines amongst the sharper lines suggesting that these lines should be split. Poor resolution of the lines above Bragg angles of 45° was characteristic of all photographs and may be due to poor crystallinity. It is however unusual that poor crystallinity should persist throughout all the methods of sample
preparation involving widely different temperatures.

The symmetry of the unit cell indicates that vanadium tetrafluoride is not isostructural with any known tetrafluoride. A large group of tetrafluorides, particularly zirconium and hafnium, and the actinide and lanthanide tetrafluorides crystallise with a monoclinic unit cell, with twelve formula units per unit cell (53). The coordination of the metal atom is not known but it has been suggested that it is greater than six (54). The molecular tetrafluorides, such as silicon and germanium tetrafluorides crystallise with a cubic unit cell in which the tetrahedral molecular units are preserved. Vanadium tetrafluoride is not isostructural with platinum tetrafluoride, which has a distorted uranium tetra-chloride structure (55).

If one uses the volatility of the tetrafluorides as an indication of the degree of molecular association, it is evident that there are three principal classes of volatility, each of which can be correlated with a certain extent of molecular association.

(a) Highly volatile - The molecular tetrafluorides such as silicon tetrafluoride and germanium tetrafluoride, in which the tetrahedral molecular unit is preserved, are highly volatile indicating that the intermolecular association is very weak.

(b) Involatile - The monoclinic tetrafluorides of the zirconium tetrafluoride type are highly involatile, subliming
only at red heat, suggesting a high degree of molecular association (51). A similar sort of involatility is found in vanadium trifluoride which has been shown to have a highly associated structure (22).

(c) Moderate volatility - To this intermediate group belong titanium tetrafluoride (51), chromium tetrafluoride (52), and vanadium tetrafluoride; all of which sublime in the range 100-250° and probably possess an intermediate degree of intermolecular association. Thus the coordination number of the central metal atom is probably between four (as found for SiF₄ etc.) and eight or twelve which is suggested for the zirconium tetrafluoride type (54). This suggests a possible coordination number of six in the moderately volatile tetrafluorides.

A recent study of the heat capacity of titanium tetrafluoride (54) shows that titanium tetrafluoride has a higher heat capacity than zirconium, hafnium or uranium tetrafluorides (54). Within an isostructural series, the heat capacity is expected to increase with the molecular weight, and this expected trend is observed for the isostructural series formed by zirconium, hafnium and uranium tetrafluorides, suggesting that titanium tetrafluoride does not belong in this series (54). The anomalous behaviour of titanium tetrafluoride was attributed to the formation of a structural type intermediate between that of the non-associated silicon tetrafluoride and
the highly associated zirconium tetrafluoride, and the structure proposed by Huckel (51) was favoured (54).

Huckel (51) proposed that titanium tetrafluoride crystallises with an infinite chain type structure of octahedral TiF$_6$ units, joined at four corners to other octahedral units by the sharing of a fluorine atom. Thus four of every six fluorines in the TiF$_6$ octahedra are shared between two titanium atoms, and two would be held by only one titanium atom, leading to a distorted octahedral unit about the titanium atom.

The similar volatilities of titanium tetrafluoride and vanadium tetrafluoride, and the indication that both are not members of the zirconium tetrafluoride structural type, suggests that the structure outlined above for titanium tetrafluoride is equally applicable to vanadium tetrafluoride. Thus vanadium tetrafluoride would be constructed from polymeric chains of VF$_6$ octahedra so that each vanadium would achieve its maximum coordination of six.

Vanadium trifluoride has been shown to contain condensed VF$_6$ octahedral units (22) with each fluorine atom shared by two vanadium atoms. It has also been suggested that vanadium pentafluoride condenses as a polymer or dimer containing hexacoordinate VF$_6$ units, each sharing two fluorines with adjacent octahedra (19,56). Thus the regular increase in volatility of the vanadium fluorides from the trifluoride to the pentafluoride appears to follow the probable order of decreasing molecular condensation.
The volume of the unit cell of a heavy metal fluoride can be approximated to the volume of the fluoride ions, since the metal atoms are relatively small and occupy the interstitial holes between the fluoride ions (57). In the uranium and lanthanum fluorides the volume occupied by each fluoride ion varies only slightly about a mean value of 18Å³; e.g., from 17Å³ in $\text{UF}_5$ and $\text{UF}_9$ to 19Å³ in $\text{UF}_4$ and $\text{UF}_6$ (57). However, this volume is not constant in all fluorides as it depends on the structural type and the extent to which the approximation of a negligible volume for the metal ion applies.

Since the ionic sizes of vanadium ions are considerably less than the sizes of uranium and lanthanide ions of the same valence (58), the approximation of the volume of the unit cell to the volume of the fluoride ions is more justifiable. In vanadium trifluoride, the bimolecular rhombohedral unit cell of dimensions $a = 5.73$ Å, $\alpha = 57.52°$ (22) has a volume of 73.5Å³, or a volume of 12.2Å³ per fluoride ion. This is not much larger than the volume of 11Å³ which is occupied by a sphere with a radius of 1.36Å, the accepted radius of the fluoride ion (11), indicating that the packing in vanadium trifluoride is very efficient. In vanadium tetrafluoride, the bimolecular hexagonal cell, suggested by powder measurements, has a volume of 129Å³, or a volume of 16Å³ per fluoride ion. This increase in the volume occupied per fluoride ion is not unexpected because the decrease in the extent of intermolecular association, which would be necessary to preserve six
coordination about the vanadium, would likely lead to a decrease in the compactness of the structure.

(ii) Chemical Properties of Vanadium Tetrafluoride

Vanadium tetrafluoride is readily oxidised to vanadium pentafluoride by fluorine gas at 100°, and by liquid bromine trifluoride. In the latter case the resulting vanadium pentafluoride could not be separated from the bromine trifluoride, and so the solution was reacted with potassium fluoride to form the potassium hexafluorovanadate (V) salt. The vigorous evolution of bromine during the dissolution of vanadium tetrafluoride in bromine trifluoride was further evidence for oxidation of vanadium which probably proceeds according to the equation:

$$2\text{VF}_4 + \text{BrF}_3 \rightarrow 3\text{VF}_5 + \frac{1}{2}\text{Br}_2$$

Iodine pentafluoride, however, is not a sufficiently strong fluorinating agent to oxidise vanadium tetrafluoride to vanadium pentafluoride. Vanadium tetrafluoride did dissolve slightly in iodine pentafluoride forming a red-brown solution, but when the more volatile iodine pentafluoride was removed, unchanged vanadium tetrafluoride remained.

Liquid nitryl fluoride did not oxidise vanadium tetrafluoride even when they were kept in contact for two months at -78°. No evidence for formation of a nitronium salt, such as \((\text{NO}_2)_2\text{VF}_6\), was observed, which may have been due to the insolubility of vanadium tetrafluoride in nitryl fluoride. Accordingly an attempt was made to prepare the nitronium salt,
by using iodine pentafluoride as a solvent, however when nitryl fluoride was mixed with an iodine pentafluoride solution of vanadium tetrafluoride a gas, presumably NO₂, was evolved and the nitronium salt of vanadium pentafluoride (59), NO₂VF₆, was obtained. There is no evidence to suggest that iodine pentafluoride was the oxidising agent or that the tetrafluoride was merely disproportionating to the tri- and pentafluorides, therefore nitryl fluoride must be regarded as the oxidising agent. Thus, in the presence of iodine pentafluoride, nitryl fluoride oxidised vanadium tetrafluoride according to the equation:

\[ \text{NO}_2\text{F} + \text{VF}_4 \rightarrow \text{VF}_5 + \text{NO}_2 \]

which was then followed by salt formation between excess nitryl fluoride and vanadium pentafluoride:

\[ \text{NO}_2\text{F} + \text{VF}_5 \rightarrow (\text{NO}_2)\text{VF}_6. \]

Since the reaction occurs only in the presence of the solvent (iodine pentafluoride) the mechanism may involve the formation of ionic species.

A comparison of the relative fluorinating powers of vanadium pentafluoride and vanadium tetrafluoride results from a consideration of the behaviour of these fluorides with sulphur dioxide and sulphur trioxide. Vanadium pentafluoride readily fluorinates both sulphur dioxide and sulphur trioxide (8) forming thionyl fluoride from the former and pyrosulphuryl fluoride from the latter, according to the equations:
\[ \text{VF}_5 + \text{SO}_2 \rightarrow \text{VOF}_3 + \text{SOF}_2 \]

\[ \text{VF}_5 + 2\text{SO}_3 \rightarrow \text{VOF}_3 + \text{S}_2\text{O}_5\text{F}_2 \]

Vanadium tetrafluoride does not react with either \text{SO}_2 or \text{SO}_3 illustrating that it is not an effective fluorinating agent for sulphur oxides. It has been suggested that the fluorination of sulphur dioxide and trioxide with vanadium pentafluoride involves the proposed autoionisation of \text{VF}_5 (8), in that the reaction proceeds through the formation of intermediate ionic complexes, such as \text{SO(VF}_6\text{)}_2 and \text{(VF}_4\text{)}_2\text{SO}_3 in the case of sulphur dioxide, and the fluorosulphonate, \text{VF}_3(\text{SO}_3\text{F}), in the case of sulphur trioxide. Vanadium tetrafluoride does not react because it does not dissolve in sulphur dioxide or sulphur trioxide to form the requisite complex intermediates. Of course, heating vanadium tetrafluoride in contact with sulphur dioxide or sulphur trioxide would result in the evolution of vanadium pentafluoride which would then react according to the above reactions. Vanadium tetrafluoride could thus function as a fluorinating agent in that it can be induced to supply the pentafluoride, the rate controlling factor being the rate of evolution of vanadium pentafluoride.

Vanadium tetrafluoride readily forms 1:1 complexes with ammonia and pyridine. Amminotetrafluorovanadium (IV) and pyridinetetrafluorovanadium (IV) were previously obtained (60) from the reaction of vanadium pentafluoride with ammonia and pyridine respectively. These complexes, which are probably electron donor-acceptor complexes, resemble the 1:1 complexes
of metal tetrafluorides, such as titanium, zirconium, silicon and molybdenum tetrafluorides, with pyridine or trimethyl amine, reported by Muetterties (61).

The 1:1 complexes obtained by Muetterties were solids, without sharp melting points. They were insoluble in polar non-protonic solvents and were readily decomposed by protonic solvents such as water. These properties suggested that the 1:1 tetrafluoride-base complexes were polymeric rather than monomeric pentacoordinate species and it was suggested (61) that polymerisation occurred through the formation of fluorine bridge bonds. The 1:1 ammonia or pyridine complexes with vanadium tetrafluoride are also non-melting, insoluble solids which are decomposed by water (60), suggesting that these complexes are fluorine bridged polymers, similar to those obtained by Muetterties (61). In these fluorine bridged polymers, vanadium is at least six coordinate.

It has been previously suggested (56) that reduction of vanadium pentafluoride by ammonia and pyridine to form 1:1 tetrafluoride-base adducts occurs because of the instability of coordination numbers greater than six for vanadium, but this does not explain why the reaction between vanadium tetrafluoride and the nitrogen bases forms only the 1:1 tetrafluoride-base adducts when many of the tetrafluorides studied by Muetterties (61) formed 1:2 tetrafluoride-base complexes as well as the 1:1 complexes which are similar to those formed
by vanadium tetrafluoride. Comparisons of the behaviour of the vanadium fluorides with the behaviour of the tetrafluorides studied by Muettterties (61) are not particularly valid because Muettterties generally prepared the adducts from solutions of the tetrafluoride, whereas vanadium pentafluoride and tetrafluoride were reacted directly with the base, in which both the fluorides and the reaction products were insoluble.

The reaction of vanadium pentafluoride with a Lewis base probably involves the initial formation of a $V\!F_5^{-}\cdot$Base adduct which is unstable and loses fluoride to form the $V\!F_4^{-}\cdot$Base product. The instability of this pentavalent intermediate suggests that vanadium pentafluoride is the only stable halide compound of pentavalent vanadium. The decomposition of the intermediate adduct is probably aided by the gain in lattice energy accompanying the transformation of a pentavalent, hexacoordinate complex of the type $V\!F_5^{-}\cdot$Base, in which the maximum coordination of vanadium has been satisfied and the complex can only form non-associated, molecular crystals of low lattice energy, to a $V\!F_4^{-}\cdot$Base complex in which association occurs to satisfy the coordination requirements of the vanadium atom and forms a "giant molecule" crystal with a high lattice energy.

The reaction between vanadium tetrafluoride and the base probably results in the formation of a 1:1 base adduct as the initial step. Presuming that vanadium tetrafluoride itself is a fluorine bridge polymer in which vanadium is hexacoordinate, this adduct now contains heptacoordinate vanadium.
To maintain hexacoordination requires only that one bridge bond revert to a normal metal-fluorine bond, leaving the solid as an associated "giant molecule" crystal with a high lattice energy. Further reaction with the base to form a \( \text{VF}_4.2\text{Base} \) complex probably does not occur because to maintain hexacoordinate vanadium this complex must be non-associated. The resulting \( \text{VF}_4.2\text{Base} \) compound can only form molecular crystals which probably have a low lattice energy, thus the reaction:

\[
\text{VF}_4.\text{Base} + \text{Base} \rightarrow \text{VF}_4.2\text{Base}
\]

involves a considerable loss in lattice energy of the solid complex. If the tetrafluoride and its complexes were soluble in the base or a solvent, the mode of reaction would probably be quite different because the loss of lattice energy on breaking down the crystal is compensated by a gain in the solvation energy upon dissolution. The lattice energy loses its importance in the reaction, and it becomes possible to form adducts with two or more base molecules, the product of the reaction depending only on the maximum coordination of the central atom. Since Muetterties formed the tetrafluoride-base complexes in solution, 1:2 complexes as well as 1:1 complexes were formed (61).

Selenium tetrafluoride, but not sulphur tetrafluoride, forms a 1:1 adduct with vanadium tetrafluoride, \( \text{SeF}_4.\text{VF}_4 \). This adduct may be either a 1:1 donor-acceptor adduct analogous to the nitrogen base adducts above; an ionic salt such as \( \text{SeF}_3^+\text{VF}_5^- \) or some equivalent structure; or finally an associated complex in which selenium and vanadium are bonded via fluorine...
bridges. Since selenium and sulphur tetrafluorides do not show any tendency to form donor-acceptor complexes (4), the 1:1 complex of selenium tetrafluoride with vanadium tetrafluoride is probably not a donor-acceptor complex similar to the VF$_4$. Base complexes with the nitrogen bases.

Recent work on the sulphur and selenium tetrafluoride complexes with boron trifluoride, antimony pentafluoride and arsenic pentafluoride (4) suggests that these complexes contain the SF$_3^+$ or SeF$_3^+$ ions. Thus it seems reasonable to formulate the VF$_4$.SeF$_4$ complex as SeF$_3^+$.VF$_5^-$. If this is so it is difficult to understand why the VF$_4$.2SeF$_4$ complex, which can be formulated as (SeF$_3^+$)$_2$.VF$_6^-$, is not formed, particularly when complex salts such as K$_2$.VF$_6$ (15,16,17) are well known whereas VF$_5^-$ salts have not been reported.

Trivalent vanadium readily forms complex salts such as K$_2$.VF$_5^-$, which apparently contain the VF$_5^-$ ion. Therefore it was possible that similar complex salts of tetravalent vanadium (eg. KVF$_5^-$) could be prepared which would confirm the existence of the VF$_5^-$ ion proposed in the SeF$_3^+$.VF$_5^-$ complex. Combination of stoichiometric amounts of potassium fluoride and vanadium tetrafluoride in iodine pentafluoride however, resulted only in the formation of K$_2$.VF$_6^-$ leaving considerable unreacted vanadium tetrafluoride. This indicates that the VF$_5^-$ ion is not too readily formed, but its formation with selenium tetrafluoride may arise from the stabilizing effect of the large SeF$_3^+$ cation. The inability of sulphur tetrafluoride
to complex with vanadium tetrafluoride can be attributed to the lesser stability of the SF$_3^+$ cation (4).

It has been suggested (23) that the pentafluorovanadate ions of trivalent vanadium (VF$_5^{-2}$) are dimeric, achieving hexacoordinate vanadium through the formation of V$_2$F$_{10}^{4-}$ fluorine-bridged species. Similarly the ionic structure of the VF$_4$.SeF$_4$ complex may be based on dimeric anions of the type: V$_2$F$_{10}^{-2}$, associated through the formation of fluorine bridge bonds. The SeF$_3^+$ ions are not associated and act as simple cations in the structure. Certainly a more satisfying picture of the structure of the SeF$_4$.VF$_4$ complex results if fluorine bridge bonding is restricted to the complex vanadium fluoride anion rather than attempting to propose polymeric structures involving fluorine bridges between selenium and vanadium, which maintain hexacoordination about both the vanadium and selenium atoms. The available evidence, however, does not permit the assignment of a definite structure to the complex.

(iii) **The Preparation and Properties of Hexafluorovanadate (IV) Salts**

The apparent solubility of vanadium tetrafluoride in iodine pentafluoride without complex formation or reaction suggested that complex salts of the alkali and alkaline earth metals, containing the VF$_6^{-2}$ ion, could be prepared in this solvent from vanadium tetrafluoride and the requisite alkali or alkaline earth fluoride. Although there is no oxidation of
vanadium tetrafluoride by iodine pentafluoride itself, unfortunately in the presence of alkali metal fluorides, extensive oxidation of the vanadium occurred, as indicated by the presence of considerable amounts of iodine in the products. The salts were mixtures of $M_2VF_6$, $MF_6$ and unreacted alkali metal fluoride. Calcium and barium fluorides did not form complex fluorides, nor did they cause oxidation of the vanadium tetrafluoride, presumably because of their insolvability in iodine pentafluoride.

Attempts to prepare tetravalent hexafluorovanadate salts of potassium and caesium from vanadium tetrafluoride in selenium tetrafluoride were successful only in the case of potassium where the product was pure potassium hexafluorovanadate (IV). The trigonal form of $K_2VF_6$ with the lattice constants $a = 5.68\text{Å}$, $c = 4.66\text{Å}$, was obtained and corresponds to the low temperature form obtained by Liebe, Weise and Klemm (17) from the fluorination of trivalent $K_2VF_5$. The pyknometric density of 2.56 g./cc. does not agree too well with the calculated density of 3.09 g./cc. nor with the value of 2.99 g./cc. obtained by Liebe et al. (17), however only one density measurement was made and errors due to slight hydrolysis of the sample may have been considerable. The magnetic properties of potassium hexafluorovanadate (IV) are discussed in Chapter 5.

Caesium fluoride reacted with vanadium tetrafluoride in selenium tetrafluoride to form an inhomogeneous product containing some hexagonal $Cs_2VF_6$ (previously obtained by Liebe
et. al. (17)) along with impurities, principally trivalent vanadium complexes as indicated by the magnetic moment of 2.5 Bohr magnetons at 295°K.

It is not known why the addition of an alkali metal fluoride to a solution of vanadium tetrafluoride in iodine pentafluoride or selenium tetrafluoride results in varying degrees of oxidation or reduction, particularly in view of the many successful preparations of salts of lower fluorides in these solvents (23, 62). However a consideration of the reaction products indicates that several factors are responsible for this behaviour.

The alkali metal fluorides are bases in the iodine pentafluoride and selenium tetrafluoride solvent systems, that is dissolution of an alkali metal fluoride increases the concentration of the basic anions IF$_6^-$ and SeF$_5^-$ respectively. The solubility of alkali metal fluorides in fluoride solvents will be partially dependent on the fluoride acceptor properties of the neutral solvent molecule; the stronger fluoride acceptors yielding the more concentrated alkali metal fluoride solution. Iodine pentafluoride shows a stronger tendency to form compounds containing its basic ion (IF$_6^-$) than selenium tetrafluoride, which appears to prefer to form its acidic ion SeF$_3^+$ (4) thus iodine pentafluoride can be regarded as the stronger fluoride acceptor. Alkali metal fluorides will thus tend to be more soluble in iodine pentafluoride than in selenium tetrafluoride.
Solubility is also governed by the lattice energies of the solids and solvation energies of the ions. For dissolution to be a feasible process the lattice energy required to dissociate the solid into the constituent ions must be balanced by the gain in energy on solvation of the ions. In general lattice energies and solvation energies increase with decreasing ionic size and increasing ionic charge, although lattice energies generally increase more rapidly than solvation energies (33). For example the increased solvation energies of divalent alkaline earth ions, relative to the alkali metal ions, is not sufficient to compensate the three fold increase in lattice energies of alkaline earth fluorides relative to alkali metal fluorides (32), and so the alkaline earth fluorides are insoluble in the fluoride solvents. Thus complex fluoride salts of alkaline earths can not be prepared in fluoride solvents.

The varying extent of oxidation and reduction observed in the preparation of alkali metal hexafluorovanadate salts in fluoride solvents is probably connected with the difference in solubility of the reactants and products. The decreasing lattice energies from potassium to caesium (32) and the slower decrease in solvation energy from potassium to caesium (33), both of which are due to the increasing ionic size of the metal, results in the solubility of an alkali metal fluoride increasing from potassium to caesium fluoride. A similar increase in solubility from potassium to caesium will probably occur for the $M_2VF_6$ salts as well, thus the concentration of hexafluorovanadate (IV) ion in the fluoride solution will probably
increase from potassium to caesium. Also as selenium tetrafluoride is a poorer solvent for a given metal fluoride than iodine pentafluoride, the solubility of a given metal fluoride or fluorovanadate salt will likely increase on going from the selenium tetrafluoride to the iodine pentafluoride solvent system.

During the preparation of the salts it was observed that considerable solution of the reagents occurred in all systems except with potassium fluoride and vanadium tetrafluoride in selenium tetrafluoride. The above trends predict that a minimum solubility will be found with potassium salts in selenium tetrafluoride, as observed. The appearance of oxidation-reduction reactions appears to be a function of the concentration of hexafluorovanadate ion in solution. This is also in agreement with the apparently greater degree of oxidation in caesium salts relative to the potassium salts in any one solvent.

