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RADIOTRACER STUDIES OF HETEROGENEOUS LEWIS ACID-BASE REACTIONS

A THESIS PRESENTED TO THE UNIVERSITY OF GLASGOW FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

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DEDICATION

To my wife and my parents without whose help I could not have completed this work.
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SUMMARY

Caesium fluoride has been widely used as a catalyst in a whole range of synthetic reactions. Mechanisms for these and related reactions are usually considered to involve intermediates related to complex fluoro-anions.

The aim of this work was to study the reactions between CsF, a solid Lewis base and several gaseous Lewis acids together with the reactions between the solid Lewis acids AlF₃, NbF₅ and β-UF₅ with SF₄, a Lewis base. This was done in an attempt to determine whether or not molecular analogies are useful in understanding the reactions which occur at metal halide surfaces.

Lewis acid base reactions between the above noted fluorides have been studied under heterogeneous conditions at room temperature, using the radiotracers C¹⁴, F¹⁸ and S³⁵. Surface adsorption of volatile acids or bases is always observed and in many systems additional bulk reactions occur.

Treatment of CsF with (CF₃)₂CO in the presence of MeCN followed by thermal decomposition of the 1:1 adduct formed is one of the methods used to activate CsF for use as a heterogeneous catalyst or reagent. In this work Kr adsorption at activated and untreated CsF has been used together with the reactions of both types of CsF with radiochemically labelled Lewis acids in order to quantify the activation effect.

Activated CsF has a B.E.T. surface area in the range 3.01 - 2.08 m² g⁻¹ (95% confidence limits), compared with 0.31 - 0.19 m²
Chemical analyses of the CsF after activation shows that a small amount of the \( \text{OCF} (\text{CF}_3)_2 \) anion is retained. Reaction results also suggest that activation of CsF produces a porous solid.

Room temperature \(^{18}\text{F} \) exchange between activated CsF and BF\(_2\)\(^{18}\text{F} \) or AsF\(_4\)\(^{18}\text{F} \) is not observed, but reaction to give BF\(_3\)\(^{18}\text{F}^- \) or AsF\(_4\)\(^{18}\text{F}^- \) is rapid, and, in the case of BF\(_3\)\(^{18}\text{F} \), complete. Uptake of AsF\(_4\)\(^{18}\text{F} \) by CsF is smaller due to sintering and due to the constraints upon adsorption of gas imposed by the pore structure. CsBF\(_4\) prepared by this means undergoes no observable room temperature \(^{18}\text{F} \) exchange with BF\(_2\)\(^{18}\text{F} \), but \(^{18}\text{F} \) exchange between BF\(_3\) and BF\(_4^- \) in MeCN is rapid and complete.

\(^{18}\text{F} \) exchange is observed between F\(^{18}\text{FCO} \) and activated CsF, together with the formation of F\(_2\)\(^{18}\text{F} \)CO\(^- \). Experiments carried out using F\(_2\)\(^{14}\text{FCO} \) show that there is more than one adsorbed species present both on the surface of the CsF and in the bulk of the solid.

No \(^{18}\text{F} \) exchange is observed between BF\(_2\)\(^{18}\text{F} \) or AsF\(_4\)\(^{18}\text{F} \) and untreated CsF. The uptakes of gas are far smaller reflecting the smaller surface area. The extent of these reactions is comparable to that between activated CsF and the weaker Lewis acid SF\(_3\)\(^{18}\text{F} \). No room temperature \(^{18}\text{F} \) exchange is observed but \(^{18}\text{F} \) and \(^{35}\text{S} \) experiments enable surface adsorption and bulk reaction to be differentiated. 15% of the surface species are strongly adsorbed SF\(_5^- \) anions. The remainder are weakly adsorbed SF\(_4 \) molecules.
Similar Lewis acid base reactions occur between untreated CsF and SF$_4$, but due to the smaller surface area only the bulk reactions can be conveniently followed. $^{18}$F exchange is observed when SF$_3^{18}$F interacts with NbF$_5$ or AlF$_3$ although experiments with $^{35}$SF$_4$ show that adsorption is weak. Surface species are only observed in the presence of a pressure of $^{35}$SF$_4$, with all surface activity being removed on removal of the gas. The reaction of $^{35}$SF$_4$ with $\beta$-UF$_5$ results in strong adsorption. Previous work has shown that $^{18}$F exchange is observed between SF$_3^{18}$F and $\beta$ - UF$_5$ at room temperature.