The extent of the oxidation-reduction reaction probably depends, in addition to the concentration effects outlined above, upon the relative ease of oxidation or reduction of the solvents. The appearance of oxidised salts and iodine in the iodine pentafluoride reactions and reduced salts and probably selenium hexafluoride in the selenium tetrafluoride reactions suggests that iodine pentafluoride is preferably reduced to iodine whereas selenium tetrafluoride is preferably oxidised to selenium hexafluoride by tetravalent vanadium. That is iodine pentafluoride tends to act as an oxidising solvent
whereas selenium tetrafluoride tends to act as a reducing solvent. This effect will influence the relative oxidation potentials of the various oxidation states of vanadium in the fluoride solvents. The stabilities of the different $\text{VF}_6^{-n}$ ions will not have a great effect on the reactions because the relative stabilities of these ions are probably somewhat similar to each other.

It must be noted that these fluoride solvents are not readily oxidised or reduced by vigorous fluorinating agents (for example selenium tetrafluoride is not oxidised by bromine trifluoride (62)) however the action of a transition metal such as vanadium may be markedly different from that of oxidising agents such as bromine trifluoride because of the possibility of catalytic effects with the transition metals.

The successful preparation of $\text{K}_2\text{VF}_6$ (IV) in selenium tetrafluoride was therefore due largely to the insolubility of the reactants and products in the fluoride solvent which prevented attack on the solvent by the hexafluorovanadate (IV) product. However because of the scarcity of quantitative information on the behaviour of the fluoride solvents in the presence of alkali metal and transition metal fluorides, it is almost impossible to predict whether a specific salt can be successfully prepared in a certain solvent.
CHAPTER 5: THE MAGNETIC PROPERTIES OF TETRAVALENT VANADIUM FLUORIDES

The magnetic susceptibilities of the tetravalent vanadium fluorides were found to obey the Curie-Weiss law (63):

\[ \chi'_M = \frac{C}{T+\Theta} \quad (5-1) \]

\( \chi'_M \) denotes the molar susceptibility, corrected for diamagnetic contributions with the values given in Selwood (64). These values were chosen because they provide a set of self-consistent corrections for the diamagnetism of all the ions encountered in this study. \( \Theta \) is the Weiss constant and \( T \) the temperature in °K. In all cases a very high Weiss constant was observed.

Magnetic moments were calculated from the Curie-Weiss law:

\[ \mu_{\text{eff}} = 2.84 \sqrt{\chi'_M (T+\Theta)} \quad (5-2) \]

and the Curie law:

\[ \mu_{\text{eff}} = 2.84 \sqrt{\chi'_M T} \quad (5-3) \]

Both calculations were made because of the dispute concerning the method of calculating the effective magnetic moment. Selwood (64) considers \( \Theta \) to be a significant quantity and that magnetic moments of substances obeying the Curie-Weiss law should be calculated from equation (5-2), thus yielding moments independent of temperature.
Other workers (63) have questioned the validity of the correction for \( \theta \) on the grounds that correction of the moment for deviations of the susceptibility from the Curie law is quite meaningless unless the source of the deviation is known. As this is rarely so, especially in cases where \( \theta \) is large, this correction can not usually be justified. The most frequently observed values of \( \Theta \) (e.g. \( 0^\circ \) to \( 40^\circ \)) are so small that they may be included or neglected in the calculation of the moment with little effect. It is only when \( \Theta \) becomes greater than \( 100^\circ \) that the problem becomes important.

Calculation of the magnetic moment from the Curie law (eqn. 5-3) when the substance obeys the Curie-Weiss law, introduces a temperature dependence into the magnetic moment, consequently if this practice is to be followed, \( \mu_{\text{eff}} \) is significant only at the temperature quoted. Since the effective magnetic moment in paramagnetic compounds can be regarded as the temperature independent contribution to the susceptibility it is probably more justifiable to calculate the moment from the same law as is obeyed by the measured susceptibility, thus following Selwood. However if moments are calculated in this way the errors contributed by \( \theta \), which are fairly large because \( \theta \) is determined by extrapolation, must be recognised and the resulting magnetic moments must always be qualified by the value of \( \theta \) used in their calculation.

Magnetic moments calculated from both the Curie-Weiss and Curie laws, as well as the parameters of the susceptibility
equation (eqn 5-1) are given in Table 4. The results of Liebe, Weise and Klemm (17) are included for comparison and in addition the room temperature moments of NH$_3$·VF$_4$ and Py·VF$_4$ (calculated from the Curie law (eqn. 5-3) are included. The experimental data are given in Tables 19, 21 and 22 in the experimental section, and the experimental data for the M$_2$VF$_6$ salts studied by Liebe, Weise and Klemm will be found in reference (17).

**TABLE 4**

**MAGNETIC PROPERTIES OF TETRAVALENT VANADIUM FLUORIDES**

<table>
<thead>
<tr>
<th>Compound</th>
<th>c (cgs units)</th>
<th>θ (degrees)</th>
<th>μ$_{\text{eff}}$ at 295°K (B.m.)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>VF$_4$</td>
<td>0.5835</td>
<td>198</td>
<td>1.68</td>
<td>2.17</td>
</tr>
<tr>
<td>VF$_4$·SeF$_4$</td>
<td>0.665</td>
<td>133</td>
<td>1.86</td>
<td>2.32°</td>
</tr>
<tr>
<td>K$_2$VF$_6$</td>
<td>0.515</td>
<td>118</td>
<td>1.71</td>
<td>2.05</td>
</tr>
<tr>
<td>NH$_3$·VF$_4$</td>
<td>-</td>
<td>-</td>
<td>1.82</td>
<td>-</td>
</tr>
<tr>
<td>Py·VF$_4$</td>
<td>-</td>
<td>-</td>
<td>1.79</td>
<td>-</td>
</tr>
<tr>
<td>K$_2$VF$_6$</td>
<td>-</td>
<td>78</td>
<td>1.63, 1.73</td>
<td>1.92, 2.01</td>
</tr>
<tr>
<td>Rb$_2$VF$_6$</td>
<td>-</td>
<td>101</td>
<td>1.60, 1.63</td>
<td>1.96, 1.99</td>
</tr>
<tr>
<td>Cs$_2$VF$_6$</td>
<td>-</td>
<td>103</td>
<td>1.62, 1.64</td>
<td>2.03</td>
</tr>
</tbody>
</table>

The agreement of the effective moments of K$_2$VF$_6$ determined in the present investigation with those of Liebe, Weise and Klemm (17) is very good. The difference in the values of θ, 118° in the present work and 78° in Liebe et al.
is largely due to the difference in the straight line chosen to represent the Curie-Weiss law. In the present work, the magnetic susceptibility of $K_2VF_6$ was measured at eight temperatures between $81^\circ$ and $295^\circ$K and all but the $81^\circ$ value coincided with the straight line representing the Curie-Weiss law. The susceptibility at $81^\circ$K was slightly higher than that indicated by this Curie-Weiss law. Liebe et al. measured the susceptibility at only three points in this temperature range and these values agree quite well with the susceptibilities obtained in the present work. The lower value of $\Theta$ obtained by Liebe et al. is due to their inclusion of the susceptibility at $81^\circ$K in their Curie-Weiss law, however the present work has shown that the susceptibility at this temperature is slightly higher than that indicated by the Curie-Weiss law which fits all the other points. The long extrapolation (about $200^\circ$) involved in establishing $\Theta$ magnifies small differences in the susceptibility measurements considerably resulting in this large difference in $\Theta$.

The small increase in the susceptibility of $K_2VF_6$ at $81^\circ$K over that predicted by the Curie-Weiss law obtained in the present work is apparently real, because of the similarity of the measured susceptibilities in both the present work and that of Liebe, Weise and Klemm (17). This increase in susceptibility at $81^\circ$K may indicate the presence of anomalous magnetic behaviour such as antiferromagnetism, however extension of the susceptibility measurements to temperatures somewhat
below 81°K would be necessary to fully establish any deviation from normal paramagnetic behaviour which may be present.

The effective magnetic moments calculated assuming Curie law behaviour (eqn. 5-3) are all fairly close to the spin-only value of 1.73 Bohr magnetons for one electron, tending in general to be low for VF$_4$ and the VF$_6^{-2}$ salts, and high in the VF$_4$ Base and VF$_4$ SeF$_4$ complexes. Correction of the effective moments for the Weiss constant, (eqn. 5-2) yields magnetic moments consistently higher (0.2 to 0.5 Bohr magnetons) than the spin-only value.

The Weiss constants of tetravalent vanadium fluoride compounds have consistently high positive values, the lowest (which is somewhat too low according to the present work) being 78°, observed by Liebe et al. (17) for K$_2$VF$_6$, and the highest 198° for vanadium tetrafluoride.

It is interesting to note that the anomalous θ values are not a function of the d$^1$ electronic configuration of vanadium (IV). Vanadium tetrachloride has a negligible Weiss constant, and a magnetic moment of 1.67 Bohr magnetons, slightly below that expected for one unpaired spin (65). The various vanadyl complexes which have been studied exhibit normal moments for one unpaired spin and have low Weiss constants of the order of 20° to 50° (66). In trivalent vanadium compounds, which have two unpaired electrons, a similar behaviour is observed. Vanadium trichloride has a magnetic moment of 2.74 Bohr magnetons, compared to the spin-only value of 2.83
Bohr magnetons, and a Weiss constant of $35^\circ$ (67), whereas vanadium trifluoride has a Weiss constant of $146^\circ$ and an effective moment of 2.71 Bohr magnetons calculated from the Curie law (eqn. 5-3) and 3.32 Bohr magnetons calculated from the Curie-Weiss law (eqn. 5-2). While all the vanadium compounds have magnetic moments, calculated from the Curie law, slightly lower than the spin-only value, only the fluorides exhibit anomalously high $\theta$ values with a concomitantly large difference between the magnetic moments calculated from the Curie law and Curie-Weiss law. The source of this high $\theta$ value is not known but it is reasonable to attribute this behaviour to intermolecular association, because in solid halides, the greatest amount of intermolecular association is usually found in fluorides.

Van Vleck (69) suggested that the behaviour of $\theta$ indicated that it could arise from two sources. Since $\theta$ is usually smallest for $S$ states having no angular moment, $\theta$ can arise from spin-orbit coupling which contributes angular momentum to the system. Alternatively as $\theta$ is usually smallest in magnetically dilute compounds, the source of $\theta$ could be some form of exchange interaction ("antiferromagnetism") which violates a basic assumption of the theory of paramagnetism; that the magnetic centres are non-interacting. It must be noted that compounds which obey the Curie-Weiss law, which is a paramagnetic susceptibility law, are not true antiferromagnetic compounds but paramagnetic compounds with
possible small interactions of an antiferromagnetic type.

Griffith has shown (70) that there is little basis for differentiating between either source for $\Theta$ from the temperature behaviour of the susceptibility especially if the antiferromagnetic interactions are small (for example when the paramagnetism is influenced but not destroyed) or if the spin-orbit couplings occur between nearly degenerate levels (eg. the splitting is less than the magnitude of the thermal energy $kT$). The magnetic susceptibility ($\chi$) of a system involving antiferromagnetic exchange interactions occurring as pure spin-spin interactions between neighbouring paramagnetic ions, to the first order in $J$ (the interaction constant), is given by (70) the expression:

$$\chi = \frac{N\beta^2}{k(T-J/4k)} \quad (5-4)$$

where $N$ is the Avogadro number, $k$ the Boltzmann constant, $T$ the absolute temperature and $\beta$ the Bohr magneton. This is exactly the form of the Curie-Weiss law (eqn. 5-1) hence $\Theta$ can be attributed to antiferromagnetic interactions.

However the magnetic moment of a spin-orbit coupled $d^1$ system is given by Kotani (71) as:

$$\mu_{\text{eff}}^2 = \frac{8 + (3x-8) e^{-3x/2}}{(2 + e^{-3x/2})} \quad (5-5)$$
where \( x = \frac{\xi}{kT} \) and \( \xi \) is the spin-orbit coupling constant.
If \( \xi \) is approximately as large as \( kT \) and the exponentials are replaced by series expansions to the first power in \( \xi \) only, then substitution of the resulting approximate expression for \( \mu_{\text{eff}}^2 \) into the Curie expression for the magnetic susceptibility (\( \chi \)):

\[
\chi = \frac{N \beta^2 \mu_{\text{eff}}^2}{3kT}
\]

(5-6)
gives an approximate expression for the magnetic susceptibility of a paramagnetic system with spin-orbit interaction;

\[
\chi = \frac{5N \beta^2}{3k(T + 2\frac{\beta^2}{5k})}
\]

(5-7)

All the symbols are as given above. This also has the form of the Curie-Weiss law. Hence antiferromagnetic interactions and spin-orbit interactions lead to the same kind of departures from true paramagnetic behaviour and therefore it is not possible to choose one or the other as being responsible for the high \( \theta \) values.

The magnetic moments of the tetravalent vanadium fluorides, calculated from the Curie-Weiss law (eqn. 5-2) are, of course, independent of temperature, but the magnetic moments calculated from the Curie law (eqn. 5-3) do decrease with decreasing temperature. Kotani (71) has predicted the temperature variation of the magnetic moment that would be expected for a paramagnetic system with spin-orbit interaction.
The decrease in moment with temperature for a d^1 electronic configuration is given by equation (5-5). Assuming the spin-orbit coupling constants of vanadium to be between 200 and 400 cm\(^{-1}\), the usual range for the first period of transition elements, magnetic moments at three representative temperatures have been calculated and are shown in Table 5. For comparison, the magnetic moments of vanadium tetrafluoride, potassium hexafluorovanadate (IV) and the adduct, VF\(_4\)·SeF\(_4\) have been calculated for the same temperatures using the experimental susceptibility equation and the Curie law (eqn. 5-2) and are also shown in Table 5.

### TABLE 5

**COMPARISON OF PREDICTED (71) AND EXPERIMENTAL MAGNETIC MOMENTS (Bohr magnetons)**

<table>
<thead>
<tr>
<th>Predicted moments by Kotani's theory (71)</th>
<th>200 cm(^{-1})</th>
<th>300 cm(^{-1})</th>
<th>400 cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>T°K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>1.77</td>
<td>1.60</td>
<td>1.40</td>
</tr>
<tr>
<td>200</td>
<td>1.60</td>
<td>1.35</td>
<td>1.15</td>
</tr>
<tr>
<td>100</td>
<td>1.15</td>
<td>0.85</td>
<td>0.65</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Experimental moments, from Curie law.</th>
<th>VF(_4)</th>
<th>K(_2)VF(_6)</th>
<th>SeF(_4)·VF(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T°K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>1.68</td>
<td>1.71</td>
<td>1.92</td>
</tr>
<tr>
<td>200</td>
<td>1.54</td>
<td>1.61</td>
<td>1.79</td>
</tr>
<tr>
<td>100</td>
<td>1.25</td>
<td>1.45</td>
<td>1.52</td>
</tr>
</tbody>
</table>
In general the Kotani theory predicts a more rapid decrease with temperature than is observed thus spin-orbit coupling is not solely responsible for the magnetic behaviour. This does not exclude the presence of spin-orbit coupling in systems which also have antiferromagnetic interactions since Kotani's predictions are based on the assumption that no antiferromagnetic exchange interactions occur (71). Because the magnetic behaviour observed in tetravalent vanadium fluorides is not that predicted by Kotani's theory alone it seems reasonable to propose that both inter-ion (antiferromagnetic) and intra-ion (spin-orbit) interactions occur.

The proposed fluorine bridge polymerisation in vanadium tetrafluoride and the 1:1 VF$_4$ complexes provides a readily available means of transmitting antiferromagnetic type interactions between the vanadium atoms. The similarity of the magnetic properties of vanadium trifluoride, which has been shown to have a highly associated, bridge bonded structure (22), to those of vanadium tetrafluoride and its complexes, suggests that the high Weiss constants may be due to exchange interactions involving fluorine bridge bonds.

The magnetic behaviour of the adduct SeF$_4$·VF$_4$ is more consistent with its formulation as (SeF$_3^+$)$_2$(V$_2$F$_{10}^-$) in which the VF$_5^-$ ions have formed a fluorine bridged complex ion with hexacoordinate vanadium, than with the formulation as a fluorine bridged VF$_4$·SeF$_4$ polymer. Exchange interaction between the vanadium atoms in the complex anion, where the
vanadium atoms are linked by fluorine bridges, is more easily visualised than in the bridged polymer, where the interactions between neighbouring vanadium atoms must be transmitted through an F-Se-F bridge.

These high Weiss constants do not necessarily indicate that formation of the fluorine bridge bonds causes antiferromagnetic exchange, because the Weiss constant can also arise from spin-orbit interactions. The sharing of two or four fluorine atoms of each $\text{VF}_6$ or $\text{VF}_5$. Base unit creates two different bond types and leads to a distortion of the octahedral coordination about the vanadium atom. This in turn leads to a splitting of the low lying ($d\pi$) orbitals, and this splitting is likely to be quite small (e.g. less than $kT$) thus creating a situation where spin-orbit coupling can occur to provide Curie-Weiss magnetic susceptibility behaviour.

Thus fluorine bridge bonding can give rise to high Weiss constants through either exchange interaction or through spin-orbit type interactions arising from distortions of the symmetry accompanying the formation of the bridge bonds. These polymeric compounds and complexes can not be regarded as "magnetically dilute", hence the simple theories of paramagnetism are likely inadequate.

It is more difficult to explain the behaviour of the hexafluorovanadate salts because the structures are most likely composed of discrete $\text{VF}_6^{-2}$ units, in which the vanadium atom is hexacoordinate and supposedly magnetically dilute.
The Weiss constants are certainly lower for the VF$_6$ salts, in agreement with the expected trend on magnetic dilution, but they are still much larger than the usually observed Weiss constants. A similar case has been reported by Hargreaves and Peacock (72) for the AMF$_6$ salts of molybdenum, rhenium and tungsten. Large positive values of the Weiss constant (as high as 218°) were observed for the molybdenum and rhenium salts. The tungsten salts were actually antiferromagnetic with Neel points in the range 110-140°K. The magnetic moment did not vary with temperature according to Kotani's predictions and thus the high θ values were attributed to antiferromagnetic interactions. These interactions were proposed for AMoF$_6$ and AReF$_6$ and actually observed in AWF$_6$ salts (72).

Hargreaves and Peacock (72) suggested that the antiferromagnetic interactions occurring between the MF$_6^-$ ions were similar to the antiferromagnetic interactions observed in IrCl$_6$ salts by Griffiths and co-workers (73). These antiferromagnetic interactions were supposed to occur through superexchange interactions involving the formation of M-X-X-M type bridges between the IrCl$_6$ ions, utilizing p orbitals on the bridging atoms as proposed by Anderson (74). The effects observed by Griffith and co-workers (73) are much smaller than observed either here or by Hargreaves and Peacock (72), as the Weiss constant for K$_2$IrCl$_6$ is only 33°.
Since the antiferromagnetic effects observed in oxides, sulphides and selenides decrease in this order (74) that is, following the decrease in electronegativity and the increase in the size of the anion, superexchange appears to increase with increasing ionic character of the bond, and with decreasing separation between exchanging centres as would be expected (74). Antiferromagnetic interactions in halides, would therefore probably increase from iodides to fluorides following the increasing ionic character of the bond and the decreasing size of the bridging ion. Exchange effects are therefore likely to be more important in fluorides than in other halides and this appears to be the case.

Anderson's theory of antiferromagnetism (74) is based on a cubic crystal structure and is not directly applicable to the present complexes or to those of Hargreaves and Peacock (72) which have lower symmetry. Hargreaves and Peacock (72) proposed that small tetragonal distortions have a disproportionately large effect on the antiferromagnetic exchange. Tetragonal distortions are observed in many $\text{AMF}_6$ salts and are quite likely to be found in the molybdenum and rhenium salts (72).

To suggest that specific antiferromagnetic effects arise from these distortions is not necessary, as crystal distortions which might influence antiferromagnetic interactions may also cause spin-orbit couplings, with the same effect on the temperature dependence of the magnetic susceptibility. Tetragonal distortions in these salts will
lead, as before, to a splitting of the lower triplet of d electrons \( (d\epsilon) \) and thus create low-lying (less than \( kT \) above the ground state) non-degenerate orbitals which can be involved in spin-orbit coupling. Tetragonal distortions of this type need not be large to provide a sufficient degree of splitting of the \( d\epsilon \) level for large coupling effects, in fact if the distortions are too large the resultant levels will probably be too greatly separated to be extensively populated by thermal excitation and coupling will not occur to any great extent.

At this time it is only possible to conclude that the observed magnetic properties of the tetravalent vanadium fluorides while considerably different from other \( d^1 \) vanadium compounds are consistent with the effects expected from associations and distortions which probably occur in the fluorides. Since the effects are large, even in the "magnetically dilute" \( \text{VF}_6^{-2} \) salts, it is likely that both exchange interactions and distortion induced spin-orbit couplings are responsible, however it is not possible to separate the two effects.
CHAPTER 6: **INFRARED SPECTRA OF VANADIUM FLUORIDES**

The infrared spectrum of vanadium pentafluoride has been obtained for the region $250 \text{ cm}^{-1}$ to $4000 \text{ cm}^{-1}$. The results are shown in Table 6 and Figure 2. Estimated intensities and such assignments as are possible at this time are also given in Table 6.

Although liquid vanadium pentafluoride is thought to be associated by means of fluorine bridge bonds, the normal vapour density (7) suggests that the pentacoordinate monomer is present in the gas phase. There are however two possible structures for a pentacoordinate molecule; the trigonal bipyramid ($D_{3h}$) or the square pyramidal ($C_{4v}$) structure. The only fluoride known to have the latter structure is bromine pentafluoride (19), however in this case the non-bonded electron pair of the bromine atom is considered to be occupying one coordination site making the coordination about the bromine atom octahedral. Thus bromine pentafluoride has a distorted octahedral rather than a square pyramidal structure.

As there are no non-bonding electrons in vanadium pentafluoride, it is reasonable to suppose that, even if octahedral coordination is achieved in the liquid, the gaseous molecule assumes the trigonal bipyramid structure and thus is isostructural with compounds such as phosphorus pentafluoride and phosphorus pentachloride. The assignment of the infrared spectrum will largely be based on previous assignments of the spectra of phosphorus pentachloride (75), antimony pentachloride...
and antimony pentafluoride (77). Spectra of phosphorus pentafluoride (78) and bromine pentafluoride (79) have been interpreted in terms of a trigonal bipyramid ($D_{3h}$) and a square pyramidal ($C_{4v}$) structure respectively but complete assignments have not been made.

Assuming that vanadium pentafluoride vapour has the trigonal bipyramid ($D_{3h}$) structure, there will be eight fundamental vibrational frequencies; two of symmetry species $a_1'$, two of species $a_2''$, three of species $e'$ and one of species $e''$. The $a_1'$ and $e''$ frequencies are only Raman active, the $a_2''$ only infrared active and the $e'$ is both Raman and infrared active, hence the infrared spectrum will have five fundamental frequencies; two of species $a_2''$ and three of species $e'$.

If the V-F bond distance in vanadium pentafluoride is assumed to be $2.00 \pm 0.1$ Å, the moments of inertia of the molecule, which is a symmetric top, are $I_Z = 380(\pm 40) \times 10^{-40}$ and $I_X = I_Y = 440(\pm 80) \times 10^{-40}$ g cm$^2$ where $I_Z$ is the moment of inertia along the Z axis (the $C_3$ axis of the molecule) and $I_X$ and $I_Y$ are moments about the $C_2$ axes, lying in the XY plane. Following the correlation of band shape with moments of inertia by Badger and Zumwalt (80), which has been applied to a trigonal bipyramid molecule by Wilmshurst (76), the parallel $a_2''$ bands should have a weak Q branch with strong PR branches. The PR branch separation, which is governed by the $I_X$ and $I_Y$ moments of inertia, (81) should be about $18 \pm 4$ cm$^{-1}$. The perpendicular $e'$ bands will have a strong Q branch and weak
### TABLE 6

**INFRARED SPECTRUM OF VANADIUM PENTAFLUORIDE VAPOR**

<table>
<thead>
<tr>
<th>Wavenumber</th>
<th>Approximate Intensity</th>
<th>Assignment and Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>271</td>
<td>1.1</td>
<td>$e'$ fundamental $\text{VF}_3$ in plane bend.</td>
</tr>
<tr>
<td>274</td>
<td>1.3</td>
<td>$e'$ fundamental $\text{VF}_2$ linear bend.</td>
</tr>
<tr>
<td>287</td>
<td>1.9</td>
<td>$e'$ fundamental $\text{VF}_3$ in plane bend.</td>
</tr>
<tr>
<td>293</td>
<td>3.1</td>
<td>$e'$ fundamental $\text{VF}_2$ linear bend.</td>
</tr>
<tr>
<td>320</td>
<td>2.5</td>
<td>$a''$ fundamental $\text{VF}_3$ out of plane bend.</td>
</tr>
<tr>
<td>326</td>
<td>sh ?</td>
<td></td>
</tr>
<tr>
<td>332</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>339</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>343</td>
<td>sh ?</td>
<td></td>
</tr>
<tr>
<td>351</td>
<td>sh ?</td>
<td></td>
</tr>
<tr>
<td>775</td>
<td></td>
<td></td>
</tr>
<tr>
<td>784</td>
<td>100</td>
<td>$e''$ fundamental and $a_2$ fundamental $\text{VF}_3$ out of plane bend.</td>
</tr>
<tr>
<td>791</td>
<td></td>
<td></td>
</tr>
<tr>
<td>810</td>
<td></td>
<td></td>
</tr>
<tr>
<td>880</td>
<td>sh</td>
<td></td>
</tr>
<tr>
<td>887</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>890</td>
<td></td>
<td></td>
</tr>
<tr>
<td>930</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>995</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>1060</td>
<td>0.6</td>
<td>$784+273=1057$</td>
</tr>
<tr>
<td>1385</td>
<td>3.0</td>
<td>$784+273=1057$</td>
</tr>
<tr>
<td>1417</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>1497</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>1520</td>
<td>sh.</td>
<td></td>
</tr>
<tr>
<td>1615</td>
<td>broad.</td>
<td>0.8</td>
</tr>
</tbody>
</table>

sh. = shoulder

$F'$ indicates axial and F indicates equatorial fluorine atoms respectively.
FIG. 2

INFRARED SPECTRA OF VANADIUM FLUORIDES

(a) $\text{VF}_5$ 250-400 cm$^{-1}$
(VAPOR, $\sim 100$ mm)

(b) $\text{VF}_5$ 700-1700 cm$^{-1}$
(VAPOR, $\sim 100$ mm)

(c) $\text{VF}_4$ 400-1100 cm$^{-1}$
(SOLID, MULL)

(d) $\text{VF}_3$ 400-1100 cm$^{-1}$
(SOLID, MULL)

WAVENUMBER (cm$^{-1}$)

ABSORPTION (%)
The most prominent bands in the spectra of trigonal bipyramid molecules are the two antisymmetric stretch frequencies, one each of $a_2^\prime$ and $e'$ symmetry. These bands, which are the antisymmetric stretch frequencies of the axial atoms and equatorial atoms respectively, are generally observed in the range $400-1000 \text{ cm}^{-1}$ in halides. The $a_2^\prime$ bands usually show a parallel structure and the $e'$ band a perpendicular structure as expected. The separation of the two bands is $75 \text{ cm}^{-1}$ in phosphorus pentafluoride (78), $127 \text{ cm}^{-1}$ in phosphorus pentachloride (75) and $14 \text{ cm}^{-1}$ in antimony pentachloride (76). Only one strong absorption band was observed for vanadium pentafluoride in the range 400 to 2000 cm$^{-1}$, and it is quite possible that the odd structure of this band (see Figure 2b), which looks like an unsymmetrical PQR band, is due to coincidence of the two antisymmetric stretch frequencies. The 775 and 791 cm$^{-1}$ peaks, separated by $16 \text{ cm}^{-1}$, are probably the PR branches of the parallel $a_2^\prime$ frequency (with the weak Q branch having a frequency of $783 \text{ cm}^{-1}$) and the peak at $784 \text{ cm}^{-1}$ is probably a combination of the strong Q branch of the perpendicular $e'$ band and the weak Q branch of the $a_2^\prime$ band; thus the antisymmetric frequencies are degenerate.

The three remaining strong frequencies at 271-4, 288-94, and at $332 \text{ cm}^{-1}$ are probably the other three infrared active fundamentals. The PQR structure of the $332 \text{ cm}^{-1}$ band, with PR separation of approximately $19 \text{ cm}^{-1}$ ($339-320 \text{ cm}^{-1}$) suggests that this is the second $a_2^\prime$ frequency (the VF$_3$ out of plane
bending). The remaining two strong frequencies are probably the \( e', VF_2 \) linear bending and the \( e', VF_3 \) in plane bending frequencies.

Few combination bands can be deduced from this infrared spectrum, and those that have been tentatively assigned are shown. Other assignments of the observed infrared fundamentals do not lead to any better agreement with the observed spectrum, nor does an assignment based on the less likely square pyramidal model. It is possible that one or more of the \( e' \) fundamentals which have been assigned to the lowest frequency peaks may be below the lower limit of the instrument and have not been observed. The three fundamentals which are only Raman active are unknown and these will also be involved in forming infrared active combination bands. One of these, the \( e'' \) frequency will likely be found in the range 300-400 cm\(^{-1}\) and the two \( \alpha \) frequencies (the symmetric stretching frequencies of axial and equatorial fluorines) will probably occur between 500 and 800 cm\(^{-1}\), by analogy with similar pentahalides. Until the Raman spectrum of vanadium pentafluoride is available, no further assignments can be made.

As it was not possible to measure the infrared spectrum of the liquid due to the reactivity of the cell window materials required to investigate the regions of interest, no comparison between liquid and vapour is available. Such a comparison could perhaps lead to further information about the association of vanadium pentafluoride in the liquid state.
The infrared spectra of vanadium trifluoride and vanadium tetrafluoride were also measured over the range 400 to 4000 cm\(^{-1}\) as mulls in Nujol, and the results are shown in Table 7 and Figure 2. Since these compounds are solids, broader peaks and less detailed spectra were obtained.

**Table 7**

**Infrared Spectra of Vanadium Trifluoride and Tetrafluoride**

<table>
<thead>
<tr>
<th><strong>VF(_3)</strong></th>
<th><strong>VF(_4)</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>1060 br. w.</td>
<td>1025 br. w</td>
</tr>
<tr>
<td>970,940 doublet, w.</td>
<td>837 s.</td>
</tr>
<tr>
<td>890 vw.</td>
<td>780 s.</td>
</tr>
<tr>
<td>540±20 s.br.</td>
<td>530±20 s.br.</td>
</tr>
</tbody>
</table>

s = strong, w = weak, vw = very weak, br = broad.

While both \(\text{VF}_3\) and \(\text{VF}_4\) have a strong broad band of somewhat similar shape at approximately 530 cm\(^{-1}\), the remainder of the spectrum is markedly different. With \(\text{VF}_3\) only a few weak bands are observed from 600 to 4000 cm\(^{-1}\), whereas vanadium tetrafluoride shows a strong doublet band at 780-837 cm\(^{-1}\). The difference in spectra may be due to the difference in the structure of the solid.

Vanadium trifluoride has a structure (22) in which each vanadium atom is coordinated by six fluorine atoms forming a nearly regular octahedron. A species with octahedral \((O_h)\) symmetry has two infrared active fundamentals (triply degenerate \(F_{\text{lu}}\) species) which are associated with the anti-
symmetric vibration frequencies. The larger value is usually denoted $v_3$ and the smaller, $v_4$. The broad band at 540 cm$^{-1}$ is probably the $v_3$ frequency, and thus similar to the value of 511 observed in $K_3VF_6$ (82). The lower frequency, $v_4$, is probably below the observed region as suggested by Peacock and Sharp (82).

If vanadium tetrafluoride exhibited regular octahedral symmetry about the vanadium, the infrared spectrum of vanadium tetrafluoride would be expected to be very similar to that of vanadium trifluoride, perhaps showing only a slight increase in the value of $v_3$ paralleling the change in $v_3$ from 511 cm$^{-1}$ in $K_3VF_6$ to 583 cm$^{-1}$ in $K_2VF_6$ (82). However the infrared spectrum of vanadium tetrafluoride has, in addition to a broad strong band similar to the $v_3$ band in vanadium trifluoride, a strong double band at 780 and 837 cm$^{-1}$ suggesting that the solid structure is not the same in the two fluorides.

It was suggested earlier that vanadium tetrafluoride has an associated structure in which four fluorines of the $VF_6$ octahedral unit are shared with adjacent octahedra (e.g. as fluorine bridge bonds) and two are unshared, probably leading to four short vanadium-fluorine bonds and two long bonds in the octahedron or vice versa. The symmetry about the vanadium is therefore tetragonal rather than octahedral. A molecule of tetragonal symmetry ($D_{4h}$) has three infrared active fundamentals (doubly degenerate $E_u$ species) rather than the two triply degenerate infrared active fundamentals of the octahedral molecule.
Assuming that small changes in symmetry such as this will not cause large shifts in the vibrational frequencies (e.g., the shifts are probably less than 100 cm$^{-1}$), the sudden appearance of the 780-837 cm$^{-1}$ band in vanadium tetrafluoride is probably due to activation of a previously inactive infrared band because of the lower symmetry of the VF$_6$ unit in vanadium tetrafluoride relative to that in vanadium trifluoride. The strong broad band at 540 cm$^{-1}$ in vanadium tetrafluoride probably corresponds to the 583 cm$^{-1}$ band observed in K$_2$VF$_6$ (82) and the third fundamental is probably below 400 cm$^{-1}$ as before.

The reason for the doublet structure (see Figure 2c) of the 780-837 cm$^{-1}$ band is not known. The two peaks are not identical, the 780 cm$^{-1}$ band being much sharper than the 837 cm$^{-1}$ band. It is possible that the degenerate vibration is split by crystal forces and differences in bonding and that the two bands are associated with non-bridge and bridge fluorines. A complete analysis of the vibrational spectrum requires a Raman spectrum but because VF$_4$ is a solid the measurement of the Raman spectrum would likely be difficult.
CHAPTER 7: THE THERMOCHEMISTRY OF VANADIUM FLUORIDES

(i) The Standard Heat of Formation of Vanadium Tetrafluoride

Vanadium tetrafluoride was dissolved in distilled water in a calorimeter, probably according to the reaction:

\[ \text{VF}_4(\text{c}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{V}^{0+2}(\text{aq}) + 4\text{F}^- (\text{aq}) + 2\text{H}^+(\text{aq}) \]

and the average heat evolved during this hydrolysis \( (H_a) \), calculated from the experimental data given in Table 24, was \(-27.5 \pm 0.5\) kcal/mole. The thermochemical cycle for the heat of formation was completed by combining reaction (a) with the following reactions:

\[ \text{(b)} \text{V}^{0+2}(\text{aq}) + 2\text{H}^+(\text{aq}) + 4\text{Cl}^- (\text{aq}) \leftrightarrow \text{VCl}_4(\text{l}) + \text{H}_2\text{O}(\text{l}) \]

\[ \text{(c)} \text{VCl}_4(\text{l}) \leftrightarrow \text{V}(\text{c}) + 2\text{Cl}_2(\text{g}) \]

\[ \text{(d)} 2\text{Cl}_2(\text{g}) \rightarrow 4\text{Cl}^- (\text{aq}) \]

\[ \text{(e)} 4\text{F}^- (\text{aq}) \leftrightarrow 2\text{F}_2(\text{g}) \]

Adding reactions (a) to (e) together results in reaction (g),

\[ \text{(g)} \text{VF}_4(\text{s}) \leftrightarrow \text{V}(\text{c}) + 2\text{F}_2(\text{g}) \]

which is the reverse of the formation reaction of vanadium tetrafluoride. The heat of reaction (g) is the negative of the standard heat of formation of vanadium tetrafluoride, and is given by:

\[ H_g = -\Delta H_f(\text{VF}_4) = H_a + H_b + H_c + H_d + H_e \]

The necessary data for the calculation and the resulting heat of formation of vanadium tetrafluoride are given in Table 8.
The experimental heats of hydrolysis of vanadium tetrafluoride (reaction (a)) and vanadium tetrachloride (reaction (b)) were measured at 298°K. All the other values are also those given (83) at 298°K.

**TABLE 8**

HEAT OF FORMATION OF VANADIUM TETRAFLUORIDE

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Description</th>
<th>Numerical Values</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_a</td>
<td>heat of hydrolysis of VF₄</td>
<td>-27.5 kcal/mole</td>
<td>Present work (Table 24)</td>
</tr>
<tr>
<td>H_b</td>
<td>-(heat of hydrolysis of VCl₄)</td>
<td>-(-68.6) kcal/mole</td>
<td>Present work (Table 26)</td>
</tr>
<tr>
<td>H_c</td>
<td>-ΔHᵦ₀(VCl₄)</td>
<td>-136.2 kcal/mole</td>
<td>84</td>
</tr>
<tr>
<td>H_d</td>
<td>4ΔHᵦ₀Cl⁻(aq)</td>
<td>4(-160.1) kcal/mole</td>
<td>83</td>
</tr>
<tr>
<td>H_e</td>
<td>4ΔHᵦ₀F⁻(aq)</td>
<td>-4(-78.66) kcal/mole</td>
<td></td>
</tr>
</tbody>
</table>

Therefore: \( H_g = -\Delta H_\text{f₀}(VF_4) = 331.8 \text{ kcal/mole}. \)

The standard heats of formation at 298°K of the ions are the values for each ion at infinite dilution. The error arising from this approximation is no greater than 0.1 kcal./mole and is not significant in this study. The only errors estimated are those arising from the experimental heats of hydrolysis, which are approximately ±0.5 kcal./mole for the heat of hydrolysis of vanadium tetrafluoride and ±1 kcal./mole for vanadium tetrachloride, giving an overall error of ±1.5 kcal./mole. Therefore the standard heat of formation of vanadium tetrafluoride is

\[
\Delta H_\text{f₀}(VF_4) = -332 \pm 1.5 \text{ kcal./mole.}
\]
Reaction (b) was the most feasible method of completing the thermochemical cycle, because it simplifies the assumption of the form in which the vanadium (IV) exists in the solution. Using reaction (b) it is only necessary to assume that vanadium tetrafluoride and vanadium tetrachloride hydrolyse to the same cationic species under similar conditions, rather than specifically assuming that vanadium tetrafluoride hydrolyses to VO$^{+2}$. However, the heat of reaction (b) was not available in the literature; the determination of the heat of formation of vanadium of vanadium tetrachloride by Ruff and Freidrich (85) from the heat of hydrolysis is not applicable because they hydrolysed VCl$_4$ in an alkaline peroxide solution, essentially measuring the heat of the reaction:

$$\text{VCl}_4(1) + \frac{9}{2}\text{OH}^-(\text{aq}) + \frac{1}{2}\text{O}_2\text{H}^-(\text{aq}) \rightarrow \text{VO}_3^-(\text{aq}) + \frac{5}{2}\text{H}_2\text{O} + 4\text{Cl}^-\text{(aq)}$$

which is a combination of the heat of hydrolysis of vanadium tetrachloride, neutralization of the evolved acid and the heat of oxidation of V(IV) to V(V) in aqueous solution.

Alternatively, the standard heat of formation of the aqueous vanadyl ion (VO$^{+2}$) could have been estimated from the standard free energy of formation which has been determined from electrochemical cell potential measurements (95). The uncertainties introduced by this approximation however could have been as large as 20 kcal/mole in the final heat of formation of vanadium tetrafluoride, so to avoid introducing
unnecessary approximations, the heat of hydrolysis of vanadium tetrachloride (reaction (b)) was also determined. The average heat of hydrolysis of vanadium tetrachloride, under similar conditions to those used in the hydrolysis of vanadium tetrafluoride, was \(-68.8 \pm 1.0\) kcal./mole (Table 26). The hydrolysis of vanadium tetrachloride is further discussed in Appendix 1, where it is shown that the standard heat of formation of \(\text{VO}^{+2}(\text{aq})\) is \(-113\) kcal./mole. Thus the approximation of \(\Delta F^\circ_\text{f} (\text{VO}^{+2}(\text{aq})) (-109\) kcal./mole) to \(\Delta H^\circ_\text{f} (\text{VO}^{+2}(\text{aq}))\) in order to calculate the heat of formation of vanadium tetrafluoride would have introduced an error of 4 kcal./mole, instead of the 20 kcal./mole estimated.

(ii) The Standard Heat of Formation of Vanadium Pentafluoride

Vanadium pentafluoride was hydrolysed in dilute alkali, probably according to the reaction:

\[
\text{(a) VF}_5(1) + 6\text{OH}^- (\text{aq}) \rightarrow \text{VO}_3^- (\text{aq}) + 3\text{H}_2\text{O}(1) + 5\text{F}^- (\text{aq})
\]

The average heat of hydrolysis of vanadium pentafluoride \((H_a)\), calculated from the experimental data in Table 25 is \(-141 \pm 3\) kcal./mole. The thermochemical cycle for the heat of formation of vanadium pentafluoride was completed by combining reaction (a) with reactions (b) to (e) inclusive:

\[
\begin{align*}
\text{(b) } \text{VO}_3^- (\text{aq}) & \quad \leftrightarrow \quad \text{V(c)} + 3/2 \text{O}_2(g) \\
\text{(c) } 3\text{H}_2(g) + 3\text{O}_2(g) & \quad \rightarrow \quad 6\text{OH}^- (\text{aq}) \\
\text{(d) } 3\text{H}_2\text{O}(1) & \quad \leftrightarrow \quad 3\text{H}_2(g) + 3/2 \text{O}_2(g) \\
\text{(e) } 5\text{F}^- (\text{aq}) & \quad \leftrightarrow \quad 5/2 \text{F}_2(g)
\end{align*}
\]
The addition of reactions (a) to (e) together results in reaction (g), which is the reverse of the standard formation reaction of vanadium pentafluoride:

\[(g) \text{VF}_5(l) \rightleftharpoons \text{V}(c) + \frac{5}{2} \text{F}_2(g)\]

The heat of reaction (g), which is the negative of the standard heat of formation of vanadium pentafluoride is given by the sum of the heats of reactions (a) to (e) inclusive, that is:

\[H_g = -\Delta H_f(\text{VF}_5(l)) = H_a + H_b + H_c + H_d + H_e.\]

The data necessary for the calculation of the standard heat of formation of vanadium pentafluoride are given in Table 9.

**TABLE 9**

**HEAT OF FORMATION OF VANADIUM PENTAFLUORIDE**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Description</th>
<th>Numerical Values</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_a</td>
<td>heat of hydrolysis of VF₅</td>
<td>-141 kcal./mole</td>
<td>Present work. (Table 25)</td>
</tr>
<tr>
<td>H_b</td>
<td>$-\Delta H_f(\text{VO}_3^{aq})$</td>
<td>$-(-224.5)$ kcal./mole</td>
<td>224.5</td>
</tr>
<tr>
<td>H_c</td>
<td>6$\Delta H_f(\text{OH}^-^{aq})$</td>
<td>$6(-54.96)$ kcal./mole</td>
<td>-329.8</td>
</tr>
<tr>
<td>H_d</td>
<td>$-3\Delta H_f(\text{H}_2\text{O}(l))$</td>
<td>$-3(-68.32)$ kcal./mole</td>
<td>204.96</td>
</tr>
<tr>
<td>H_e</td>
<td>$-5\Delta H_f(\text{F}^-^{aq})$</td>
<td>$-5(-78.66)$ kcal./mole</td>
<td>393.3</td>
</tr>
</tbody>
</table>

Therefore: \[H_g = -\Delta H_f(\text{VF}_5(l)) = 351.9 \text{ kcal./mole.}\]

No error is calculated for the standard values used in the thermochemical cycle. All heat values used are those given for 298°K as before and the standard heat of formation of each ion is the given heat of formation of the ion at infinite
dilution (83). The error contributed by this approximation is negligible amounting to no more than 0.1 kcal./mole. The only error estimated is that arising from the experimental heat of hydrolysis which is probably about \( \pm 3 \) kcal./mole. Therefore the standard heat of formation of vanadium pentafluoride at \( 298^\circ K \) is:

\[
\Delta H_f(\text{VF}_5(l)) = -352 \pm 3 \text{ kcal./mole}
\]

(iii) **Theoretical Estimation of Heats of Formation from Lattice Energies**

The Born-Haber cycle relates the thermodynamic properties of a crystalline compound to the thermodynamic properties of its constituent elements. The component enthalpies of a fluoride, \( \text{MF}_n \), are shown below in the familiar graphical representation (32).

\[
\begin{align*}
\text{MF}_n(c) & \quad \xrightarrow{U} \quad \text{M}^{+n}(g) + n\text{F}^{-}(g) \\
\Delta H_f(\text{MF}_n) & \quad \downarrow \quad \downarrow \\
\text{M}(s) + n/2 \text{F}_2(g) & \quad \xleftarrow{(-L - nD/2)} \quad \text{M}(g) + \text{F}(g)
\end{align*}
\]

where: \( U \) is the lattice energy of \( \text{MF}_n \). Strictly, at \( 298^\circ K \) the lattice enthalpy \( (U + (n+1)RT) \) should be used, however for the higher fluorides at \( 298^\circ K \) the difference in lattice energy and enthalpy is about 1 part in 1000
and much smaller than the errors in estimating $U$ itself. All the remaining values are those given for $298^\circ K$.