The reaction between CO$_2$ and CsF has been the subject of much debate in the literature. In an effort to clarify the situation a radiotracer study was undertaken.

The reaction between CO$_2$ and activated CsF is barely detectable but experiments carried out using $^{14}$CO$_2$ confirm that uptake of gas occurs and that more than one adsorbed species is present on the surface of the CsF.

The results obtained in this work show that molecular analogies can be very useful in describing the reactions which occur at metal halide surfaces.

ooOoo
CHAPTER ONE
INTRODUCTION

In catalysis by supported metals analogies have been made with the chemistry of metal atom clusters and with organometallic compounds in general.

The aim of this work was to examine the usefulness of molecular behaviour in explaining the reactions which occur at metal halide surfaces, in an attempt to determine to what extent molecular analogies are useful in understanding catalysis by metal halide surfaces.

Metal halides can behave as Lewis bases, that is halide ion donors or as Lewis acids, that is halide ion acceptors. Complete transfer of the halide ion is not always observed, resulting in complexes with bridging halides. A brief discussion of some of the chemistry of the fluorides studied in this work is given in sections 1.2 - 1.4. Section 1.1 reviews the various acid-base definitions and includes a more detailed discussion of the proposals of G.N. Lewis.

1.1 ACID-BASE DEFINITIONS

The earliest studies of acids and bases were restricted to aqueous solutions and were made with an inadequate understanding of the peculiarities of water. Arrhenius\(^1\) defined acids as substances which dissociated in water to give hydrogen ions and bases as substances which dissociated to give hydroxide ions. This definition does not hold for solutions in other solvents and does not even give a true representation of the situation in
aqueous solution. Thermodynamic studies have shown that hydration of a free proton is a highly exothermic reaction and hence free H\(^+\) ions are unlikely to exist in any appreciable concentration in water\(^2\). The dissociation of an acid in water is therefore presumed to lead to a hydrated proton H\(^+\)(aq), usually represented by H\(_3\)O\(^+\) and referred to as the hydroxonium ion. When an acid dissociates in anhydrous ethyl alcohol it gives the C\(_2\)H\(_5\)OH\(^+\) cation and in liquid ammonia it gives the NH\(_4\)\(^+\) cation.

Similarly with bases. Sodium hydroxide is a strong base in water giving the hydroxide ion, OH\(^-\), but in anhydrous alcohol the anion present is C\(_2\)H\(_5\)O\(^-\). This anion is also present in solutions of amines in ethyl alcohol. In liquid ammonia the anion present is NH\(_2\)\(^-\).

These examples clearly show that acids and bases cannot be defined simply as substances which dissociate in water to give the ions H\(^+\) and OH\(^-\) respectively.

1.1.1 **LOWRY - BRONSTED THEORY OF ACIDS AND BASES**

In 1923 Lowry\(^3\) and Brönsted\(^4\) independently defined an acid as a compound or ion with a tendency to lose a proton, and a base as a compound or ion with a tendency to gain a proton. This can be expressed by the general equilibrium shown below

\[
A \rightleftharpoons B + H^+
\]

Acid Base + Proton
On losing a proton the acid A becomes a base B. The base will then tend to regain the proton and revert to the acid A. The acid and base arising from this equilibrium are commonly referred to as a conjugate acid - base pair.

The Lowry - Brønsted definition allows for three different types of acid, molecular, cationic and anionic. Molecular acids are those such as hydrochloric and sulphuric which lose protons to give the chloride and hydrogen sulphate ions as conjugate bases. Cationic acids like the hydroxonium and ammonium ions lose protons to give water and ammonia as conjugate bases. Anionic acids are anions such as hydrogen sulphate which lose a proton to form their conjugate base.

The definition also allows for two different types of base. Molecular bases such as ammonia and ethylamine, which combine with protons to give the corresponding cations, and anion bases such as the hydroxide and acetate ions, which combine with protons to give uncharged molecules.

Although this definition applies to a wide range of systems it suffers from two major faults. The acid must contain hydrogen and nothing is specified about the atomic structure of the base.

1.1.2 THE SOLVENT SYSTEM DEFINITION

The solvent system definition was developed from the
fundamental ideas of E.C. Franklin by chemists exploring the chemistry of a number of non aqueous systems. 5

Within this classification an acid is defined as any substance that yields, either by direct dissociation or by interaction with the solvent, the cation characteristic of that solvent. A base is defined as any substance that yields either by direct dissociation or by interaction with the solvent, the anion characteristic of the solvent. Both donor and acceptor acids and bases can be defined. A donor acid is a substance that can split off solvent cations or unite with solvent molecules to form cations. An acceptor acid is a substance that can combine with solvent anions. Similarly for bases, a donor base is a substance that can split off solvent anions or unite with solvent molecules to form anions, and an acceptor base is a substance that can combine with solvent cations.