$I_1$ represents the successive ionization potentials of the metal $M$.

$E$ is the electron affinity of fluorine.

$L$ is the enthalpy of sublimation of the metal.

$D$ is the enthalpy of dissociation of fluorine.

$\Delta H_{fo}(MF_n)$ is the heat of formation of $MF_n$ from its elements.

As the sum of all terms in the cycle must be zero, the heat of formation is given by:

$$\Delta H_{fo}(MF_n) = \sum I_1 + L - n(E - D/2) - U. \quad (7-1)$$

Since all the quantities on the right hand side of equation (7-1) except the lattice energy ($U$) are readily available in thermodynamic tables, the problem of calculating the heat of formation becomes one of evaluating the lattice energy.

Exact lattice energy calculations are lengthy and rather involved, however sufficient accuracy for the present purposes may be obtained with the simple formula of Born and Mayer (32) which considers only the coulombic forces and the nearest neighbour repulsive forces within the crystal. The lattice energy ($U$) is given (32) by:

$$U = \frac{N M Z A Z C e^2}{r_o} \left[ 1 - \frac{b}{r_o} \right] \quad (7-2)$$
where: $M$ is the Madelung constant,

$N$ is the Avogadro number,

$Z_A$ and $Z_C$ are the anionic and cationic charges respectively,

$r_o$ is the internuclear separation,

e is the electronic charge,

and $b$ is the interionic repulsion constant.

The Madelung constant is a function of the crystal structure and its calculation requires a detailed knowledge of the crystal structure. Furthermore the difficulty of the calculation increases with decreasing crystal symmetry. Further simplification is achieved by replacing (32) the Madelung constant ($M$), which is proportional to the number of ions in a molecule, by a constant ($\alpha$) which is the "Madelung constant per ion" and is given by:

$$\alpha = \frac{2M}{v}$$ (7-3)

where $v$ is the number of ions in a formula unit.

The lattice energy is then given (32) by:

$$U = \frac{N\alpha v Z_A Z_C e^2}{2r_o^2} \left[ 1 - \frac{b}{r_o} \right]$$ (7-4)

where all symbols are the same as given above.

Although the "Madelung constant per ion" ($\alpha$) is not identical for different lattice types, changes in $\alpha$ with lattice type are proportional to the internuclear separation of the ions (32). According to Kapustinskii, every crystal
can be represented by a sodium chloride lattice with suitable modifications to the coefficients $\alpha$ and $r_o$ without change in lattice energy (86). The lattice energy can therefore be calculated by assuming $\alpha = 1.754$, the value for the sodium chloride lattice, and that $r_o = r_A + r_C$, the sum of the ionic radii (in Angstrom units) for six coordination of the ions; the coordination found in sodium chloride. Making these substitutions and taking $b = 0.345$, and $Ne^2 = 329.7$ kcal./mole, the Kapustinskii formula (32, 86) is obtained:

$$U = \frac{287.2 vZ_A Z_B}{r_A + r_C} \left[ 1 - \frac{0.345}{r_A + r_C} \right]$$

(7-5)

The lattice energy of a crystal ($U$) can therefore be calculated from only the ionic radii of the ions ($r_A$ and $r_C$). As before, $v$ is the number of ions in a formula unit and $Z_A$ and $Z_B$ are the anionic and cationic charges respectively.

Lattice energies resulting from the Kapustinskii formula are not as exact as those obtained by elaborate calculations (32) however the formula readily gives useful estimates of lattice energies where exact calculations are often difficult or impossible. Lattice energies were estimated from the Kapustinskii formula (eqn. 7-5) for a series of tri- and tetrafluorides of the first long period transition metals and the highest fluorides of two transition metals of the second long period, zirconium and niobium. These lattice energies were used in equation (7-3) to calculate the heats of formation of the fluorides.
The ionic radii of the metals chosen for the calculations were Pauling's crystal radii (58) which form a self-consistent set of six coordinate radii for all possible valencies of a metal ion and yield closer agreement with measured interatomic distances in the fluorides. Where such radii were not available (eg. for iron and cobalt) empirical ionic radii (Pauling, (58)) or estimated ionic radii were used. These radii are in general larger than crystal radii and yield lower values of the lattice energy and hence of the heat of formation ($\Delta H_{fo}$). The actual values used are shown in Table 10. The radius of fluoride was taken as 1.36 Å(11). The resulting lattice energies of the tri- and tetrafluorides of the first long period elements from titanium to cobalt, of zirconium tetrafluoride and niobium pentafluoride are shown in Table 11.

Using the calculated lattice energies and the thermochemical data given in Table 10, the standard heats of formation were calculated for the same fluorides as above. The results are shown in Table 11 along with the available experimental heats of formation of these fluorides.

Where the ionic radii were extremely uncertain, that is for Mn$^{+4}$, Fe$^{+4}$ and Co$^{+4}$, upper and lower limits were assigned to the radii and the two values given for each lattice energy and heat of formation represent the extreme values of these quantities for the range of ionic radius.
<table>
<thead>
<tr>
<th>Element</th>
<th>Latent heat of subl. (87) (L) (kcal./mole)</th>
<th>Ionisation Potentials (88) ( (I_n, n = \text{valence of ion}) ) (kcal./mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>112</td>
<td>147 314 649 997</td>
</tr>
<tr>
<td>V</td>
<td>122</td>
<td>155 327 685 1106</td>
</tr>
<tr>
<td>Cr</td>
<td>94</td>
<td>156 380 713 1143</td>
</tr>
<tr>
<td>Mn</td>
<td>68</td>
<td>171 360 777 1199</td>
</tr>
<tr>
<td>Fe</td>
<td>99</td>
<td>182 373 706 1153</td>
</tr>
<tr>
<td>Co</td>
<td>102</td>
<td>182 392 772 (1153)(^a)</td>
</tr>
<tr>
<td>Zr</td>
<td>125</td>
<td>160 323 572 783</td>
</tr>
<tr>
<td>Nb</td>
<td>185</td>
<td>156 323 648 883(^b)</td>
</tr>
</tbody>
</table>

\((E - D/2)\) for fluorine = 66.3 kcal./mole (89).

\(^a\) estimated value

\(^b\) \(I_5\) for Nb = 1153 kcal./mole.
## TABLE 11

LATTICE ENERGIES AND HEATS OF FORMATION OF FLUORIDES

<table>
<thead>
<tr>
<th>Element</th>
<th>$r^+n$</th>
<th>$U(MF_n)$</th>
<th>$\xi_{n}I^-$</th>
<th>$\Delta H_f(MF_n)$</th>
<th>$\Delta H_f(MF_n)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>kc/mole</td>
<td>kc/mole</td>
<td>(calc)</td>
<td>(exptl)</td>
</tr>
<tr>
<td>TRIFLUORIDES, $v = 4, n = 3, n(E - D/2) = 199$ kcal./mole</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>0.73</td>
<td>1376</td>
<td>1121</td>
<td>-345</td>
<td>-315</td>
</tr>
<tr>
<td>V</td>
<td>0.67</td>
<td>1409</td>
<td>1167</td>
<td>-319</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>0.64</td>
<td>1426</td>
<td>1250</td>
<td>-281</td>
<td>-265</td>
</tr>
<tr>
<td>Mn</td>
<td>0.62</td>
<td>1438</td>
<td>1308</td>
<td>-261</td>
<td>-238</td>
</tr>
<tr>
<td>Fe</td>
<td>0.60</td>
<td>1449</td>
<td>1261</td>
<td>-288</td>
<td>-</td>
</tr>
<tr>
<td>Co</td>
<td>0.63</td>
<td>1432</td>
<td>1346</td>
<td>-183</td>
<td>-187</td>
</tr>
</tbody>
</table>

TETRAFLUORIDES, $v = 5, n = 4, n(E - D/2) = 265$ kcal./mole.

| Ti      | 0.68   | 2339      | 2114           | -385              | -393              | 28   |
| V       | 0.62   | 2413      | 2241           | -315              | -332              | Present work. |
| Cr      | 0.56   | 2454      | 2412           | -233              | -287              | 90   |
| Mn to 0.60 | 2474 | 2507 | -165 | -105 | - |
| to 0.54 | 2415 | 2414 | -246 | -167 | - |
| (Fe) to 0.60 | 2494 | 2414 | -246 | -167 | - |
| (Co) to 0.60 | 2516 | (2499)* | -180 | -79 | - |
| Zr      | 0.80   | 2234      | 1825           | -536              | -457              | 26   |

PENTAFLUORIDES, $v = 6, n = 5, n(E - D/2) = 332$ kcal./mole.

| V       | 0.59   | . . . . . . not calculated . . . . . . . -352 | Present work |
| Nb      | 0.70   | 3482      | 3163           | -466              | -432              | 31   |

*includes an estimated value.
Considering the approximate nature of the lattice energy calculations, the agreement between the experimental and calculated heats of formation, when both values are available, is surprisingly good. The agreement indicates that calculated values of the heat of formation may be used when experimental values are not available, such as in the case of vanadium trifluoride.

In general, calculated heats of formation of the tri-fluorides of the elements of the first long period are greater than the experimental values, whereas the calculated values for the tetrafluorides of the same elements are generally lower than the experimental ones. The only calculations done for fluorides of the second long period elements are those on niobium pentafluoride and zirconium tetrafluoride, both of which are higher than experimental values.

The discrepancies between experimental and calculated values are probably due to small errors in the lattice energy estimation. The Kapustinskii formula appears to overestimate the lattice energy of the trifluorides of the elements of the first long period whereas it underestimates the lattice energy of the tetrafluorides of the same elements probably because of the increase in covalent character of the M-F bonds accompanying the increased valence. The calculated values of the heat of formation of zirconium tetrafluoride and niobium pentafluoride are larger than the experimental values, indicating that the Kapustinskii formula probably overestimates the lattice energies of fluorides of elements in the second long
period. Again this overestimation is probably due to the larger degree of ionic character in the bonds formed by second long period elements relative to first long period elements, because of the larger ionic size in the second long period elements. Effectively the Kapustinskii formula arbitrarily compensates for a constant amount of covalent character, whereas in fact covalent character changes with valence and ionic size.

There are a few anomalies in the calculated heat of formation values in Table 11 which cannot be attributed to systematic variations of covalent character. The value of the heat of formation calculated for iron trifluoride does not obey the fairly regular decrease of calculated heat of formation values observed for the trifluorides from titanium to cobalt. This may be due to the use of empirical radii rather than crystal radii and it is possible that the radius of Fe$^{+3}$ should be taken as somewhat greater than 0.60Å.

Barber, Linnet and Taylor (89), using a much more approximate formula for the lattice energy, have also calculated heat of formation values for the trifluorides of the first long period elements. In general their results exhibit the same trend as those in Table 11 but were about 100 kcal./mole greater than the present calculated values, and thus showed a poorer agreement with the experimental values. In general the more approximate method of evaluating the lattice energy which they used to calculate the heats of formation of mono, di-, and trihalides of the transition metals of the first long period, yielded heats of formation which showed good
agreement with experimental values only in the case of chlorides. The present evaluation of the lattice energy yields heats of formation of fluorides which are in fairly good agreement with experimental values. This suggests that agreement with experiment is obtained through a rather fortuitous cancellation of unevaluated factors, such as the effect of various amounts of covalency in the M-X bonds, rather than the achievement of a complete evaluation of the lattice energy through a valid theoretical expression.

The heat of formation of vanadium pentafluoride was not calculated in the above manner because vanadium pentafluoride is a liquid at 298°K, hence evaluation of a lattice energy and a heat of formation from it is completely meaningless for comparison with the experimental value. The experimental value of the heat of formation of vanadium pentafluoride is included in the table to facilitate comparison with the heats of formation of vanadium tetrafluoride and niobium pentafluoride.

(iv) Thermodynamic Stability of Vanadium Fluorides

Consider first the disproportionation of vanadium tetrafluoride into the tri- and pentafluorides:

$$2VF_4 \rightarrow VF_5 + VF_3.$$ 

The heat of the disproportionation reaction ($\Delta H_D$) is given by the difference between the total heat of formation of the products and reactants, that is:

$$\Delta H_D = \Delta H_{f0}(VF_5) + \Delta H_{f0}(VF_3) - 2 \Delta H_{f0}(VF_4)$$
Using the experimental values of -332 and -352 kcal./mole for the heats of formation of vanadium tetrafluoride and vanadium pentafluoride respectively, and the calculated value of -319 kcal./mole for the heat of formation of vanadium trifluoride, the heat of the above disproportionation reaction is:

\[ \Delta H_D = -352 - 319 - 2(-332) = -7 \text{ kcal./mole.} \]

Considering \( \Delta H_D \) to be an approximate criterion, the disproportionation reaction is spontaneous. The assumption that \( \Delta S_D \) is positive for the above reaction, as is the general case for reactions which produce gaseous products (89), means that \( \Delta F_D \), which is given by \( \Delta F = \Delta H - T\Delta S \), will have a greater magnitude than \( \Delta H_D \), thus confirming the spontaneity. Certainly the observed rapid disproportionation of vanadium tetrafluoride into vanadium pentafluoride and vanadium trifluoride supports the thermodynamic indication of spontaneity.

Approximating \( \Delta H_D \) to \( \Delta F_D \), the equilibrium constant \( (K) \) of the above disproportionation reaction can be estimated from the relation

\[ \Delta F_D = \Delta H_D = RT\ln K \]

Using -7 kcal./mole for \( \Delta H_D \), \( K = 10^5 \), certainly strongly in favour of disproportionation. This suggests that vanadium pentafluoride will not readily combine with vanadium trifluoride to form vanadium tetrafluoride.

It is possible to prepare and study vanadium tetrafluoride in spite of the exothermic nature of the disproportionation into the tri- and pentafluorides because the actual
stability of the compound also depends on the kinetics of the disproportionation reaction. Vanadium tetrafluoride disproportionates quite slowly, even at 120°, requiring about 20-30 hrs. to decompose approximately four grams, suggesting that the activation energy of the reaction is quite high. This may indicate that the reaction mechanism involves the simultaneous breaking of several bonds. A complete kinetic study of this reaction would be of interest.

Through similar calculations the disproportionation can be shown to be the favoured mode of decomposition of vanadium tetrafluoride. The heat of dissociation of vanadium tetrafluoride into the trifluoride and fluorine according to the equation

\[ \text{VF}_4 \rightarrow \text{VF}_3 + \frac{1}{2} \text{F}_2 \]

is given by the relation:

\[ \Delta H_{\text{diss}}(\text{VF}_4) = \Delta H_{\text{f0}}(\text{VF}_3) - \Delta H_{\text{f0}}(\text{VF}_4) \]

Using the experimental value of -332 kcal./mole for \( \Delta H_{\text{f0}}(\text{VF}_4) \) and the calculated value of -319 kcal./mole for \( \Delta H_{\text{f0}}(\text{VF}_3) \), the heat of dissociation is

\[ \Delta H_{\text{diss}}(\text{VF}_4) = -319 - (-332) = +13 \text{ kcal./mole} \]

That is, the dissociation of vanadium tetrafluoride into the trifluoride and fluorine is endothermic and much less favourable than the disproportionation into vanadium trifluoride and vanadium pentafluoride. Certainly, there is no experimental evidence to suggest that vanadium tetrafluoride dissociates into vanadium trifluoride and fluorine.
The possibility of forming vanadium tetrafluoride by dissociation of vanadium pentafluoride can be estimated from the heat of the reaction:

\[ \text{VF}_5 \rightarrow \text{VF}_4 + \frac{1}{2} \text{F}_2 \]

which is given by:

\[ \Delta H_{\text{diss}}(\text{VF}_5) = \Delta H_f(\text{VF}_4) - \Delta H_f(\text{VF}_5). \]

Substituting the experimental values for the heats of formation of vanadium tetrafluoride and vanadium pentafluoride gives, for the heat of dissociation of vanadium pentafluoride,

\[ \Delta H_{\text{diss}}(\text{VF}_5) = -332 - (-352) = 20 \text{ kcal./mole}, \]

indicating that the dissociation of vanadium pentafluoride into vanadium tetrafluoride and fluorine is extremely unlikely. The reverse reaction is highly exothermic and thus spontaneous. The reaction of vanadium tetrafluoride and fluorine has been found to proceed quite rapidly and there is no experimental evidence to suggest that vanadium pentafluoride dissociates into vanadium tetrafluoride and fluorine.

(v) Thermodynamic Stability of the First Period Tetrafluorides

Following the lines of the discussion of the thermodynamic stability of vanadium fluorides, it is of interest to consider the thermodynamic stability of the tetrafluorides of the first long period in general, particularly with respect to the dissociation:

\[ \text{MF}_4 \rightarrow \text{MF}_3 + \frac{1}{2} \text{F}_2 \]
where the heat of reaction ($\Delta H$) is given by:

$$\Delta H = \Delta H_f(MF_3) - \Delta H_f(MF_4)$$

The required heats of formation are taken from Table 11 and are shown with the resulting heats of reaction in Table 12.

Unfortunately, the necessary ionization potentials and ionic radii to calculate the heats of formation of $MF_5$ compounds are not available for the first period transition elements of group VIII, therefore the stability of these tetrafluorides with respect to the disproportionation

$$2MF_4 \rightarrow MF_5 + MF_3$$
could not be evaluated.

**TABLE 12**

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H_{f}(MF_3)$</th>
<th>$\Delta H_{f}(MF_4)$</th>
<th>$\Delta H$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kcal./mole (Table 11)</td>
<td>kcal./mole (Table 11)</td>
<td>kcal./mole</td>
</tr>
<tr>
<td>Ti</td>
<td>345</td>
<td>385</td>
<td>+ 40</td>
</tr>
<tr>
<td></td>
<td>315</td>
<td>393</td>
<td>+ 78</td>
</tr>
<tr>
<td>V</td>
<td>319</td>
<td>315</td>
<td>- 4</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>332</td>
<td>+ 13</td>
</tr>
<tr>
<td>Cr</td>
<td>281</td>
<td>233</td>
<td>- 48</td>
</tr>
<tr>
<td></td>
<td>265</td>
<td>287</td>
<td>+ 22</td>
</tr>
<tr>
<td>Mn</td>
<td>261</td>
<td>165 (calc.)</td>
<td>- 96</td>
</tr>
<tr>
<td></td>
<td>238</td>
<td>105</td>
<td>- 156</td>
</tr>
<tr>
<td>Fe</td>
<td>288</td>
<td>246 (calc.)</td>
<td>- 53</td>
</tr>
<tr>
<td></td>
<td>167</td>
<td>105</td>
<td>- 33</td>
</tr>
<tr>
<td>Co</td>
<td>183</td>
<td>180 (calc.)</td>
<td>- 121</td>
</tr>
<tr>
<td></td>
<td>79</td>
<td>79</td>
<td>- 104</td>
</tr>
<tr>
<td></td>
<td>187 (calc.)</td>
<td>180 (calc.)</td>
<td>- 7</td>
</tr>
<tr>
<td></td>
<td>79</td>
<td>79</td>
<td>- 108</td>
</tr>
</tbody>
</table>

*the values in brackets represent upper and lower limits to the calculated heat of formation.*
The results in Table 12 are quite striking. The heats of dissociation of the tetrafluorides of titanium, vanadium and chromium into the trifluorides of these elements are quite endothermic, particularly if the available experimental values are chosen in preference to calculated heats of formation. Heats of reaction obtained from calculated heats of formation ($\Delta H_f^\circ$) tend to overestimate the exothermicity of the dissociation and to suggest that the dissociation is more feasible than it actually is. Beyond chromium tetrafluoride, the calculated heat of reaction ($\Delta H$) becomes highly exothermic, and even considering the tendency to overestimation of exothermicity it is apparent that manganese tetrafluoride and iron tetrafluoride will show a strong tendency to dissociate into the trifluorides and fluorine. Manganese tetrafluoride has recently been prepared (92) and does indeed dissociate into manganese trifluoride and fluorine (93). Iron and cobalt tetrafluorides have not been prepared.