The solvent system definition is unsatisfactory because acid base phenomena are not restricted to self ionising solvents.

The Arrhenius, Lowry, Brønsted and solvent system definitions of acids and bases all have their faults and are restricted in their application. A much more wide ranging definition was first proposed by G.N. Lewis in 1923 6 and further emphasised in 1938 7.
1.1.3 THE LEWIS ACID-BASE DEFINITION

Lewis defined a basic substance as one "which has a lone pair of electrons which may be used to complete the stable group of another atom," and an acidic substance as one "which can employ a lone pair from another molecule in completing the stable group of its own atoms." He also proposed that one of the main operational criteria of an acid be that a stronger acid be able to displace a weaker acid from its acid base complexes.

The fundamental acid base reaction is the forward step of equilibrium 1.

$$\begin{align*}
A & \quad + \quad B \quad \Rightarrow \quad A : B \\
\text{Acid} & \quad \text{Base} & \quad \text{Adduct}
\end{align*}$$

Equilibria 2 - 4 show the related heterolytic processes which follow from the fundamental relationship.

$$\begin{align*}
A^1 + A^2 : B \quad &\Rightarrow \quad A^2 + A^1 : B \\
B^1: + A : B^2 \quad &\Rightarrow \quad B^2: + A : B^1 \\
A^1: B^1 + A^2: B^2 \quad &\Rightarrow \quad A^1B^2 + A^2B^1
\end{align*}$$

The Lewis definition covers the previously discussed definitions due to Lowry and Brönsted and the solvent system definitions. For example equilibrium 5 shows a typical Brönsted-Lowry acid-base equilibrium. This is equivalent to equilibrium 3 with the proton in 5 representing the Lewis acid in 3.
Similarly for the solvent system's approach.

Equilibrium 6 shows the reaction occurring in liquid ammonia between the solvent system's acid $\text{NH}_4\text{Cl}$ and the solvent system's base $\text{NaNH}_2$.

$$\text{NH}_4^+ + \text{Cl}^- + \text{Na}^+ + \text{NH}_2^- \rightleftharpoons 2\text{NH}_3 + \text{Na}^+ + \text{Cl}^- \quad 6$$

This equilibrium can be rewritten as shown in 7.

$$\text{NH}_4^+ + \text{NH}_2^- \rightleftharpoons \text{NH}_3 + \text{NH}_3 \quad 7$$

The Lewis definitions are widely applicable. Unfortunately they suffer from the absence of a uniform scale of acid or base strengths. Instead these are made variable by dependence upon the reaction or method used for their evaluation hence the evolution of the hard/soft acid/base formalism of R.G. Pearson.

Lewis proposed that a strong acid should be able to displace a weaker acid from its acid base complexes. Accordingly the study of a large number of displacement reactions of the type shown in equation 1.1 should allow an ordering of the strengths of acids in a given series towards a particular base.

$$A^1 + B : A \rightarrow B : A^1 + A \quad \text{equation 1.1}$$
A more quantitative measure may be obtained by measuring the enthalpy change accompanying the following reaction for a series of acids and a reference base.

\[ A + B \rightarrow A : B \]

Based on Hess's Law and the assumption that the displacement that occurs has a negative \( \Delta H \), the order of acidity toward the reference base may be taken as the order of exothermicity of the reaction. In practice this type of reaction has been studied most frequently in solution, occasionally with formation of an insoluble product or reactant or both. Indirectly related properties such as solubilities or sublimation temperatures have also been used as criteria for acidity orders. In these cases differences in solvation energies of products and reactants, or lattice energy effects, or both, may obscure acidity differences. A further complication occurs in the assumption that the order of the acid strength is independent of the reference base. Within recent years it has been shown that the order of acid strengths is indeed affected by the reference base chosen. 9, 10