(vi) Bond Energies of Vanadium Fluorides

If the heat of dissociation of a compound is defined as the heat required to dissociate the molecule into its constituent atoms in the gas phase, it can be shown that this is related to the heat of formation of the compound by a simple Born-Haber cycle. The cycle is illustrated below for a compound of the type $MF_n$. 
where $\Delta H_D$ is the heat of dissociation of $\text{MX}_n$

$L$ is the heat of sublimation of $\text{M}$

$D(X_2)$ is the heat of dissociation of the halogen $X_2$

and $\Delta H_{fo}$ is the standard heat of formation of $\text{MX}_n$. Since the sum of all terms in the cycle must be zero, the heat of dissociation is given by:

$$\Delta H_D = - \Delta H_{fo}(\text{MX}_n) + L + \frac{n}{2} D(X_2). \quad (7-6)$$

The bond energy is defined as the average dissociation energy per M-X bond, eg. $E_b = \Delta H_D/n$, and is given by the expression:

$$E_b = \frac{1}{n} \left[ - \Delta H_{fo}(\text{MX}_n) + L \right] + \frac{1}{2} D(X_2) \quad (7-7)$$

The bond energies of vanadium and niobium fluorides have been calculated by substituting the appropriate thermochemical data into equation (7-7). The dissociation energy of fluorine ($D(F_2)$) was taken as 38 kcal./mole (11). The results are shown in Table 13.
TABLE 13
BOND ENERGIES OF SOME GROUP IV AND V FLUORIDES

<table>
<thead>
<tr>
<th>MF_n</th>
<th>L</th>
<th>$-\Delta H_f^0$ (exptl)</th>
<th>$\Delta H_D$</th>
<th>$E_b$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kcal.</td>
<td>kcal.</td>
<td>kcal.</td>
<td>kcal.</td>
<td>($\Delta H_f^0$ exptl.)</td>
</tr>
<tr>
<td>VF_3</td>
<td>122</td>
<td>319+30 (calc)</td>
<td>(498+30)</td>
<td>(166+10)</td>
<td>calc. (Present work)</td>
</tr>
<tr>
<td>VF_4</td>
<td>122</td>
<td>332</td>
<td>530</td>
<td>132</td>
<td></td>
</tr>
<tr>
<td>VF_5</td>
<td>122</td>
<td>352</td>
<td>569</td>
<td>114</td>
<td></td>
</tr>
<tr>
<td>NbF_5</td>
<td>185</td>
<td>432</td>
<td>712</td>
<td>142</td>
<td>31</td>
</tr>
<tr>
<td>TiF_4</td>
<td>112</td>
<td>393</td>
<td>581</td>
<td>145</td>
<td>28</td>
</tr>
<tr>
<td>ZrF_4</td>
<td>125</td>
<td>457</td>
<td>677</td>
<td>169</td>
<td>26</td>
</tr>
</tbody>
</table>

The bond energies of the vanadium chlorides, calculated in the same manner, using $D(\text{Cl}_2) = 58$ kcal./mole (11), are shown in Table 14 for comparison.

TABLE 14
BOND ENERGIES OF VANADIUM CHLORIDES

<table>
<thead>
<tr>
<th>MF_n</th>
<th>L</th>
<th>$-\Delta H_f^0$</th>
<th>$\Delta H_D$</th>
<th>$E_b$</th>
<th>Reference ($\Delta H_f^0$ exptl.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kcal.</td>
<td>kcal.</td>
<td>kcal.</td>
<td>kcal.</td>
<td></td>
</tr>
<tr>
<td>VCl_2</td>
<td></td>
<td>108</td>
<td>288</td>
<td>144</td>
<td></td>
</tr>
<tr>
<td>VCl_3</td>
<td>122</td>
<td>137</td>
<td>346</td>
<td>115</td>
<td>83</td>
</tr>
<tr>
<td>VCl_4</td>
<td></td>
<td>136</td>
<td>374</td>
<td>93</td>
<td>84</td>
</tr>
</tbody>
</table>

The results in Tables 13 and 14 show that the bond energies of vanadium fluorides are approximately 40% greater than those of vanadium chlorides with the same valence. This
increase in bond energy from chloride to fluoride follows the probable increase in ionic character of the metal-halogen bond, since ionic character will tend to decrease with increasing polarizability and size of the halogen, i.e. from chloride to fluoride.

The bond energy within the chloride and fluoride series decreases with increasing valence of the metal, thus the bond energy again decreases with ionic character of the metal-halogen bond. The bond energy of the fluorides also increases from vanadium pentafluoride to niobium pentafluoride, and from titanium tetrafluoride to zirconium tetrafluoride, that is the bond energy increases with increasing ionic character of the bond. These last two trends can be related to the increase of ionic bond character with increasing ionic size. Thus lower valence ions, with a larger metal ion size, will form bonds of greater ionic character than high valence ions, and elements in the second long period will, due to their greater ionic size, form bonds of greater ionic character than elements in the first long period. The trends exhibited by the bond energies in Tables 13 and 14 are consistent with the generally expected behaviour of metal halide bonds.(105).

The reliability of the preceding thermodynamic calculations on vanadium fluorides would be greatly increased if the calculated heat of formation of vanadium trifluoride could be replaced by an experimental value. Unfortunately the heat of hydrolysis cannot be measured in the same manner
as for the tetrafluoride and pentafluoride because of the extreme slowness of the dissolution of vanadium trifluoride in water. Direct measurement of the heat of combination of the elements in a bomb according to the methods of the workers at the Argonne laboratory (26) would not be straightforward as the higher fluorides are more likely to be formed because of the large excess of fluorine present in the bomb. Perhaps the reaction of vanadium metal with hydrogen fluoride in a bomb calorimeter would provide a means of obtaining the heat of formation of vanadium trifluoride as Muetterties and Castle (94) have reported that this reaction apparently leads to quantitative formation of vanadium trifluoride. If this can be done the result would be of interest as it would complete the series of heats of formation of the vanadium fluorides, and provide a further check of the reliability of the heats of formation obtained from estimated lattice energies.
CHAPTER 8: EXPERIMENTAL

GENERAL TECHNIQUES

Most of the early literature contains reports that fluorides attack glass, thus manipulation of these fluorides required metal or fluorocarbon plastic apparatus. Recent studies (6,7) have shown, however, that when freed of all traces of moisture, volatile fluorides can be readily manipulated in glass apparatus.

The marked susceptibility of volatile fluorides to moisture in glass apparatus arises from an extremely rapid, self-propagating chain reaction involving the glass itself.

\[
\begin{align*}
\text{eg. } & MF_n + H_2O \rightarrow MOF_{n-2} + 2HF \\
& 4HF + SiO_2 \rightarrow SiF_4 + 2H_2O \\
& MF_n + H_2O \rightarrow \text{etc.}
\end{align*}
\]

Thus even minute traces of moisture will eventually result in complete hydrolysis of the fluoride. Any study of the properties of volatile fluorides therefore requires techniques which permit the ready manipulation and purification of the fluorides by simple trap-to-trap distillations in moisture-free vacuum systems. Hydrocarbon vacuum greases cannot be tolerated as they are attacked by most fluorides, and fluorocarbon greases, while withstanding chemical attack by volatile fluorides, often contain traces of moisture and thus must also be avoided.
Such conditions can easily be achieved with simple all-glass systems consisting of a number of traps connected with combinations of capillary seal-off constrictions and breakseals instead of the greased taps used in conventional vacuum systems. These all-glass systems can be readily dried prior to use by evacuation and heating the glass with a blowtorch. After the system has been thoroughly dried under vacuum, the capillary leading to the vacuum manifold is sealed off leaving an evacuated, all-glass, grease and moisture-free system in which the fluoride can be readily manipulated. Materials can be transferred from one system to another by sealing into a trap equipped with a breakseal, which is then connected to the new system. After the new trapline has been thoroughly dried the breakseal is broken with a glass covered, magnetically operated breaker and the fluoride transferred by distillation. Many simple physical measurements can also be made with standard glass apparatus modified to provide a completely dry and enclosed system.

The disadvantage of such techniques is that each experiment requires the construction of a new vacuum trapline. In some cases this disadvantage can be overcome with the use of a standard vacuum system in which greased stopcocks are replaced by packless metal bellows valves (6) (eg. Hoke type 431) which are united to the glass with metal-glass seals, hard soldered to the metal valve. Metal valves however, are not universally applicable to the study of
fluorides as the metals are sometimes subject to attack, particularly by the more active fluoride solvents. The valves are also difficult to clean, especially if the bellows becomes dirty, and the metal to Pyrex seals are a point of weakness being subject to breakage and the development of pinhole leaks.

The careful drying of the manipulative system is of little effect if the volatile fluoride to be studied already contains traces of moisture. Every effort must be made to prepare the fluoride under strictly anhydrous conditions, applying somewhat the same means as outlined above for drying the preparative apparatus, with a few changes in procedure because preparations are often most conveniently done at atmospheric pressure in a flow system. Careful preliminary drying of the apparatus and reagents under vacuum followed by admission of dry nitrogen and opening the system to the atmosphere only through a series of cold traps is usually adequate to exclude moisture from even exceptionally sensitive materials such as vanadium pentafluoride. Hydrolysis can be minimised by storing the fluoride in contact with dry sodium fluoride, which combines with hydrogen fluoride to form the stable sodium bifluoride, and thus interrupts the hydrolysis cycle outlined above. Obviously, to be used in this manner the sodium fluoride must not form a stable complex with the volatile fluoride.
Studies on involatile, solid fluorides, which are generally less rapidly attacked by moisture, require similar precautions against hydrolysis. Transfers are made in a dry-box in which a dry atmosphere is maintained through the use of phosphoric oxide desiccant. Carefully dried apparatus and containers should be used and the manipulations should be performed as quickly as possible. All reagents placed in contact with hydrolysable fluorides should be rigorously dried prior to use.

In this investigation solid fluorides were generally characterised by X-ray powder photography, magnetic susceptibility and analysis.

X-ray powder photographs were taken on a General Electric X-ray unit using a copper target and nickel filters. The camera, also supplied by General Electric, was of conventional design with a circumference of 45 cm. Samples were sealed in dry, thin-walled, 0.5 mm. diameter Pyrex or quartz capillaries (Pantak Ltd.) to prevent hydrolysis during the exposure.

Magnetic susceptibilities were measured with a Gouy balance incorporating a Varian #4004 electromagnet with 2 inch diameter tapered pole faces, which generated a field of approximately 8,000 gauss. Most susceptibility measurements were done at room temperature using mercuric-cobaltitetrathio-cyanate (II) (96) as a calibration standard. Where indicated, the temperature dependence of the magnetic susceptibility was measured in the range 80° to 300°K using a thermostatted sample.
compartment, adapted from the design of Figgis and Nyholm (97). The particulars of this apparatus have been described elsewhere (98).

The analyses were done with standard techniques. Vanadium was estimated by titration of vanadium (IV), previously reduced with sulphur dioxide if necessary, with standard (0.01N) potassium permanganate in approximately 2N sulphuric acid solution. Sulphur dioxide, if used, was removed by boiling the solution prior to titration. Ratios of vanadium (IV) to vanadium (V) were determined by titrating the sample immediately after hydrolysis, followed by reduction of the titrated sample with sulphur dioxide and titration as above. Interfering anions (such as I\(^-\), IO\(_3^-\), SeO\(_2^2^-\), etc.) were removed by reducing all the vanadium to vanadium (IV) with sulphur dioxide followed by adsorption of the vanadyl (VO\(_{2}^+\)) cation on a Dowex 50W cation exchange resin. The anions were washed out of the column with distilled water; the vanadium was eluted with 6N sulphuric acid; the vanadyl solution was then diluted and titrated with standard permanganate solution.

Fluoride was best estimated (56) by distillation as fluorosilicic acid from a constant boiling mixture (135°) of perchloric acid (99), followed by precipitation as lead chloride fluoride from an alkaline (sodium acetate buffer) solution, containing an excess of chloride ion and lead nitrate. The precipitate was digested at 95° for one hour,
filtered on a tared glass crucible and weighed.

Selenium was determined by precipitation of the element from concentrated (3N) hydrochloric acid solution and weighing on a tared glass crucible.

PREPARATION AND PHYSICAL PROPERTIES OF VANADIUM PENTAFLUORIDE

(i) The Preparation of Vanadium Pentafluoride

Vanadium pentafluoride was prepared by fluorination of vanadium metal as previously described (7,14). Fluorine was supplied by Allied Chemical Company in a steel gas cylinder which was permanently installed in a walk-in fume hood. The pressure regulating and gas delivery system has been described elsewhere (56).

Vanadium metal was placed in a nickel boat and inserted into a one inch diameter nickel tube, twelve inches long, which was placed in a tube furnace and connected to the fluorine supply line. The exit of the nickel reactor tube was connected to a glass trapline, consisting of four or five traps equipped with breakseals and capillary constrictions. The connection was made by means of a nickel flange to which was welded one half of the body of a 3"/4 inch brass compression union. The flange was bolted to the nickel reactor, the seal being made with a compressible lead washer. The trapline was connected to the flange with a neoprene gasket and the compression fitting nut. This provided a very large diameter exit from
the reactor tube, thus preventing the blockages due to condensation of less volatile fluorides which frequently occurred in the previous apparatus (56) which had a narrow exit tube.

The apparatus was evacuated and "flamed-out" to remove all trace of moisture. Dry nitrogen gas was admitted, the vanadium metal heated to 350-360°C, and fluorine passed over the heated metal. The volatile pentafluoride was condensed in traps cooled to -78°C with alcohol-dry-ice baths. After the reaction was completed the fluorine was shut off and nitrogen passed to flush any traces of fluorine out of the system. The system was evacuated and the traps containing the product were sealed off.

The impure product obtained from this reaction, largely a mixture of vanadium tetrafluoride and vanadium pentafluoride, was connected to a simple distillation system containing sodium fluoride, and volatile materials were repeatedly distilled from sodium fluoride. The purified vanadium pentafluoride was stored in sealed glass traps equipped with break-seals.

The purified volatile material was typically a white solid, melting about room temperature (m.p. 19.5°C(7)) to a straw coloured liquid. A typical analysis gave V, 35.3; F, 63.2%. Calc. for VF$_5$: V, 34.95; F, 65.05%.

The residue remaining in the trap in which the products were first condensed was a light brown powder which was a mixture of vanadium tetrafluoride and vanadium
trifluoride, the former predominating, as shown by X-ray powder photography and analysis (Found: V, 42.1%. Calc. for VF₄: V, 40.3; for VF₃: V, 47.3%).

(ii) The Density of Vanadium Pentafluoride

A silica dilatometer, consisting of a bulb approximately 6 mm. diameter, 2 cm. long, and a 2 mm. diameter capillary 13 cm. long, with a reference mark engraved at the base of the capillary, was calibrated with mercury. The volume of the dilatometer was given by the relation:

\[ V = 0.6889 + 0.02883h \text{ cc.} \]

where \( V \) is the volume of liquid in cc. contained in the dilatometer and \( h \) is the height of the liquid, in cm. above the engraved reference mark.

The dilatometer was sealed to a trapline and dried by heating under vacuum. Sufficient vanadium pentafluoride to bring the level of liquid into the capillary was distilled into the dilatometer and it was sealed off and weighed. The dilatometer was immersed in a thermostatically controlled water bath (+ 0.05° variation) and the height of liquid in the capillary measured with a vertical travelling microscope outside the bath. The height of liquid in the capillary was measured at each temperature, with both increasing and decreasing temperature to check on reproducibility. The
temperature was varied from 20° to 45°, this being the liquid range of vanadium pentafluoride. After the series of volume measurements was completed, the vanadium pentafluoride was frozen in the dilatometer. The dilatometer was then carefully broken open and the contained vanadium pentafluoride distilled out under vacuum. The pieces of the dilatometer were weighed to obtain the weight of the vanadium pentafluoride by difference. Two experiments were performed and the results are shown, in chronological order, in Table 15.

**TABLE 15**

**DENSITY OF VANADIUM PENTAFLUORIDE**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Volume (cc.)</th>
<th>Density (g/cc.)</th>
<th>Temperature (°C)</th>
<th>Volume (cc.)</th>
<th>Density (g/cc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.0</td>
<td>0.8706</td>
<td>2.508</td>
<td>20.6</td>
<td>0.8330</td>
<td>2.491</td>
</tr>
<tr>
<td>25.2</td>
<td>0.8772</td>
<td>2.489</td>
<td>25.3</td>
<td>0.8388</td>
<td>2.474</td>
</tr>
<tr>
<td>30.2</td>
<td>0.8811</td>
<td>2.478</td>
<td>30.9</td>
<td>0.8440</td>
<td>2.459</td>
</tr>
<tr>
<td>34.7</td>
<td>0.8887</td>
<td>2.457</td>
<td>35.1</td>
<td>0.8492</td>
<td>2.444</td>
</tr>
<tr>
<td>39.8</td>
<td>0.8945</td>
<td>2.435</td>
<td>40.4</td>
<td>0.8563</td>
<td>2.424</td>
</tr>
<tr>
<td>44.9</td>
<td>0.9043</td>
<td>2.414</td>
<td>45.0</td>
<td>0.8626</td>
<td>2.406</td>
</tr>
<tr>
<td>30.1</td>
<td>0.8841</td>
<td>2.470</td>
<td>37.7</td>
<td>0.8522</td>
<td>2.435</td>
</tr>
<tr>
<td>24.3</td>
<td>0.8771</td>
<td>2.489</td>
<td>30.3</td>
<td>0.8431</td>
<td>2.462</td>
</tr>
<tr>
<td>20.4</td>
<td>0.8733</td>
<td>2.500</td>
<td>25.0</td>
<td>0.8371</td>
<td>2.479</td>
</tr>
<tr>
<td>26.6</td>
<td>0.8797</td>
<td>2.482</td>
<td>20.2</td>
<td>0.8323</td>
<td>2.494</td>
</tr>
<tr>
<td>33.4</td>
<td>0.8890</td>
<td>2.456</td>
<td>38.4</td>
<td>0.8948</td>
<td>2.440</td>
</tr>
<tr>
<td>38.0</td>
<td>0.9018</td>
<td>2.421</td>
<td>43.0</td>
<td>0.8780</td>
<td>2.485</td>
</tr>
</tbody>
</table>

*average of two determinations.*
In the range 25° to 40° the graphs of volume \((V)\) and density \((\varphi)\) against temperature \((t)\) were linear and obeyed the equations:

\[
\frac{dV_1}{dt} = 1.312 \times 10^{-3} \text{ cc/deg.} \quad \frac{dV_2}{dt} = 1.215 \times 10^{-3} \text{ cc/deg.}
\]

\[
\frac{d\varphi_1}{dt} = -0.00356 \text{ g/cc/deg.} \quad \frac{d\varphi_2}{dt} = -0.00341 \text{ g/cc/deg.}
\]

\[
\varphi_1 = 2.487 - 0.00356 (t-25°) \quad \varphi_2 = 2.479 - 0.00341(t-25°)
\]

The average expression for the density from the two experiments, including standard deviations, is:

\[
\varphi = 2.483 (+0.004) - 0.00349(t-25°) + 0.00008 \text{ g./cc.}
\]

and the average coefficient of expansion is:

\[
\frac{dV}{dt} = 1.263 (+0.05) \times 10^{-3} \text{ cc./deg.}
\]

(iii) The Viscosity of Vanadium Pentafluoride

A viscometer based on the Ostwald design was constructed with special provisions for handling a volatile, easily hydrolysed liquid. The Pyrex viscometer consisted of a 15 cm. length of one mm. capillary between an upper bulb of approximately one ml. capacity and a lower bulb of about two ml. capacity. Calibration marks were provided above and below the upper bulb. The capillary was bent into a U-shape near to the large bulb so that the liquid flowed into the lower reservoir at the bottom of this reservoir. An 8 mm. diameter tube,
joined to the top of the large reservoir, was parallel to the capillary tube. A metal tap (Hoke type 431) was joined to the top of the 8 mm. tube by means of a Kovar-Pyrex graded seal. A second tap, below this first tap and affixed in the same manner, provided a connection between the two arms of the viscometer which permitted a variation in the relative pressure between the arms.

The apparatus was sealed to a vacuum line and "baked" under vacuum at 100° for two days to ensure complete drying. Two ml. of vanadium pentafluoride was distilled into the viscometer, which was then sealed off. The viscometer was sealed to a vacuum line consisting of an evacuated 5 litre bulb, a 5 litre bulb with dry nitrogen at atmospheric pressure and the necessary arrangement of metal taps, through the main tap on the viscometer. With the tap connecting the two arms of the viscometer closed, the application of pressure through the main tap forced the liquid into the upper chamber. Opening the tap between the two arms of the viscometer equalised the pressure on both sides of the capillary and allowed the liquid to flow under the influence of its hydrostatic pressure into the lower reservoir. Reducing the pressure by opening the viscometer to the evacuated bulb allowed repetition of this procedure without requiring increasingly greater pressures of inert gas. The viscometer was immersed in a thermostatted water bath and where possible several measurements of the flow time for each temperature were made. The results, shown in Table 16, were fairly reproducible and a reasonable straight
line can be drawn (Figure 1a). Measurements were made with ascending and descending temperature and are given in chronological order in Table 16. Densities were calculated from the preceding equation.

**TABLE 16**

**VISCOSITY OF VANADIUM PENTAFLUORIDE**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>No. of det$^*$s of flow time</th>
<th>Density (g./cc)</th>
<th>Viscosity (centipoise)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.35</td>
<td>3</td>
<td>2.482</td>
<td>124.2</td>
</tr>
<tr>
<td>25.45</td>
<td>2</td>
<td>2.482</td>
<td>125.7</td>
</tr>
<tr>
<td>31.9</td>
<td>1</td>
<td>2.458</td>
<td>86.8*</td>
</tr>
<tr>
<td>32.0</td>
<td>3</td>
<td>2.458</td>
<td>76.4</td>
</tr>
<tr>
<td>27.3</td>
<td>1</td>
<td>2.475</td>
<td>110.4*</td>
</tr>
<tr>
<td>27.3</td>
<td>1</td>
<td>2.475</td>
<td>120.0*</td>
</tr>
</tbody>
</table>

*these points deviate from the straight line by about 10%.

The viscosity of vanadium pentafluoride can be expressed by the equation:

$$\eta = 124 - 7.2(t-25^\circ) \text{ centipoise}.$$  

The occasional point at each temperature except 25° deviated considerably (about 10%) from the straight line, thus the reproducibility is not exceptionally good. Considerable experimental difficulties were encountered through the volatility of vanadium pentafluoride which seriously limited the accessible temperature range and also caused some of the pentafluoride to distill out of the viscometer during the pressure reduction steps. Decomposition of the vanadium
pentafluoride caused an increasing darkening of the liquid colour during the experiment. Formation of solids during this decomposition may have been responsible for the deviations from the straight line plot. Calibration of the viscometer is ideally done with a liquid of similar density and viscosity. Concentrated sulphuric acid (94.3 weight-percent, density 1.8318 g./cc.) was the only liquid of reliably known viscosity which was at all close to matching the density and surface tension of vanadium pentafluoride. The necessary extrapolation from the viscosity of sulphuric acid (19.8 centipoise) to that of vanadium pentafluoride ($\sim$100 centipoise) is another source of error. Considering the large errors arising from these sources, the viscosity of vanadium pentafluoride given by the above equation is probably reliable within $\pm20\%$.

(iv) The Surface Tension of Vanadium Pentafluoride

Two types of capillary rise apparatus were used. In the first apparatus a bundle of four capillaries ranging in size from approximately 1.5 mm. to 0.5 mm. internal diameter were placed in a silica bulb, and thoroughly dried. About two ml. of vanadium pentafluoride were distilled into the bulb. The bulb was sealed off, immersed in a thermostatically controlled bath and the height of liquid in the capillaries above the surface of liquid in the bulb was determined with a vertical travelling microscope as before. Only three of the capillaries gave a measurable rise of the liquid and at any
one temperature it was not possible to measure the rise in all of these three capillaries due to the formation of bubbles in the capillaries. The temperature was varied from 20° to 40° and readings taken with ascending and descending temperature. After the capillary rise of vanadium pentafluoride had been measured, the apparatus was emptied, cleaned and calibrated by measuring the capillary rise for distilled water in the same manner.

A second experiment was done with a differential capillary tensiometer, similar to that shown in Figure 156(a) of Dodd and Robinson (100), with two different capillaries, 1.0 and 0.5 mm. diameter, sealed to a bulb of about 2 ml. capacity. A side arm of 5 mm. tubing was also sealed to the sample bulb to facilitate the condensation of the sample in the bulb. The apparatus was sealed to a simple distillation system, to which was also sealed a breakseal bottle containing vanadium pentafluoride. The entire apparatus was evacuated and the tensiometer was heated to 100° for two days under vacuum to ensure complete drying of the capillaries. The remainder of the apparatus was heated with a torch intermittently during this period as usual.

Sufficient vanadium pentafluoride to fill the sample bulb was distilled into the tensiometer which was then sealed off and immersed in a thermostatted water bath. The differential capillary rise was measured with the travelling microscope as before. After the capillary rise of vanadium pentafluoride had been measured, the vanadium pentafluoride was
distilled out under vacuum and the apparatus was calibrated by measuring the capillary rise for distilled water and benzene as before.

The surface tension ($\gamma$) of vanadium pentafluoride was calculated from the expression:

$$\gamma = \frac{f \Delta h}{\rho}$$

where $f$ is the apparatus factor

$\Delta h$ is the difference in level of liquid in each of the two capillaries or the height of liquid in the capillary above the level of liquid in the reservoir.

and $\rho$ is the density of the liquid.

The apparatus factor ($f$) was determined for each apparatus by measuring the $\Delta h$ of a liquid of known density and surface tension such as water or benzene. The density of vanadium pentafluoride at each temperature was calculated from the previously determined expression. The results of both surface tension experiments are given in Table 17 and the temperature variation of the surface tension is shown graphically in Figure 1b.
TABLE 17
SURFACE TENSION OF VANADIUM PENTAFLUORIDE

<table>
<thead>
<tr>
<th>Experiment A</th>
<th></th>
<th>Experiment B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>Surface Tension</td>
<td>Temperature</td>
</tr>
<tr>
<td>°C</td>
<td>dynes/cm²</td>
<td>°C</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>24.5</td>
<td>-</td>
<td>18.35</td>
</tr>
<tr>
<td>29.7</td>
<td>17.96</td>
<td>-</td>
</tr>
<tr>
<td>34.8</td>
<td>16.75</td>
<td>-</td>
</tr>
<tr>
<td>40.0</td>
<td>12.35</td>
<td>-</td>
</tr>
</tbody>
</table>

Apparatus Factor 11.12 27.47 46.45 17.65

Least squares analyses of the data for both experiments for points in the range 24.5 to 37.0 gives for the surface tension of vanadium pentafluoride:

\[ \gamma = 18.2 - 0.142(t-25) \text{ dynes/cm}^2 \]

with a probable error of ± 0.2 and a standard deviation of ± 0.3.

The molar surface energy (\( \mathcal{T} \)) was calculated from the expression:

\[ \mathcal{T} = \gamma (Mv)^{2/3} \]

where \( M \) is the molecular weight

\( v \) is the specific volume which is equal to the reciprocal of the density

and \( \gamma \) is the surface tension.

The values of the surface tension and density of vanadium pentafluoride were taken from the previous expressions. The results are shown in Table 18.
TABLE 18
MOLAR SURFACE ENERGY OF VANADIUM PENTAFLUORIDE

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Density (g/cc.)</th>
<th>Surface Tension (dynes/cm²)</th>
<th>Molar Surface Energy (dynes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>2.500</td>
<td>18.92</td>
<td>284.5</td>
</tr>
<tr>
<td>25</td>
<td>2.483</td>
<td>18.22</td>
<td>275.4</td>
</tr>
<tr>
<td>30</td>
<td>2.466</td>
<td>17.50</td>
<td>265.9</td>
</tr>
<tr>
<td>35</td>
<td>2.448</td>
<td>16.77</td>
<td>256.4</td>
</tr>
</tbody>
</table>

A graph of the molar surface energy (\(\Gamma\)) against temperature yields a straight line with a slope:

\[
\frac{d\Gamma}{dt} = -1.9
\]

(v) The Infrared Spectrum of Vanadium Pentfluoride

The infrared spectra were measured on Perkin-Elmer model 21 infrared recording spectrometers, fitted with sodium chloride optics for the 2 to 15 micron region and caesium bromide optics for the 15 to 40 micron region, using two different gas cells.

The metal cell was a two cm. diameter stainless steel tube, nine cm. long, with a large diameter (6 cm.), 0.5 cm. thick stainless steel flange welded to each end. The surface of each flange was flat except for a concentric ridge about 0.5 mm. high about 0.5 cm. from the inner edge of the flange. Polyethylene windows, 0.5 mm. thick, were sealed to the cell by clamping them between the flange and a matching, 0.5 cm. thick, flat compression plate by means of heavy screws passing through the compression plate and screwing into the flanges.
welded to the body of the cell. Sufficient pressure was applied by means of the screws to squeeze the polyethylene into the small ridge on the cell flange without cutting it, thus providing a vacuum tight seal. A Kovar-Pyrex graded seal was welded to the body of the cell and a glass cold finger, breakseal and capillary constriction sealed to the glass portion of the graded seal.

The cell was sealed to a vacuum line through the capillary constriction, evacuated and dried by heating gently under vacuum. A small amount of vanadium pentafluoride was distilled into the cold finger and the cell was sealed off at the capillary constriction. The concentration of vanadium pentafluoride vapour in the cell was controlled by varying the temperature of the cold finger. With this cell, the region from 42 to 11 microns could be observed as polyethylene has only two weak absorption bands at 13.7 and 13.9 microns.

The second cell was a 10 cm. long glass cell, 3 cm. internal diameter with flat ground flanges on each end. Potassium bromide windows were sealed to the glass with Araldite (Ciba Ltd.) epoxy resin glue. The inner surfaces of the potassium bromide windows had been previously coated with a thin film of paraffin wax to prevent attack of the window material by vanadium pentafluoride. These windows were transparent from 30 to 2.5 microns, except for the sharp paraffin absorption bands at 3.45, 6.8, 6.85, 13.7 and 13.9 microns which were quite weak, because of the thinness of the
film, and did not obscure a large region of the spectrum. A glass cold finger, breakseal and capillary seal off were sealed to the cell as before. The cell was dried, and the spectrum determined as described above.

Spectra were measured on two different samples in each cell over the entire accessible range for each cell, with no appreciable differences being observed. The positions of the absorption bands and estimated relative intensities are shown in Table 9 and Figure 2.

CHEMICAL PROPERTIES OF VANADIUM PENTAFLUORIDE

(1) The Reaction of Vanadium Pentafluoride with Selenium Tetrafluoride

An excess of selenium tetrafluoride (prepared as described by Aynsley, Peacock and Robinson (10)) was distilled into a silica reaction vessel which contained about 2 g. of vanadium pentafluoride. Removal of the volatiles at 0° left a white solid which could be slowly sublimed at room temperatures. Analysis indicated a composition close to a 1:1 complex of selenium tetrafluoride with vanadium pentafluoride.

Found: V, 17.05; F, 50.3; Se, 32.5.

$\text{VF}_5\cdot\text{SeF}_4$ requires: V, 16.95; F, 56.8; Se, 26.25.

$\text{VF}_5\cdot2\text{SeF}_4$ requires: V, 11.2; F, 54.6; Se, 34.65.

and $\text{VF}_5\cdot0.5\text{SeF}_4$ requires: V, 22.9; F, 59.5; Se 17.7.

However the instability of the product made analytical definition difficult.
(ii) **The Reaction of Vanadium Pentafluoride with Sulphur Tetrafluoride**

An excess of sulphur tetrafluoride (Dupont Co.) was distilled into a silica vessel containing about 2 g. of vanadium pentafluoride. Removal of the volatile materials at room temperature left no residue in the reaction vessel. However removal of the volatile materials with the container held at \(-78^\circ\) left a white solid which readily lost sulphur tetrafluoride on standing. A small amount of this solid was shaken into a side arm while the entire apparatus was maintained at \(-78^\circ\). The side arm was sealed off and the contents taken for analyses. On melting the solid, a clear white liquid was formed. The composition of the solid indicated by analysis was somewhere between a 1:1 and a 2:1 ratio of vanadium pentafluoride to selenium tetrafluoride.

(Found: V, 23.7; F, 57.7. \(\text{VF}_5\cdot\text{SF}_4\) requires: V, 20.1; F, 66.6. \(\text{VF}_5\cdot\frac{1}{2}\text{SF}_4\) requires: V, 25.5%). The instability of the product makes analytical definition even more difficult than in the case of the selenium tetrafluoride complex. Little can be said about the complex because a definite composition could not be established.
PREPARATION AND PHYSICAL PROPERTIES OF VANADIUM TETRAFLUORIDE

(1) The Preparation of Vanadium Tetrafluoride

Vanadium tetrafluoride was prepared in large quantities of 10 to 20 grams from vanadium tetrachloride by the method of Ruff and Lickfett (12) and in smaller quantities of 0.5 to 1 gram by fluorination of vanadium metal at low temperatures.

Vanadium tetrachloride was prepared by passing chlorine gas (Matheson Co.) over vanadium metal heated to 300-350° (102) in a Pyrex reaction tube. The product was collected in a glass trap cooled to -78° and transferred, with a minimum exposure to the air, to an all-glass still. The fraction distilling between 152° and 154° was collected. A typical analysis gave: V, 26.4; Cl, 73.5%. Calc. for VCl₄: V, 26.4; Cl, 73.6%.

(a) Preparation from Vanadium Tetrachloride

The procedure described by Ruff and Lickfett (12) was used except for two modifications to provide a solvent and continuous stirring of the reaction mixture to improve the purity of the product. About 10. g. of vanadium tetrachloride was placed in a 250 ml. polyethylene reactor vessel containing a Teflon coated magnetic stirring bar. The reactor was connected to a polyethylene condenser, and 20 g. of trichlorofluoromethane (Freon-11, Dupont Co.) was added and the reactor chilled to -78°. A vigorous stream of nitrogen
was maintained throughout the operation to flush out moisture. The solution was stirred continually by means of an external magnetic stirrer motor. Twenty five to thirty ml. of anhydrous hydrogen fluoride was condensed into the reactor at -78 degrees. The vessel was then permitted to return to room temperature over a period of three hours. At this point the reaction was complete and the trichlorofluoromethane (bp. 24°) and any excess hydrogen fluoride (bp. 19°) was boiled off by warming the reactor to about 30° with a bath of warm water. The product obtained in this manner was invariably pure vanadium tetrafluoride (Found: V, 40.0, 40.4; F, 59.0, 59.6. \(\text{VF}_4\) requires: V, 40.3; F, 59.7%).

The magnetic moment of vanadium tetrafluoride at room temperature calculated from the relationship:

\[
\mu_{\text{eff}} = 2.84 \sqrt{\chi M T}
\]

was 1.64 Bohr magnetons.

A sample of the tetrafluoride prepared in the above manner but without a solvent and continuous stirring, (eg. exactly as described by Ruff and Lickfett (12)) was contaminated with about 3.5% of \(\text{VF}_3\) (Found: V, 41.2%). The magnetic moment (calculated as above) was 1.9 Bohr magnetons, this high value also indicating the presence of vanadium trifluoride.
(b) **Preparation from Vanadium Metal and Fluorine**

Approximately 5 g. of vanadium metal in a nickel boat was placed in a 1 inch diameter nickel reactor, and a series of glass traps was fitted to the exit. After heating the reactor to 150-200°, fluorine diluted with nitrogen was passed for two hours. A small amount of white solid sublimed into the glass traps which were cooled to -78°. The reactor was sealed off and dismantled in the dry-box. Around the exit of the reactor was found a mass of dark green solid which was identified as vanadium tetrafluoride (Found: V, 40.5; F, 57.2%).

The solid deliquesced in air to a blue paste although not as quickly as powdered vanadium tetrafluoride prepared from vanadium tetrachloride and hydrogen fluoride.

The X-ray photograph of the residue remaining upon distillation of vanadium pentafluoride from the impure brown product obtained by fluorination of vanadium metal at 350-360° indicated that this light brown powder was impure vanadium tetrafluoride. The residue showed an X-ray diffraction pattern identical to that of vanadium tetrafluoride prepared by other methods, plus a weak line arising from small amounts of vanadium trifluoride. Analysis confirmed the identification of the residue as impure vanadium tetrafluoride (Found V, 42.1%).
(ii) **General Properties of Vanadium Tetrafluoride**

Pure vanadium tetrafluoride is a bright, lime green powder which becomes brown on exposure to small amounts of moisture in the dry-box. On exposure to the atmosphere it deliquesced to a blue paste. It dissolved rapidly in water yielding an acidic solution with the characteristic rich blue colour of vanadium (IV) in aqueous solution. It was insoluble in carbon tetrachloride, trichlorofluoromethane, ether, benzene and nitrobenzene, and in inorganic solvents such as sulphur dioxide, ammonia and hydrogen fluoride. In pyridine, acetonitrile, tetrahydrofuran, and ethoxymethoxyethane, vanadium tetrafluoride formed a greenish solution with a brown residue remaining, which was apparently a reaction product. Chlorobenzene, toluene and pentane converted vanadium tetrafluoride to a black solid while the solvent remained uncoloured. Two determinations of the specific gravity under carbon tetrachloride gave 3.28 g/cc (at 28°) and 3.02 g/cc (at 19.5°). A determination under toluene gave a specific gravity of 2.2 g/cc, however as vanadium tetrafluoride appears to react with toluene, this result is not reliable. The infrared spectrum of vanadium tetrafluoride as a Nujol mull was measured from 400 to 2000 cm⁻¹ and the results are shown in Table 9 and Figure 2.
(iii) The Magnetic Susceptibility of Vanadium Tetrafluoride

The magnetic susceptibility was measured from $81^\circ$ to $295^\circ K$ with the apparatus described previously. The susceptibility obeys the Curie-Weiss law and the magnetic moment at $293^\circ K$, calculated according to the Curie-Weiss law is 2.17 Bohr magnetons, and according to the Curie law is 1.68 Bohr magnetons. The results are given in Table 19.

TABLE 19

<table>
<thead>
<tr>
<th>$T^\circ K$</th>
<th>$10^4 \chi_M$</th>
<th>$\mu_{\text{eff}}$ (Curie-Weiss)</th>
<th>$\mu_{\text{eff}}$ (Curie)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>11.91</td>
<td>2.17</td>
<td>1.68</td>
</tr>
<tr>
<td>252</td>
<td>12.97</td>
<td>2.17</td>
<td>1.62</td>
</tr>
<tr>
<td>243</td>
<td>13.11</td>
<td>2.16</td>
<td>1.59</td>
</tr>
<tr>
<td>204</td>
<td>14.49</td>
<td>2.17</td>
<td>1.54</td>
</tr>
<tr>
<td>181</td>
<td>15.23</td>
<td>2.16</td>
<td>1.49</td>
</tr>
<tr>
<td>132</td>
<td>17.71</td>
<td>2.17</td>
<td>1.37</td>
</tr>
<tr>
<td>83</td>
<td>21.01</td>
<td>2.17</td>
<td>1.18</td>
</tr>
</tbody>
</table>

$\Theta = 198^\circ$  \hspace{1cm} $C = 0.5835$ cg su.

(iv) Thermal Disproportionation of Vanadium Tetrafluoride

Approximately 4 g. of vanadium tetrafluoride was placed in a silica pyrolysis tube, 1 inch in diameter and 12 inches long, surrounded by an electric furnace, and connected, through a spray trap, to a glass trapline. One trap was chilled to $-78^\circ$, the system evacuated and the temperature of the sample in the silica tube slowly increased. At $100^\circ$ the evolution of gas was vigorous and powdered vanadium tetrafluoride was carried into the spray trap. The
temperature was maintained between 100° and 120° for 20-30 hr. until gas evolution ceased. The pale yellow solid residue was vanadium trifluoride. (Found: V, 47.4; F, 52.8. Calc. for VF₃: V, 47.3; F, 52.7%). The -78° trap contained vanadium pentafluoride as a white solid which melted to a pale yellow liquid at 20°. (Found: V, 33.5; F, 61.9. Ratio F/V, 4.97/1. Calc. for VF₅: V, 34.9; F, 65.1%. Mp. VF₅: 19.5° (7)).

High temperatures are not required for thermal disproportionation of vanadium tetrafluoride. Samples of vanadium tetrafluoride sealed in dry glass tubes initially at atmospheric pressure rapidly formed an excess internal pressure of gas. The bright green solid became noticeably darker in colour, eventually becoming a dark brown powder. Analysis of a sample of vanadium tetrafluoride which had been kept for about 10 days at room temperature showed that 7.5% of the vanadium was present as V (III) (Found: V, 41.6%).

(v) The Sublimation of Vanadium Tetrafluoride

During one pyrolysis in vacuum at 100°, as described above, the cool portion of the silica tube, i.e. the narrow neck leading to the spray trap and vacuum line, became completely blocked with a glassy dark green solid, which was identified as slightly impure vanadium tetrafluoride (Found: V, 41.5%). The appearance and location of the green deposit indicated that it could only have been formed by sublimation
of the vanadium tetrafluoride. This sublimed solid showed an X-ray powder pattern identical to that of the lime-green powdered vanadium tetrafluoride obtained from the tetrachloride.

(vi) The X-ray Diffraction of Powdered Vanadium Tetrafluoride

The X-ray diffraction diagrams of powdered vanadium tetrafluoride, sealed in thin walled glass capillaries, were taken on the unit described earlier. The diffraction diagrams obtained (a) from several preparations of vanadium tetrafluoride from the tetrachloride and hydrogen fluoride (b) from the sublimed product mentioned above, (c) from two samples from the fluorination of vanadium metal at 200° C and, finally, (d) from the residue from impure vanadium pentfluoride were essentially identical. In no case was the resolution of lines with diffraction angles greater than 45° exceptionally good. In all pictures certain lines were sharp, and certain lines were diffuse.

A typical set of data for vanadium tetrafluoride is given in Table 20. The hkl indices were assigned on the basis of a hexagonal unit cell of dimensions \(a = 5.37\) A, \(c = 5.16\) A, containing two molecules per unit cell \((\rho_{\text{calc.}} = 3.28 \text{ g/cc}; \rho_{\text{exp.}} = 3.15 \pm 0.15 \text{ g/cc.})\). Numerical intensity values for the lines on the photograph were measured with a Hilger and Watts FA-17 photometer, equipped with a Leeds and Northrup "Speedomax G" recording potentiometer. Where the lines were too weak to measure with the photometer visual estimates of intensity were made.
### TABLE 20

X-RAY DIFFRACTION DATA FOR VF$_4$

(Hexagonal System)

<table>
<thead>
<tr>
<th>hkl</th>
<th>$Q_{(\text{calc})}$</th>
<th>$1/a^2_{(\text{obs})}$</th>
<th>Approximate Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>001</td>
<td>0.0376</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100</td>
<td>0.0462</td>
<td>0.0475</td>
<td>38</td>
</tr>
<tr>
<td>101</td>
<td>0.0838</td>
<td>0.0862</td>
<td>100</td>
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<td>0.1386</td>
<td>0.1433</td>
<td>32</td>
</tr>
<tr>
<td>002</td>
<td>0.1504</td>
<td>0.1527</td>
<td>w</td>
</tr>
<tr>
<td>200</td>
<td>0.1848</td>
<td>0.1867</td>
<td>45</td>
</tr>
<tr>
<td>102</td>
<td>0.1962</td>
<td>0.1990</td>
<td>64</td>
</tr>
<tr>
<td>201</td>
<td>0.2224</td>
<td>0.2252</td>
<td>92</td>
</tr>
<tr>
<td>112</td>
<td>0.2890</td>
<td>0.2938</td>
<td>185</td>
</tr>
<tr>
<td>003</td>
<td>0.3390</td>
<td>0.3393</td>
<td>144</td>
</tr>
<tr>
<td>202</td>
<td>0.3352</td>
<td></td>
<td></td>
</tr>
<tr>
<td>211</td>
<td>0.3614</td>
<td>0.3619</td>
<td>314 (broad and diffuse)</td>
</tr>
<tr>
<td>103</td>
<td>0.3852</td>
<td>0.3872</td>
<td>118</td>
</tr>
<tr>
<td>300</td>
<td>0.4158</td>
<td>0.4167</td>
<td>19</td>
</tr>
<tr>
<td>220</td>
<td>0.4624</td>
<td>0.4616</td>
<td>vw.</td>
</tr>
<tr>
<td>113</td>
<td>0.4773</td>
<td>0.4790</td>
<td>126</td>
</tr>
<tr>
<td>212</td>
<td>0.4738</td>
<td></td>
<td></td>
</tr>
<tr>
<td>302</td>
<td>0.5662</td>
<td>0.5675</td>
<td>7</td>
</tr>
<tr>
<td>311</td>
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<td>0.6382</td>
<td></td>
</tr>
<tr>
<td>104</td>
<td>0.6478</td>
<td>0.6515</td>
<td>30 (broad and diffuse)</td>
</tr>
<tr>
<td>213</td>
<td>0.6624</td>
<td>0.6633</td>
<td>23</td>
</tr>
<tr>
<td>303</td>
<td>0.7548</td>
<td>0.7575</td>
<td>vw.</td>
</tr>
<tr>
<td>204</td>
<td>0.7860</td>
<td>0.7890</td>
<td>vww.</td>
</tr>
<tr>
<td>214</td>
<td>0.9250</td>
<td>0.9286</td>
<td>vww.</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\sqrt{\frac{4}{3} \left( \frac{h^2 + hk + k^2}{Q_{hk0}} \right)} &= \sqrt{\frac{4}{3} \frac{1}{Q_{100}}} = \sqrt{\frac{4}{3} \frac{1}{0.0462}} = 5.37 \text{ Å} \\
\sqrt{\frac{1}{Q_{001}}} &= \sqrt{\frac{1}{0.0376}} = 5.16 \text{ Å}
\end{align*}
\]

Volume of unit cell ($V$) $a^2c \sin 60^\circ = 128.9 \text{ Å}^3$

\[
\varrho = \frac{MZ \times 1.66 \times 10^{-24}}{V \times 10^{-24}} = 3.28 \text{ g./cc, for } Z = 2,
\]

ie. 2 molecules per unit cell; $M =$ molecular wt. $= 127$. 

\[\text{a} = \sqrt{\frac{4}{3} \left( \frac{h^2 + hk + k^2}{Q_{hk0}} \right)} = \sqrt{\frac{4}{3} \frac{1}{Q_{100}}} = \sqrt{\frac{4}{3} \frac{1}{0.0462}} = 5.37 \text{ Å} \]

\[\text{c} = \sqrt{\frac{1}{Q_{001}}} = \sqrt{\frac{1}{0.0376}} = 5.16 \text{ Å} \]
CHEMICAL PROPERTIES OF VANADIUM TETRAFLUORIDE

(i) Reaction of Vanadium Tetrafluoride with Selenium Tetrafluoride

An excess of selenium tetrafluoride was distilled into a silica vessel containing vanadium tetrafluoride (0.88 g., 6.9 m. mole) and refluxed at atmospheric pressure (b.p. 106° (101)) for 15 minutes. An orange-brown solid was formed which was partially soluble in selenium tetrafluoride. Cooling the trap to room temperature and removing unreacted selenium tetrafluoride in vacuum left 1.903 g. of a light brown solid which was identified as the 1:1 adduct \( \text{SeF}_4 \cdot \text{VF}_4 \) (Found: Se, 28.5; V, 18.2; F, 50.6. \( \text{SeVF}_8 \) requires: Se, 28.0; V, 18.1; F, 53.9%. Weight expected for 1:1 adduct 1.95 g.).