Fluoride ion affinities are most commonly used when comparing the acidities of inorganic fluorides. There have been several investigations of the relative additives of inorganic fluorides based on fluoride ion affinities. The results of these studies in which a wide variety of approaches and fluoride ion donors have been used are summarised in table 1.1.
<table>
<thead>
<tr>
<th>ORDER</th>
<th>FLUORIDE DONOR</th>
<th>REFERENCE</th>
<th>METHOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{BF}_3 &gt; \text{TaF}_5 &gt; \text{NbF}_5 &gt; \text{TiF}_4 &gt; \text{PF}_5 &gt; \text{SbF}_3 &gt; \text{WF}_6$</td>
<td>HF + xylene</td>
<td>11</td>
<td>Solvent extraction of $\text{ArH}^+ \text{MF}_n^- + 1$</td>
</tr>
<tr>
<td>$&gt; \text{SiF}_4 \sim \text{CrF}_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{AsF}_5 \sim \text{BF}_3 &gt; \text{PF}_5 &gt; \text{WF}_6 &gt; \text{TaF}_5 &gt; \text{SiF}_4$</td>
<td>MF and/or HF</td>
<td>12</td>
<td>Solubility of MF or Lewis acid</td>
</tr>
<tr>
<td>$\sim \text{SbF}_3 \sim \text{CrF}_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{SbF}_5 &gt; \text{AsF}_5 &gt; \text{BF}_3 &gt; \text{PF}_5$</td>
<td>$\text{CF}_3^- \text{SF}_3$</td>
<td>13</td>
<td>Decomposition pressure</td>
</tr>
<tr>
<td>$\text{AsF}_5 &gt; \text{PF}_5 &gt; \text{BF}_3$</td>
<td>$\text{MF}^- x + 1$ in $\text{CH}_2\text{Cl}_2$</td>
<td>14</td>
<td>Displacement reaction</td>
</tr>
<tr>
<td>$\text{SbF}_5 &gt; \text{AsF}_5 &gt; \text{PF}_5 &gt; \text{BF}_3$</td>
<td>HF</td>
<td>15</td>
<td>Cryoscopy conductivity</td>
</tr>
<tr>
<td>$\text{AsF}_3 &gt; \text{BF}_3 &gt; \text{SiF}_4 &gt; \text{AsF}_5 &gt; \text{PF}_5 &gt; \text{PF}_3$</td>
<td>$\text{SF}_6^-$</td>
<td>16</td>
<td>Rate of $\text{F}^-$ Transfer</td>
</tr>
<tr>
<td>$\text{AsF}_5 &gt; \text{BCl}_3 &gt; \text{PF}_5 &gt; \text{BF}_3 &gt; \text{SiF}_4 &gt; \text{AsF}_3 \sim \text{HCl}$</td>
<td></td>
<td>17</td>
<td>Ion cyclotron resonance studies</td>
</tr>
<tr>
<td>$&gt; \text{SO}_2 &gt; \text{SF}_5 \sim \text{SF}_4$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The orders obtained are similar although there are occasional positional changes between studies emphasising the dependance of the order on the fluoride ion donor and reaction method used.

The most recent order of acidities is based on an ion cyclotron resonance study of gas phase ion affinities. The gas phase ion affinity is defined as the negative enthalpy change for the reaction.

\[ A(g) + X^-(g) \rightarrow AX^-(g) \]

All comparisons of Lewis acidity discussed in this work are based on this scale as it is independant of external factors.

Although ion cyclotron resonance studies give an acidity scale which is independant of extraneous factors, the reliability of individual measurements such as F\(^-\) ion affinities will depend on the reliability of ancillary data used in the appropriate enthalpy cycle. An example of this is the disagreement over the fluoride ion affinity of boron trifluoride. Altshuller\(^{16}\) published a value of \(-296\text{ KJ mol}^{-1}\) which was accepted by several authors\(^{17,19}\) as the basis for other fluoride ion affinities and electron affinities. Sharpe\(^{20}\) proposed a value of \(-380\text{ KJ mol}^{-1}\) based on the data of Bills and Cotton.\(^{21}\) Although this value is in agreement with other fluoride ion affinities and electron affinities it was only confirmed in 1983 by Bartlett and coworkers\(^{22}\) who calculated a value of
It is therefore most important to check the validity of all data used in these calculations very carefully.

Although the original Lewis definitions were based on homogeneous systems they can be applied to heterogeneous gas-solid reactions if the acid-base definitions are restated as follows.

A Lewis acid site on a solid surface is a site which has an unoccupied orbital with a high affinity for an electron pair, so that a major decrease in energy is obtained when such a site shares an electron pair donated by an adsorbed base molecule. Lewis base sites on the surface are those which have electron pairs available at a high energy level and a major decrease in energy is obtained if they share this electron pair with an adsorbed electron pair acceptor.

It would seem therefore that the Lewis acid base definitions are the most suitable for describing heterogeneous gas solid reactions, and that ion cyclotron resonance studies give the most reliable measure of Lewis acidity so long as the reliance of the absolute values of fluoride affinities on the accuracy of the data used to calculate them is noted.
The chemistry of the fluorides studied is briefly discussed in section 1.2 to 1.4. As CsF and SF₄ were involved more often than any of the other fluorides, a more detailed review of their properties is presented.

1.2 CHEMISTRY OF THE LEWIS ACIDS

The reactions of the Lewis acids AsF₅, BF₃, and F₂CO with CsF have been studied. In addition to these systems the reactions of AlF₃, NbF₅, CsF and BuF₅ with SF₄ which can behave as both a Lewis acid and a Lewis base have also been studied.

AsF₅, BF₃, CO₂ and F₂CO are all gases at room temperature their Lewis acid strengths increase in the order:

\[
\text{CO}_2 < \text{F}_2\text{CO} < \text{BF}_3 < \text{AsF}_5
\]

AsF₅ and BF₃ are both strong Lewis acids and react readily with fluorides ion donors to form adducts containing the AsF₆⁻ and BF₄⁻ anions respectively. 23, 24

The AsF₆⁻ anion is octahedral as shown in figure 1.1 BF₄⁻ is slightly distorted from tetrahedral symmetry. Figure 1.2 shows the atomic arrangement in \((\text{SF}_3)^+ (\text{BF}_4)^-\). 25

Carbonyl fluoride is a weak Lewis acid which is used in organic synthesis to fluorinate unsaturated compounds. Its reaction with
Figure 1.1 The structure of AsF$_6^-$

Figure 1.2 The structure of BF$_4^-$SF$_3^+$
CsF has been widely studied and it has been shown that if the reaction is carried out in the presence of acetonitrile Cs$^+$ OCF$_3$ is formed.$^{27}$ No reaction has been reported in the absence of acetonitrile.

Spectroscopic studies of the OCF$_3^-$ anion have indicated that it has $C_{3v}$ symmetry. Examination of the band positions indicates that the C-O bond is intermediate between a single and a double bond, thus suggesting that resonance species are involved. This is supported by the x-ray single crystal diffraction analysis of TAS$^+$ CF$_3$O$^-$ (figure 1.3) which shows that the C-F bonds of the CF$_3$O$^-$ anion are exceptionally long and the C-O bond short compared with the corresponding gas-phase experimental values for CF$_3$OR. The C-O bond length approaches that for the C=O bond in CF$_2$=O.

The presence of resonance structures is also indicated by the results of Mulliken population analysis which show that each F in the CF$_3$O$^-$ carries an additional charge. Figure 1.4 shows the four hyperconjugative resonance structures which are proposed to contribute to the bonding in CF$_3$O$^-$.

The reaction between caesium fluoride and CO$_2$ is more complex and the published results have aroused a great deal of controversy.

In 1971 Martineau and Milne$^{30}$ reported the preparation of Cs$_2$CO$_2$F$_2$ from the reaction of CO$_2$ with CsF in acetonitrile.
Figure 1.3 The structure of \( \text{TAS}^+\text{CF}_3\text{O}^- \)

\( \text{TAS} = \text{tris(dimethylamino)} \) sulfonium
Figure 1.4 $\text{CF}_3^-$ Resonance structures
the product being characterised spectroscopically and on the basis of Cs and F analyses.

Subsequent attempts to reproduce these results have not been successful. In 1979 Lawlor and Passmore\textsuperscript{31} suggested that rather than observing the $\text{CO}_2\text{F}^{2-}_2$ anion, Martineau and Milne were in fact observing hydrolysis products caused by the presence of water in their acetonitrile.

Further doubt was cast on the validity of Martineau and Milne's results by David and Ault\textsuperscript{32} in 1985. They carried out a matrix isolation study of the $\text{CO}_2\text{F}^{2-}_2$ anion and their infra-red data did not agree with that of Martineau and Milne. David and Ault explained this disagreement by suggesting like Lawlor and Passmore in 1979 that Martineau and Milne had obtained infra-red spectra of a hydrolysis product rather than of $\text{Cs}_2\text{CO}_2\text{F}_2$.