The magnetic susceptibility of the \( \text{VF}_4 \cdot \text{SeF}_4 \) adduct was determined over the range 88° to 295°K as for vanadium tetrafluoride. The results, given in Table 21, show that the susceptibility obeys the Curie-Weiss law. The magnetic moment of the adduct at 295°K, calculated from the Curie law, is 1.86 Bohr magnetons, and from the Curie-Weiss law, is 2.3 Bohr magnetons.
(ii) **Reaction of Vanadium Tetrafluoride with Ammonia**

A large excess of anhydrous ammonia (Matheson Co.) was condensed on to vanadium tetrafluoride. On melting the ammonia an orange-brown slurry was formed. Removal of excess ammonia and heating the remaining solid to 100° in vacuum yielded a buff solid, amminotetrafluorovanadium (IV) (60) (Found: V, 35.5. Calc. for NH₃VF₄: V, 35.4%). The compound readily gave a brown aqueous solution which, when acidified, could be titrated for vanadium (IV) with standard potassium permanganate. The magnetic moment of amminotetrafluorovanadium (IV) was 1.83 Bohr magnetons at 293°K.

### TABLE 21

**THE MAGNETIC SUSCEPTIBILITY OF THE VF₄·SeF₄ ADDUCT**

<table>
<thead>
<tr>
<th>T°K</th>
<th>10⁺⁴χ'ₘ</th>
<th>μ&lt;sub&gt;eff&lt;/sub&gt; (Curie-Weiss)</th>
<th>μ&lt;sub&gt;eff&lt;/sub&gt; (Curie)</th>
</tr>
</thead>
<tbody>
<tr>
<td>294.5</td>
<td>15.59</td>
<td>2.32</td>
<td>1.92</td>
</tr>
<tr>
<td>273</td>
<td>16.32</td>
<td>2.31</td>
<td>1.90</td>
</tr>
<tr>
<td>245</td>
<td>17.65</td>
<td>2.32</td>
<td>1.87</td>
</tr>
<tr>
<td>215</td>
<td>18.70</td>
<td>2.29</td>
<td>1.80</td>
</tr>
<tr>
<td>193</td>
<td>20.18</td>
<td>2.31</td>
<td>1.77</td>
</tr>
<tr>
<td>165</td>
<td>21.87</td>
<td>2.29</td>
<td>1.71</td>
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<tr>
<td>138</td>
<td>24.30</td>
<td>2.31</td>
<td>1.64</td>
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<tr>
<td>124</td>
<td>25.88</td>
<td>2.32</td>
<td>1.61</td>
</tr>
<tr>
<td>88</td>
<td>30.15</td>
<td>2.32</td>
<td>1.46</td>
</tr>
</tbody>
</table>

θ = 134°  C = 0.665 cgsu.
(iii) **Reaction of Vanadium Tetrafluoride with Pyridine**

Excess dry pyridine was condensed on to 0.628 g. (4.94 m. mole) of vanadium tetrafluoride. Reaction occurred immediately on melting the pyridine, forming a brown solid. Removal of excess pyridine under vacuum left 1.036 g. (Calc. for $C_5H_5NVF_4$ 1.02 g.) of a grey-pink powder which was identified as $VF_4Py$ (Found: V, 24.7; Calc. for $C_5H_5NVF_4$: V, 24.7%).

Pyridinetetrafluorovanadium (IV) (60) dissolved readily in water to form a green solution which, after acidification, was titrated with standard permanganate solution. Comparison of the titration with permanganate immediately after dissolution with the vanadium analysis showed that all the vanadium was present in the tetravalent state. The magnetic moment of pyridinetetrafluorovanadium (IV) was 1.73 Bohr magnetons at 293°K.

(iv) **Reaction of Vanadium Tetrafluoride with Bromine Trifluoride**

Excess bromine trifluoride (Matheson Co.) was condensed on to 0.55 g. (4.3 m. mole) of vanadium tetrafluoride in a silica vessel. The vanadium tetrafluoride dissolved immediately in molten bromine trifluoride and bromine was liberated. The contents of the reaction vessel, which were completely volatile, were distilled on to 0.324 g. (4.3 m. mole) potassium chloride. Removal of volatile material under vacuum left 0.83 g. of potassium hexafluorovanadate (V) (14). (Found: V, 25.6;
F, 54.0. Calc. for KVF₆: V, 25.0; F, 55.9%. 4.3 m. mole VF₄ requires 0.88 g. KVF₆).

(v) Reaction of Vanadium Tetrafluoride with Fluorine

A mixture of fluorine and nitrogen was passed over vanadium tetrafluoride heated to 100° in a nickel reactor. Reaction began immediately on admission of fluorine and a white solid, identified as vanadium pentafluoride, was condensed in a -78° trap connected to the reactor exit. When evolution of vanadium pentafluoride ceased and the reactor was dismantled, no residue remained in the boat.

(vi) Reaction of Vanadium Tetrafluoride with Nitryl Fluoride

An excess of nitryl fluoride, prepared as described by Aynsley, Hetherington and Robinson (103), was condensed on to vanadium tetrafluoride. The vessel was sealed and kept at -78° to maintain liquid nitryl fluoride in contact with vanadium tetrafluoride. No reaction was evident. Removal of the volatile materials after a period of 47 days left unchanged vanadium tetrafluoride, according to the X-ray powder photograph, plus a small amount of (NO₂)₂SiF₆ resulting from attack of nitryl fluoride on the glass.

In a second experiment iodine pentafluoride was distilled on to vanadium tetrafluoride in a silica vessel, followed by nitryl fluoride. Upon melting, a brown-red suspension formed and vigorous evolution of a gas occurred.
which condensed to a brownish solid. The mixture was maintained at room temperature for one hour, then the excess NO₂F which had escaped was distilled back and held for 30 minutes to ensure as complete a reaction as possible. Removal of the volatile materials left NO₂VF₆ (14) (Found: V, 23.8; Calc. for NO₂VF₆: V, 24.2%). However, the product had a magnetic moment of 0.4 Bohr magnetons at 293°C, indicating contamination of the salt with vanadium trifluoride or tetrafluoride.

(vii) Reaction of Vanadium Tetrafluoride with Sulphur Tetrafluoride

A large excess of sulphur tetrafluoride (Dupont Co.) was distilled into a silica vessel containing vanadium tetrafluoride. Vanadium tetrafluoride did not appear to be soluble in sulphur tetrafluoride and removal of the volatile material in vacuum left unchanged vanadium tetrafluoride. (Found: V, 40.4%).

(viii) Reaction of Vanadium Tetrafluoride with Iodine Pentafluoride

A large excess of iodine pentafluoride (Matheson Co.) was condensed onto vanadium tetrafluoride in a silica vessel. On warming and refluxing the iodine pentafluoride at atmospheric pressure (b.p. 98°C (100)), some vanadium tetrafluoride dissolved yielding a red brown solution. Removal of iodine pentafluoride under vacuum left a dark brown solid which was
shown by analysis (Found: V, 40.5; 40.7%) and X-ray to be unchanged vanadium tetrafluoride.

(ix) Reaction of Vanadium Tetrafluoride with Sulphur Trioxide

Pure, dry α-sulphur trioxide, prepared by dehydrating fuming sulphuric acid with phosphorus pentoxide, was condensed on to vanadium tetrafluoride. On warming the mixture the sulphur trioxide polymerised, but no reaction occurred. Complete removal of the sulphur trioxide under vacuum was difficult and the vanadium tetrafluoride remaining was contaminated with a nonstoichiometric amount of sulphur trioxide.

(x) Reaction of Vanadium Tetrafluoride with Sulphur Dioxide

An excess of anhydrous sulphur dioxide (Matheson Co.) was distilled on to vanadium tetrafluoride and allowed to melt and warm up to its boiling point (-10°). No reaction occurred and no evidence of solution was observed. Removal of sulphur dioxide left unchanged vanadium tetrafluoride (Found: V, 40.4%).

An excess of potassium fluoride, mixed with vanadium tetrafluoride, was allowed to stand in boiling sulphur dioxide for one-half hour. On removal of the sulphur dioxide only a mixture of unreacted potassium fluoride and vanadium tetrafluoride remained, as confirmed by an X-ray diffraction powder photograph.
THE PREPARATION AND PROPERTIES OF HEXAFLUOROVANADATE (IV) SALTS

(i) Preparation of Potassium Hexafluorovanadate (IV) from Vanadium Tetrafluoride

Potassium fluoride and vanadium tetrafluoride (2:1 molar ratio) were mixed in a silica reaction vessel, together with 10 ml. of selenium tetrafluoride. A dark red solution was formed above the mixed solid reactants. After the mixture had stood for 30 minutes at room temperature, the SeF₄ was removed under vacuum and the salt was heated to 150°C for several hours. The residue, a pale pink powder, was potassium hexafluorovanadate (IV) (Found: V, 21.25; F, 47.3. Calc. for K₂VF₆: V, 21.0; F, 46.9%). Titration of a freshly dissolved sample, without prior treatment with sulphur dioxide confirmed that all vanadium was present as vanadium (IV).

(ii) Properties of Potassium Hexafluorovanadate (IV)

The magnetic susceptibility of potassium hexafluorovanadate obeys the Curie-Weiss law in the range 105°C to 296°C. The magnetic moment at 296°C, calculated from the Curie-Weiss law, is 2.05 Bohr magnetons, and from the Curie law is 1.71 Bohr magnetons. The present results, given in Table 22, are similar to those recently reported by Liebe et al. (17) including the 81°C measurement, which in the present case does not fall on the straight line which can be drawn through the points in the range 105°C to 296°C.
### Table 22

The magnetic susceptibility of potassium hexafluorovanadate (IV)

<table>
<thead>
<tr>
<th>(T^\circ K)</th>
<th>(10^4 \chi_M^1)</th>
<th>(\mu\text{-eff (Curie-Weiss)})</th>
<th>(\mu\text{-eff (Curie)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>296</td>
<td>12.56</td>
<td>2.05</td>
<td>1.74</td>
</tr>
<tr>
<td>266</td>
<td>13.42</td>
<td>2.04</td>
<td>1.70</td>
</tr>
<tr>
<td>241</td>
<td>14.16</td>
<td>2.03</td>
<td>1.66</td>
</tr>
<tr>
<td>226</td>
<td>15.01</td>
<td>2.04</td>
<td>1.66</td>
</tr>
<tr>
<td>209</td>
<td>15.47</td>
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<td>1.61</td>
</tr>
<tr>
<td>189</td>
<td>17.03</td>
<td>2.05</td>
<td>1.61</td>
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<tr>
<td>186</td>
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<td>1.48</td>
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<tr>
<td>105</td>
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</tr>
<tr>
<td>83</td>
<td>28.96</td>
<td>2.17</td>
<td>1.39</td>
</tr>
</tbody>
</table>

\(\theta = 118^\circ\)  \(C = 0.515\) cgsu.

The X-ray powder photograph of \(K_2VF_6\) was indexed on the basis of a trigonal unit cell of \(a = 5.68\), \(c = 4.66\), containing one molecule per unit cell. The data, which are given in Table 23 are in agreement with those of Liebe et al. (17). The specific gravity under carbon tetrachloride was found to be 2.5 g./cc., not in very good agreement with the X-ray density of 3.09 g./cc.
## Table 23

X-Ray Diffraction Data for Trigonal $K_2VF_6$

<table>
<thead>
<tr>
<th>hkl</th>
<th>$Q = \frac{1}{d^2}$ (calc.)</th>
<th>$Q = \frac{1}{d^2}$ (obs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.0413</td>
<td>0.0414</td>
</tr>
<tr>
<td>001</td>
<td>0.0466</td>
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</tr>
<tr>
<td>101</td>
<td>0.0873</td>
<td>0.0882</td>
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<tr>
<td>110</td>
<td>0.1239</td>
<td>0.1250</td>
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<tr>
<td>200</td>
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<td>0.5423</td>
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<td>0.5829</td>
<td>0.5848</td>
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<td>400</td>
<td>0.6608 abs.</td>
<td>0.7080</td>
</tr>
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<td>213</td>
<td>0.7031</td>
<td>0.7080</td>
</tr>
<tr>
<td>312</td>
<td>0.7209</td>
<td>0.7249</td>
</tr>
<tr>
<td>320</td>
<td>0.7847</td>
<td>0.7884</td>
</tr>
</tbody>
</table>

\[
a = \sqrt[4]{\frac{1}{3}(h^2 + h k + k^2)} = \sqrt[3]{\frac{1}{3}0.1239} = 5.68 \text{ Å}
\]

\[
c = \sqrt[3]{\frac{1}{Q_{001}}} = 4.66 \text{ Å}
\]

Volume = $a^2 c^2 \sin 120^\circ = 130.3 \text{ Å}^3$

\[
\rho = \frac{1.6604 \times M \times Z}{V} = 3.09 \text{ g./cc. for } Z = 1, \text{ i.e. } 1 \text{ molecule per unit cell. } M = \text{Molecular weight} = 243.
\]
(iii) Attempted Preparation of Other Hexafluorovanadate(IV) Salts

Reaction of caesium fluoride with vanadium tetrafluoride (2:1 molar ratio) in selenium tetrafluoride as above yielded a bright pink powder which tenaciously retained selenium tetrafluoride. After prolonged evacuation with heating, a pale pink powder, which was impure caesium hexafluorovanadate (IV) was obtained (Found: V, 11.6. Calc. for Cs$_2$VF$_6$: V, 11.8%). Direct titration of a freshly dissolved sample indicated that not all the vanadium was present as vanadium (IV). The magnetic moment was 2.48 Bohr magnetons at 293°K. The X-ray powder photograph indicated hexagonal Cs$_2$VF$_6$, plus impurity lines which could have been due to CsVF$_6$ and possibly Cs$_3$VF$_6$ or Cs$_2$VF$_5$.

Potassium fluoride and vanadium tetrafluoride (2:1 molar ratio) were reacted in iodine pentafluoride (Matheson Co.) solution. The pale pink product contained much free iodine and was a mixture of K$_2$VF$_6$ and KVF$_6$ (Found: V, 20.6. Calc. for K$_2$VF$_6$: V, 21.0. Calc. for KVF$_6$: V, 25.0%). Titration of a freshly dissolved sample indicated that about 20% of vanadium was present as vanadium (V) (Found: V, 15.8, Ratio V(V)/V (total): 0.77/1.). The magnetic moment was 1.15 Bohr magnetons at 296°K. The X-ray powder photograph showed lines which could have been due to both K$_2$VF$_6$ and KVF$_6$.

Caesium fluoride and vanadium tetrafluoride (2:1 molar ratio) were also reacted in IF$_5$. The pink product was a
mixture of Cs$_2$VF$_6$ and CsVF$_6$ (Found: V, 11.4. Calc. for Cs$_2$VF$_6$: V, 11.8. Calc. for Cs$_2$VF$_6$: V, 17.1%). Titration of a freshly dissolved sample indicated a pentavalent vanadium content of about 35% (Found: V(IV), 7.65. Ratio V(IV)/V (total): 0.67/1). The magnetic moment was 1.27 Bohr magnetons at 293°K.

When calcium or barium fluoride were mixed with vanadium tetrafluoride (1:1 molar ratio) in iodine pentafluoride solution, the green solid product was found by X-ray powder photography to consist of the unchanged reactants.

The reaction of an equimolar mixture of potassium fluoride and vanadium tetrafluoride in iodine pentafluoride gave a non-homogeneous product which, according to the X-ray powder photograph, appeared to be a mixture of K$_2$VF$_6$ and unreacted vanadium tetrafluoride.

THERMOCHEMISTRY OF VANADIUM FLUORIDES

(i) The Calorimeter

A solution calorimeter was constructed from a simple Parr bomb calorimeter. The metal internal vessel and bomb assembly were removed and replaced with a one litre polyethylene vessel and a hollow shaft brass stirrer. The brass stirrer shaft passed through a hole in the lid of the calorimeter and a large aluminum wheel was affixed to the stirrer shaft, where it emerged from the calorimeter, by means of a set screw in the
wheel. The depth of immersion of the stirrer could be varied by adjusting the position of the aluminum wheel on the shaft. Polyethylene bearings were provided in the lid of the calorimeter to hold the stirrer shaft firmly in position so as to obtain smooth stirring with a minimum of friction. Since independent adjustment of the position of the stirrer blades on the shaft was also desirable, the blades were fixed to a collar which was held in position on the shaft by means of a set screw. A small electric motor, fixed to the outer wall of the calorimeter with an insulating bracket was used to drive the stirrer. A belt drive was used between the motor and the aluminum wheel at the top of the stirrer shaft to minimize heat transfer to the stirrer. The original bakelite double-walled calorimeter jacket was unchanged although additional insulation in the form of cotton wool was provided around the inner vessel because it was somewhat smaller than the original vessel.

An eight ohm heater, consisting of nichrome wire wound about a polyethylene tube was immersed in the plastic calorimeter vessel. In determining the water equivalent of the system the bare wires could be exposed to the water in the vessel without effect. In vanadium fluoride solution however, passage of current resulted in electrochemical corrosion of the nichrome wire which produced changes in the resistance of the heater. To combat this difficulty a very thin coating of paraffin was applied to the heater wire. This was sufficient
to prevent corrosion of the wire but had little effect on the heat transfer to the solution. The current was supplied to the heater from a freshly charged 12 volt lead storage cell and this current was measured by determining with a potentiometer the potential difference across an accurately measured standard resistor of manganin wire. A stopwatch graduated to 0.2 sec. was used for time measurements.

The temperature was measured with a standard Beckmann thermometer, graduated to 0.01° C. Since the presence of glass in the solution was undesirable, because of the possibility of a side reaction between the hydrofluoric acid produced in the hydrolysis reaction and the glass, the part of the Beckmann thermometer which was immersed in the solution was coated with a thin film of paraffin, which was sufficient to prevent attack on the glass but with little effect on the thermal response of the thermometer.

Because a slightly different sample delivery system was used for each compound studied, it was necessary to determine the water equivalent for each system. Typically, a known amount of heat (Q), calculated from time and electrical measurements according to the expression \( Q = 0.2389RI^2t \) (where \( R \) is the heater resistance in ohms, \( I \) is the current in amps and \( t \) is the time in seconds) was delivered to the calorimeter by means of the heater coil, and the increase in temperature measured by means of the Beckmann thermometer. A graph of temperature (in arbitrary degrees C) against time was prepared.
for each measurement and used to correct the temperature increase for heat losses during heating by extrapolating the cooling curves and measuring on the graph, the temperature increase at the mid-point of the heating period (104). The water equivalent (WE) was calculated from the expression:

\[ WE = \frac{Q - (W \times s \times \Delta T)}{\Delta T} \]

(where \( Q \) is the heat applied in calories, \( W \) is the weight of water in grams, \( s \) is the specific heat of the solution and \( \Delta T \) is the temperature change in degrees). A constant weight of water, measured on the same balance, was used for every measurement of the water equivalent, heat of hydrolysis and specific heat of the resultant solution.

The specific heat was determined for each solution immediately after the hydrolysis of the vanadium compound, by the same procedure as outlined above for the water equivalent. Time-temperature graphs were used to determine \( \Delta T \) as before. Two measurements were made on each solution and the specific heat was calculated from the expression

\[ s = \frac{Q - (WE \times \Delta T)}{Wt \times \Delta T} \]

where \( s \), \( Q \), \( WE \), and \( \Delta T \) are as before and \( Wt \) is now the weight of solution resulting from the hydrolysis.