Both aluminium trifluoride and niobium pentfluoride are white crystalline solids. The $\text{AlF}_3$ unit cell has a distorted hexagonal close packed structure with each aluminium surrounded by three fluorine atoms at a distance of 1.70Å and three at 1.89Å. $\text{NbF}_5$ adopts the molybdenum pentfluoride structure. This consists of tetrameric units containing four metal atoms with four coplanar bridging fluorine atoms as shown in figure 1.\textsuperscript{34} The $\text{AlF}_3$ is involatile at room temperature whereas $\text{NbF}_5$ is slightly volatile and is readily hydrolised by moist air. $\text{NbF}_5$ forms a number of fluorine bridged complexes with Lewis bases such as $\text{SeF}_4$\textsuperscript{23} hence radiotracer studies of $\text{NbF}_5$ with gaseous
Figure 1.5 The structure of NbF$_5$
Lewis bases should provide information on the formation of these fluorine bridged species.

Like caesium fluoride, aluminium trifluoride is a widely used catalyst in organic chemistry so its use in this work allows comparison of the reactions of both a solid Lewis acid, that is AlF$_3$ and a solid Lewis base that is CsF with SF$_4$.

1.3 STRUCTURE AND CHEMISTRY OF SULPHUR TETRAFLUORIDE

SF$_4$ is a colourless gas at room temperature. Its structure is that of a distorted trigonal bipyramid in which two fluorine atoms and the unshared electron pair are in the equatorial positions and the other two fluorines are in the axial positions. (figure 1.6)$^{36,37}$

SF$_4$ reacts with a wide range of Lewis acids as shown below to form adducts containing the SF$_3^+$ cation.

$$\text{SF}_4 + \text{MF}_n \rightarrow \text{SF}_{3n}^+ \text{MF}_n^- + 1$$

MF = BF$_3$, PF$_5$, AsF$_5$, SbF$_5$, HF, IrF$_5$, AsF$_3$

The SF$_3^+$ cation exhibits $C_{3v}$ symmetry as shown in figure 1.7.

Figures 1.2 and 1.8 show the crystal structures of the adducts SF$_3^+\text{BF}_4^-$ and (SF$_3^+$)$_2\text{GeF}_6^-$. $^{26}$ $^{22}$
Figure 1.6 The structure of $SF_4$

Figure 1.7 The structure of $SF_3^+$
Figure 1.8  The structure of $(\text{SF}^+)\text{GeF}_3^2$.

Figure 1.9  The structure of $\text{SF}_5^-$.
Sulphur tetrafluoride also reacts with CsF or Me₄NF to form adducts containing the SF₅⁻ anion. The structure of the anion has been characterised spectroscopically as being square pyramidal (C₄ᵥ). (Figure 1.9)

In addition to the Lewis acid base type reactions previously described, SF₄ is also widely used in organic reactions as a fluorinating agent most commonly for fluorination of a carbonyl group as indicated in the following examples:

1. \[
\begin{align*}
\text{CH} = \text{C} & \quad \text{CHO} \\
& \quad \text{SF}_4 \quad 150^\circ \quad \text{8hr} \\
\end{align*}
\]

2. \[
\begin{align*}
\text{CH}_3(\text{CH}_2)_n \text{CHO} & \quad \text{SF}_4 \quad 50-60^\circ \quad \text{8hr} \\
& \quad \text{CH}_3(\text{CH}_2)_n\text{CHF}_2
\end{align*}
\]

3. \[
\begin{align*}
\text{RCO}_2\text{H} + \text{SF}_4 & \rightarrow \text{RCOF} + \text{HF} + \text{SOF}_2
\end{align*}
\]

4. \[
\begin{align*}
\text{RCOF} + \text{SF}_4 & \rightarrow \text{RCF}_3 + \text{SOF}_2
\end{align*}
\]

Fluorination by SF₄ is not restricted to carbonyl oxygen. Oxygen doubly bonded to arsenic, iodine or phosphorus is similarly replaced by two fluorine atoms. SF₄ is also very useful for replacing the hydroxyl groups of primary, secondary and tertiary alcohols, carboxylic acids and sulphonic acids with a fluorine atom.

SF₄ can also be used to introduce fluorine into organic compounds by replacement of chlorine, bromine or iodine atoms.
by fluorine, although relatively high temperatures are required. For example metathesis of carbon tetrachloride with sulphur tetrafluoride requires a temperature of 225-235°C.

\[
\text{CCI}_4 + \text{SF}_4 \xrightarrow{225-235^\circ} \text{CCI}_3\text{F} + \text{CCI}_2\text{F}_2 + \text{CCIF}_3
\]

The previous examples show that SF₄ can undergo a wide range of chemical reactions, and exhibit both Lewis acid and Lewis base behaviour. This, together with the availability of ¹⁸F and ³⁵S radiotracers makes SF₄ a very useful substance for the study of Lewis acid-base reactions.

1.4 CAESIUM FLUORIDE AS A CATALYST AND A BASE

Alkali metal fluorides have been widely used as catalysts in a whole range of synthetic reactions. They are fairly strong bases and have a number of advantages over other bases. Reactions conducted in the presence of alkali metal fluorides give high yields, proceed selectively and without formation of any by-products. Reactions involving conventional bases such as hydroxides or alkali metal carbonates usually result in the formation of unwanted by-products. The ability of a metal fluoride to act as a catalyst depends on the nucleophilic properties of F⁻ so it is vitally important that the CsF is dry because of the strength of the hydrogen bonds formed by the fluoride ion.

Studies carried out with various alkali metal fluorides have shown caesium fluoride to be the most active. The overall
order of activity generally found in synthetic and catalytic work is: 42

\[
\text{CsF} > \text{RbF} > \text{KF} > \text{NaF} > \text{LiF}.
\]

Illustrative examples of the use of alkali metal fluorides in synthetic reactions are given below.

1.4.1 Elimination of hydrogen halides

The basic properties of alkali metal fluorides were first observed in dehydrohalogenation reactions. In the reaction of 3-chloropropanoic acid with potassium fluoride, the formation of acrylic acid was observed. 43

\[
\text{Cl} - \text{CH}_2 - \text{CH}_2 - \text{COOH} \xrightarrow{\text{KF}} \text{H}_2\text{C} = \text{CH} - \text{COOH} \quad 68\%
\]

In the presence of alkali metal fluorides fluoro-amo groups are converted to fluoroimino and nitrile groups.

\[
\text{F}_2\text{N} - \text{CH}_2 - \text{CH} - \text{NF}_2 \xrightarrow{\text{CsF}} \text{N} = \text{C} - \text{CF} = \text{NF} \quad 44
\]

Reaction of haloorganic compounds with alcohols or phenols in the presence of metal fluorides leads to the formation of ethers.

\[
\begin{array}{c}
\text{X} \\
\text{NO}_2 \\
\text{NO}_2 \\
+ \text{R - OH} \\
\xrightarrow{\text{CsF}} \\
\text{OR} \\
\text{NO}_2 \\
\text{NO}_2 \\
\end{array}
\]

\[
x = \text{Cl, F, Br}, \quad \text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5
\]
1.4.2 MICHAEL REACTIONS

The nucleophilic addition of an enolate or analogous anion to the carbon-carbon double bond of an unsaturated ketone, aldehyde, nitrile or carboxylic acid derivative is a process known as the Michael reaction. The use of alkali metal fluorides in these reactions instead of the traditionally used amines, alkoxides, ammonium salts of organic acids, or alkali hydroxides makes it possible to carry out the reactions under milder conditions and increases the yields of reaction products. 46

\[
\begin{align*}
\text{H}_3\text{C} - \text{CH} = \text{CH} - \text{COOC}_2\text{H}_5 + \text{H}_2\text{C} - \text{CN} & \overset{\text{KF}}{\rightarrow} \text{H}_3\text{C} - \text{CH} - \text{CH}_2 - \text{COOC}_2\text{H}_5 \times \text{CN} \\
\end{align*}
\]

1.4.3 KNOEVENAGEL REACTIONS

The condensation of an active methylene compound and an aldehyde or ketone with elimination of water from the intermediate aldol product is known as the Knoevenagel reaction. 46

\[
\begin{align*}
\text{Me COCH}_2\text{Me} + \text{NCCH}_2\text{CO}_2\text{Et} & \overset{\text{KF}}{\rightarrow} \text{MeC(Et)} = \text{C(CN) CO}_2\text{Et} \\
\end{align*}
\]
1.4.4 DECARBOXYLATION

The use of alkali metal fluorides as decarboxylating agents was first discovered in 1948 by Nesmeyanov and coworkers when they isolated chloroform when attempting to obtain trifluoroacetic acid from trichloroacetic acid in the presence of potassium fluoride.

\[
\text{Cl}_3C - \text{COOH} \xrightarrow{\text{KF}} \text{Cl}_3\text{CH} \quad 70\text{-}100\%
\]

This reaction proved to be applicable to a wide range of acids. Heating of dicarboxylic acids with potassium fluoride results in partial decarboxylation which leads to cyclic ketones.

\[
\text{H}_2\text{C} - \text{CH}_2\text{COOH} \xrightarrow{\text{KF}} \text{H}_2\text{C} - \text{CH}_2\text{COOH}
\]

1.4.5 REACTIONS OF FLUORINE CONTAINING COMPOUNDS

When heated with caesium fluoride in the presence of a solvent, F-buta-1,3-diene is transformed to F-but-2-yne.

\[
\text{F}_2\text{C} = \text{CF} - \text{CF} = \text{CF}_2 \xrightarrow{\text{CsF}} \text{F}_3\text{C} - \text{C} = \text{C} - \text{CF}_3
\]

In the presence of caesium or potassium fluoride,
F-methylenecyclopentane is almost quantitatively isomerised to give F-1 methylcyclopentene.