(ii) The Heat of Hydrolysis of Vanadium Tetrafluoride

The sample holder designed for powdered solids such as vanadium tetrafluoride is shown in Figure 3. It consisted of a 13 mm. diameter brass tube approximately 6 cm. long, the top of which could be screwed into the base of the hollow stirrer shaft. A 0.01 mm. Parafilm 'M' (Marathon Chemical Co.) diaphragm was sealed to the bottom of the container by means
FIG. 3
SAMPLE HOLDERS for $V_F_5$ and $V_F_4$

$V_F_5$

- $\frac{3}{10}/30$ CONE
- BREAKSEAL
- 10 mm PYREX TUBE 5 cm long
- 5 mm thin walled 316 stainless steel 135 cm long
- CAPILLARY SEAL OFF
- 5 mm tube
- KOVAR-PYREX SEAL
- LIQUID CONTAINER 3 cm long
- PLATINUM DIAPHRAGM 0.002 mm thick
- STIRRER SHAFT
- PIERCING DEVICE FOR $V_F_5$
- SPIKE - 15 mm long
- FRAME 30 mm dia.

$V_F_4$

- POLYETHYLENE PLUNGER - 11 mm dia.
- TO FIT STIRRER SHAFT
- POWDER SAMPLE HOLDER 60 mm long
- SPIKE
- PARAFILM DIAPHRAGM 0.010 mm thick
of a wide threaded flange and compression nut. A close fitting polyethylene plug containing a sharp spike for piercing the diaphragm was inserted into the top of the sample tube. With the polyethylene plug and the Parafilm diaphragm in place a completely enclosed volume of about 3 ml. was available for the solid sample.

A typical determination of the heat of hydrolysis of vanadium tetrafluoride was done as follows.

The sample holder was carefully dried and weighed with the polyethylene plunger and Parafilm diaphragm in place. In the dry-box, the Parafilm diaphragm was removed and about two grams of vanadium tetrafluoride were loaded into the tared sample holder. The diaphragm was then replaced and the sample holder reweighed. The sample container was then screwed to the base of the stirrer shaft; and immersed into the calorimeter vessel, which already contained a weighed amount of water. The system was then allowed to reach thermal equilibrium.

At the appropriate moment the polyethylene plug was pushed through the sample holder by means of a long fibre rod which reached down the hollow stirrer shaft. The spike held in the plug pierced the diaphragm and the plug was forced into the solution pushing all of the solid into the water. When the plug left the holder, the solution entered and washed the inner walls free of any traces of vanadium tetrafluoride that may have adhered to them. In this manner complete solution of the solid was ensured. Temperature readings were taken at one minute intervals before and after the vanadium tetrafluoride
was hydrolyzed and the temperature increase upon hydrolysis was corrected for heat losses to the surroundings by the graphical procedure used above. Four measurements of the heat of hydrolysis of vanadium tetrafluoride were made and the results are given in Table 24.

The specific heat was determined with two runs on each resultant solution, and the average value for all experiments, $0.985 \pm 0.002 \text{ cal.g}^{-1}\text{deg}^{-1}$, was used in the calculations.

The solutions were titrated for vanadium with standard 0.01N potassium permanganate solution after each experiment and the results indicated that all the vanadium had dissolved as vanadium (IV). The vanadium analyses were within 0.5 of the theoretical value of 40.3% vanadium for vanadium tetrafluoride.

### Table 24

**HEAT OF HYDROLYSIS OF VANADIUM TETRAFLUORIDE**

<table>
<thead>
<tr>
<th></th>
<th>1.</th>
<th>2.</th>
<th>3.</th>
<th>4.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. of VF$_4$(g.)</td>
<td>2.7763</td>
<td>2.3875</td>
<td>2.1476</td>
<td>2.3377</td>
</tr>
<tr>
<td>Wt. of water(g.)</td>
<td>956.2</td>
<td>956.25</td>
<td>956.2</td>
<td>956.2</td>
</tr>
<tr>
<td>% V (by titration)</td>
<td>39.7</td>
<td>40.0</td>
<td>40.5</td>
<td>40.0</td>
</tr>
<tr>
<td>Water equivalent of calorimeter(cal./deg.)</td>
<td>49.5 ± 0.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta T$ (graphical) (degrees)</td>
<td>0.601</td>
<td>0.522</td>
<td>0.471</td>
<td>0.509</td>
</tr>
<tr>
<td>Heat liberated by wt. of VF$_4$(cal.)</td>
<td>597.45</td>
<td>518.74</td>
<td>467.92</td>
<td>505.77</td>
</tr>
<tr>
<td>Heat liberated per mole(cal.)</td>
<td>27,330</td>
<td>27,593</td>
<td>27,671</td>
<td>27,476</td>
</tr>
</tbody>
</table>
The average heat of hydrolysis of vanadium tetrafluoride is:

$$\Delta H_{\text{hyd}} = -27,520 \text{ cal.}$$

The standard deviation shown by the results is $\pm 120 \text{ cal}.$

The results were quite reproducibility, as indicated by the low value of $\pm 120 \text{ cal}$ for the standard deviation. Considering the possibility that unknown errors may arise in the experiment the results are to be considered reliable to within $\pm 0.5 \text{ kcal}$ or about 1.5%.

(iii) The Heat of Hydrolysis of Vanadium Pentafluoride

Since vanadium pentafluoride is a liquid at 25°, the sample holding device described for vanadium tetrafluoride could not be used. The sample holder designed for liquid vanadium pentafluoride is shown in Figure 3. The sample was contained in an approximately 2 ml. cylindrical stainless steel chamber, 6 mm. internal diameter and 30 mm. long which was attached to a 13 cm. long, 4 mm. diameter thin-walled stainless steel tube. A platinum diaphragm, 0.002 mm. thick, was welded to the bottom of the sample chamber to provide a vacuum tight seal. The top of the long stainless steel tube was welded to a Kovar-Pyrex graded seal. Glass was used at the top of the sample holder to simplify the manipulations required to introduce vanadium pentafluoride into the sample holder. There was no danger of an etching reaction occurring in the presence of the glass during the hydrolysis because the glass portions of the apparatus were not in contact with the resulting solution.
The glass end of the graded seal was sealed to a break-seal and a capillary constriction inlet. The sample holder was connected to the vanadium pentafluoride supply system by means of a B-10 joint attached to the arm of the holder with the capillary constriction. The B-10 joint was sealed with a Teflon sleeve, lightly smeared with fluorocarbon grease. An inner tube passed through the joint to minimize contact of the vanadium pentafluoride with the greased joint.

The weighed sample holder was evacuated and carefully dried. About one gram of vanadium pentafluoride was distilled into the sample holder which was then sealed off at the capillary constriction and reweighed. The sample holder containing the vanadium pentafluoride was then suspended in the calorimeter vessel, through the hollow shaft of the stirrer, and the system was permitted to come to thermal equilibrium with the standard sodium hydroxide solution contained in the calorimeter vessel.

Below the diaphragm a small sharp spike was held in a vertical position in a nichrome frame, as shown in Figure 3. The frame was fixed to the bottom of the stirrer shaft by means of a threaded brass collar so that the spike was held concentric with the stirrer shaft, and thus with the sample holder which was held in the hollow stirrer shaft.

When thermal equilibrium had been reached, a slight pressure of dry nitrogen was applied at the top of the sample holder and the breakseal was broken. The sample holder was
then gently forced down onto the sharp spike, rupturing the platinum diaphragm and allowing the nitrogen to force the vanadium pentafluoride into the sodium hydroxide solution. The nitrogen pressure was then released and a little suction applied to pull the solution up to the top of the metal part of the container and thus hydrolyze any vanadium pentafluoride adhering to the walls of the container. The sample system was then opened to the atmosphere and the water level in the holder was allowed to come to equilibrium with the level in the calorimeter vessel. Temperature measurements were taken at one minute intervals for several minutes before and after hydrolysis, and the temperature rise on hydrolysis was corrected for heat losses to the surroundings by the graphical method used above. Four determinations of the heat of hydrolysis of vanadium pentafluoride were done in the above manner. The results are shown in Table 25.

Specific heat measurements were made on each of the resultant solutions and the average result of six experiments on the four solutions, \(0.978 \pm 0.005 \text{ cal g}^{-1} \text{deg}^{-1}\) was used in subsequent calculations of the heat of hydrolysis of vanadium pentafluoride.

The normality of the resultant alkaline vanadate solutions was determined by titrations with standard 0.1N hydrochloric acid solution and the amount of vanadium pentafluoride dissolved was calculated from the difference between the initial and final normalities according to the
hydrolysis scheme:

$$\text{VF}_5(\text{l}) + 60\text{H}^- (\text{aq}) \rightarrow \text{VO}_3^- (\text{aq}) + 5\text{F}^- (\text{aq}) + 3\text{H}_2\text{O}.$$  

The solutions were also analysed for vanadium. The results for two solutions were about 2% higher than the 35.0% vanadium expected for pure vanadium pentafluoride. Two other solutions agreed well with the expected result for vanadium pentafluoride. The analytical figures for vanadium were also used to calculate the weight of vanadium pentafluoride which had been dissolved. In all cases the weight of vanadium pentafluoride calculated from the vanadium analysis agreed with the weight of vanadium pentafluoride calculated from the neutralization of sodium hydroxide as above, however only in experiments 3 and 4 did this agree with the weight of vanadium pentafluoride determined by the gross and tare weights of the sample holders both before and after hydrolysis. The reason for this discrepancy is not known, but it does not appear to affect the heat of hydrolysis in a systematic manner, because solutions with higher vanadium concentrations than expected gave heats of hydrolysis both higher and lower than those solutions which gave the expected concentrations of vanadium. Therefore the error resulting from this source can not be estimated, and is probably included in the standard deviation of the results.

Titration of the vanadate solutions immediately after the hydrolysis experiment indicated no detectable amounts of reduced species such as tetravalent vanadium.
TABLE 25

THE HEAT OF HYDROLYSIS OF VANADIUM PENTAFLUORIDE

<table>
<thead>
<tr>
<th>Wt. NaOH Solution (g)</th>
<th>1.</th>
<th>2.</th>
<th>3.</th>
<th>4.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. ( \text{VF}_5 ) in sample container (g)</td>
<td>0.9993</td>
<td>0.9971</td>
<td>1.0891</td>
<td>1.1552</td>
</tr>
<tr>
<td>Initial normality NaOH Solution (N)</td>
<td>0.1845</td>
<td>0.1845</td>
<td>0.1115</td>
<td>0.1115</td>
</tr>
<tr>
<td>Final normality NaOH Solution (N)</td>
<td>0.1370</td>
<td>0.1370</td>
<td>0.0610</td>
<td>0.0595</td>
</tr>
<tr>
<td>Wt. ( \text{VF}_5 ) dissolved (calc. from normality change) (g)</td>
<td>1.05</td>
<td>1.07</td>
<td>1.12</td>
<td>1.15</td>
</tr>
<tr>
<td>%V by titration with ( \text{KMnO}_4 )</td>
<td>37.0</td>
<td>37.2</td>
<td>35.7</td>
<td>35.0</td>
</tr>
<tr>
<td>Water equivalent (cal/deg)</td>
<td>-</td>
<td>79±1</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>( \Delta T ) (graphical) (°C)</td>
<td>1.000</td>
<td>1.014</td>
<td>1.110</td>
<td>1.145</td>
</tr>
<tr>
<td>Heat evolved by wt. of ( \text{VF}_5 ) (cal.)</td>
<td>960.18</td>
<td>973.62</td>
<td>1062.65</td>
<td>1099.58</td>
</tr>
<tr>
<td>Heat evolved per mole of ( \text{VF}_5 ) (cal.)</td>
<td>140,284</td>
<td>142,562</td>
<td>142,454</td>
<td>138,970</td>
</tr>
</tbody>
</table>

The average heat of hydrolysis of vanadium pentfluoride is:

\[ \Delta H_{\text{hyd}} = -141,100 \text{ cal.} \]

The standard deviation of the results is ± 1,750 cal.

The standard deviation in the hydrolysis of vanadium pentafluoride appears to be much higher than that for vanadium tetrafluoride, but the greater magnitude of the heat of hydrolysis of the former results in the relative errors being
comparable. The standard deviation of $\pm 1.8$ kcal in 141 kcal observed in the heat of hydrolysis of vanadium pentafluoride represents a relative error of about 1%, whereas the errors in the vanadium tetrafluoride hydrolysis were $\pm 0.12$ kcal in 27 kcal, or about 0.5%. The larger error in the hydrolysis of vanadium pentafluoride reflects the greater difficulties encountered in dissolving a reactive volatile liquid compared with a solid. It is estimated as before that unknown sources of error will possibly contribute additional errors of comparable magnitude to the error already appearing in the standard deviation, so the results are probably reliable to $\pm 3$ kcal or 2%.

(iii) The Heat of Hydrolysis of Vanadium Tetrachloride

Since there is no danger of attack of glass in the hydrolysis of a chloride, a glass sample holder was used. The sample was contained in a bulb of about 3 ml. capacity with a fragile glass tip at the bottom and a breakseal at the top. The breakseal was sealed to a 25 cm. length of 8 mm. tubing so that it could be suspended in the calorimeter through the hollow stirrer shaft. Vanadium tetrachloride, prepared as described previously, was distilled into tared sample holders through the fragile glass tip, the fractions distilling between $152^\circ$ and $154^\circ$ being taken. The sample containers were sealed at atmospheric pressure, weighed and immersed in the calorimeter, through the hollow stirrer shaft,
with the top end of the long 8 mm. tube emerging from the hollow shaft. The bulb containing the vanadium tetrachloride was then sitting in the calorimeter vessel which contained a tared amount of water. The system was allowed to reach thermal equilibrium.

A slight pressure of nitrogen gas was applied through the tube emerging from the calorimeter, and the breakseal was broken to admit the nitrogen to the sample vessel. The fragile tip of the sample bulb was broken by jerking the holder upwards against the end of the stirrer shaft. The extra pressure of nitrogen in the sample container forced the vanadium tetrachloride into the water and prevented the hydrolysis products from blocking the exit of the sample container. The nitrogen pressure was released and the water allowed to flow into the container to remove any last traces of vanadium tetrachloride. This technique is similar to that used by Ruff and Freidrich (85) in their studies of the heat of hydrolysis of vanadium tetrachloride in alkaline peroxide solution.

Four determinations of the heat of hydrolysis were made and the results are shown in Table 26. Temperatures were corrected graphically for heat loss to the surroundings as before. The specific heat of each resultant vanadyl chloride solution was determined immediately after the hydrolysis experiment and the average value for six determinations, 0.980±0.005 cal.g.⁻¹.deg.⁻¹, was used in subsequent calculations of the heat of hydrolysis. The solutions were analyzed after each experiment and the results were found to be within 0.6
of the theoretical value of 26.4% vanadium expected for vanadium tetrachloride. All the results were slightly high which may indicate that the weight of water taken, while it is constant and reproducible throughout, is not exactly known. This will not affect the calorimetric values because the apparatus was calibrated with the same amount of water as is used in the hydrolysis experiments, hence any deviation of the measured weight of water from the true weight will be incorporated into the water equivalent of the system.

**TABLE 26**

**HEAT OF HYDROLYSIS OF VANADIUM TETRACHLORIDE**

| Wt. of VCl₄ (g.) | 2.5098 | 2.3686 | 2.5000 | 2.0053 |
| Wt. of H₂O (g.) | 900.0 | 900.0 | 900.0 | 900.0 |
| %V          | 26.6 | 27.0 | 26.7 | 26.9 |
| Water equivalent (cal. deg.) | 99 | 95.3 | 95.3 | 95.3 |
| ΔT(graphical)(deg.) | 0.899 | 0.858 | 0.903 | 0.740 |
| Heat liberated by wt. of VCl₄ (cal.) | 884.1 | 840.5 | 884.7 | 724.9 |
| Heat liberated per mole VCl₄ (cal.) | 67,994 | 68,488 | 68,302 | 69,650 |

The average heat of hydrolysis of vanadium tetrachloride is:

\[ \Delta H_{\text{hyd}} = -68,630 \text{ cal.} \]
The standard deviation of the results is $\pm 440$ cal., or approximately 0.6%. The fairly low standard deviation indicates that the use of nitrogen gas to force the vanadium tetrachloride from the sample container into the solution does not introduce excessively large errors. Unevaluated errors will probably double this error as before, hence the results are probably reliable to $\pm 1$ kcal or about 1.3%.
APPENDIX: THE THERMOCHEMISTRY OF THE VANADYL ION

The measured heat of hydrolysis of vanadium tetrachloride (reaction a) in water was combined with the standard heat of formation of vanadium tetrachloride (reaction b) and the thermochemical cycle completed by reactions (c) to (e) to give a reaction (g) representing the previously unknown standard heat of formation of the VO$^{++}$(aq) ion.

\[
\begin{align*}
(a) \quad & \text{VCl}_4(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{VO}^{++}(\text{aq}) + 2\text{H}^+(\text{ag}) + 4\text{Cl}^- \\
(b) \quad & \text{V}(\text{c}) + 2\text{Cl}_2(\text{g}) \rightarrow \text{VCl}_4(\text{l}) \\
(c) \quad & 4\text{Cl}^-(\text{aq}) + 4\text{H}^+(\text{aq}) \rightarrow 2\text{Cl}_2(\text{g}) + 2\text{H}_2(\text{g}) \\
(d) \quad & \text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}) \\
(e) \quad & \text{H}_2(\text{g}) \rightarrow 2\text{H}^+(\text{aq})
\end{align*}
\]

The addition of reactions (a) to (e) together results in reaction (g):

\[
(g) \quad \text{V}(\text{c}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{VO}^{++}(\text{aq}) ,
\]

which is the formation reaction for the aqueous vanadyl ion from its elements in their standard states. The heat of reaction (g) which is the heat of formation of VO$^{++}$(aq), is given by the expression:

\[
H_g = H_a + H_b + H_c + H_d + H_e.
\]

The required data for the calculation of $H_g$ are shown in Table 27.
TABLE 27
STANDARD HEAT OF FORMATION OF THE VO^{2+}(aq) ION

<table>
<thead>
<tr>
<th>Heat of reaction</th>
<th>Description</th>
<th>Numerical Values</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_a$</td>
<td>heat of hydrolysis of VCl_4</td>
<td>-68.6</td>
<td>Present work. (Table 26)</td>
</tr>
<tr>
<td>$H_b$</td>
<td>$\Delta H^\circ (\text{VCl}_4)$</td>
<td>-136</td>
<td>84</td>
</tr>
<tr>
<td>$H_c$</td>
<td>$-4(\Delta H^\circ (\text{HCl})(aq))$</td>
<td>-4(-40.02)</td>
<td>160</td>
</tr>
<tr>
<td>$H_d$</td>
<td>$\Delta H^\circ (\text{H}_2\text{O}(1))$</td>
<td>-68.32</td>
<td>83</td>
</tr>
<tr>
<td>$H_e$</td>
<td>$\Delta H^\circ (\text{H}^+(aq))$</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

Therefore:

$H_g = -113$ kcal./mole

As before the only errors estimated are those arising from the hydrolysis reaction, which in the case of vanadium tetra-chloride are probably about $\pm 1$ kcal./mole. The heats of formation of each of the ions are the values given at infinite dilution as before. All numerical values are those given for 298°K.

Therefore the heat of formation of the vanadyl ion at 298°K is:

$\Delta H^\circ (\text{VO}^{2+}(aq)) = -113 \pm 1$ kcal./mole.

The standard free energy of formation of VO^{2+}(aq), obtained from measurements on electrochemical cell potentials is;

$\Delta F^\circ (\text{VO}^{2+}(aq)) = -109$ kcal./mole (95).
Substituting this value for \( \Delta F_{\text{f}0} \) and the present value for the heat of formation of the vanadyl ion into the equation,

\[
\Delta F_{\text{f}0} = \Delta H_{\text{f}0} - T \Delta S_{\text{f}0}
\]

gives a value of -13.4 entropy units for the entropy change of formation, \( \Delta S_{\text{f}0} \). The corresponding value for the vanadate (\( \text{VO}_3^- \)) ion is not known (95) therefore comparisons are not possible.

Ruff and Freidrich (85) measured the heat of the reaction

\[
(\text{h}) \text{VO}^{++}(\text{aq}) + \frac{5}{2} \text{OH}^- (\text{aq}) + \frac{1}{2} \text{O}_2 \text{H}^- (\text{aq}) \longrightarrow \text{VO}_3^-(\text{aq}) + \frac{5}{2} \text{H}_2\text{O} + 4\text{Cl}^- (\text{aq})
\]

and found a value of -161 kcal./mole. This can be added to the reverse of the present hydrolysis reaction of vanadium tetrafluoride, (eg. reaction a'),

\[
(\text{a}') \text{VO}^{++}(\text{aq}) + 4\text{Cl}^- (\text{aq}) + 2\text{H}^+ (\text{aq}) \Longleftrightarrow \text{VCl}_4(\text{aq}) + \text{H}_2\text{O}(\text{l})
\]

to yield reaction (j);

\[
(\text{j}) \text{VO}^{++}(\text{aq}) + \frac{5}{2} \text{OH}^- (\text{aq}) + \frac{1}{2} \text{O}_2 \text{H}^- \longrightarrow \text{VO}_3^-(\text{aq}) + \frac{7}{2} \text{H}_2\text{O}(\text{l}),
\]

which represents the oxidation of tetravalent vanadium to pentavalent vanadium in alkaline peroxide solution.

Since the heat of reaction (a') is the negative of the measured heat of hydrolysis of vanadium tetrachloride, that is
\[ H_{f} = 68.6 \text{ kcal./mole}, \] the heat of reaction \( j \) is given by:

\[ H_{j} = H_{h} + H_{a} = -161 + 68.6 = -92.4 \text{ kcal./mole}. \]

Thus the heat of oxidation of tetravalent vanadium to pentavalent vanadium in alkaline peroxide solution is about -92 kcal./mole.
REFERENCES:


65. Machin, D.J., Personal communication.


93. Hoppe, R., Personal communication to N. Bartlett, U.B.C.