Alkali metal fluorides also catalyse a number of processes which lead to fluorine containing long chain polymers.

\[
n \text{F}_2 \text{C} = \text{CF}_2 \xrightarrow{\text{CsF}} \text{C}_8 \text{F}_{18} + \text{C}_{10} \text{F}_{21} + \text{C}_{12} \text{F}_{24} \]

\[
\text{F}_3 \text{C} = \text{O} \xrightarrow{\Delta, \text{CsF}} 100^\circ \text{C} \left[ \begin{array}{c} \text{CF}_3 \\ \text{CF}_3 \\ \text{C} - \text{O} - \text{CH}_2 - \text{CH}_2 - \text{O} - \end{array} \right]_n
\]

mol mass = 118000

1.4.6 REACTIONS OF CARBONYL CONTAINING COMPOUNDS

\(\text{CF}_3 \text{OC}l, \text{C}_2 \text{F}_5 \text{OC}l\) and other similar compounds can be prepared at low temperature by caesium fluoride catalysed addition of chlorine monofluoride to the appropriate carbonyl compound.
Similarly

\[ \text{F}_2\text{CO} + \text{Cl}_2\text{O} \xrightarrow{\text{CsF}, -20^\circ} \text{CF}_3\text{OCl} + (\text{CsOCl}) \]

Carbon dioxide and carbonyl fluoride both react with fluorine in the presence of caesium fluoride.

\[ \text{CO}_2 + \text{F}_2 \xrightarrow{\text{CsF}} \text{OF} \]

\[ \text{C} = \text{O} + \text{F}_2 \xrightarrow{\text{CsF}} \text{OF} \]

1.4.7 THE CHLOROFLUORINATION OF SF\(_4\)

\[ \text{SF}_4 + \text{ClF} \rightarrow \text{SF}_5\text{Cl} \]

When no caesium fluoride is present a temperature of 350°C is required. In the presence of caesium fluoride this reaction occurs readily at room temperature.
1.5 DISCUSSION OF GENERALLY ACCEPTED MECHANISMS

Ionic fluorides with their variable basicity and relatively low nucleophilicity towards carbon have proved to be versatile proton abstractions in a variety of base assisted reactions where the strength of the base required has varied from weak to very strong and the role of the base has been catalytic and non catalytic. The fluoride ion method is particularly well suited to reactions such as Michael additions, alkylations, esterifications, eliminations and Knoevenagel condensations. These reactions are thought to occur via strong H bonding of the electron donating fluoride ion to the acceptor molecule with resulting enhancement of the nucleophilicity of the acceptor molecule. The role of the metal fluoride in reactions such as the chlorofluorination of sulphur tetrafluoride and halogen addition reactions is not as clearly understood. Mechanisms proposed for these reactions have usually involved intermediates related to complex fluoroanions, but in many cases the validity of this approach has been questioned.

In 1973 Kennedy and Cady studied the reaction of carbonyl fluoride with fluorine in the presence of various fluorides as catalysts. In the presence of CsF, RbF or KF the reaction proceeds as shown below at -78°C

\[ \text{CF}_2\text{O} + \text{F}_2 \rightarrow \text{CF}_3\text{OF} \]
The mode of action of the CsF is proposed to be:

\[
\begin{align*}
\text{CF}_2\text{O} + \text{CsF} & \rightarrow \text{Cs}^+ \text{CF}_3\text{O}^- \\
\text{CsCF}_3\text{O} + \text{F}_2 & \rightarrow \text{CsF} + \text{CF}_3\text{OF}
\end{align*}
\]

Doubts about this mechanism were first expressed by Lustig and coworkers in 1967. Their explanation stated "It is probable that the metal fluoride either reacts directly with or polarizes the carbon-oxygen double bond to such an extent that a polar intermediate is formed, which is the active species in the fluorination." One reason for their caution is that some compounds which are catalytically fluorinated do not appear to involve extensive combination with the metal fluoride. For example the uptake of CO\(_2\) by CsF is very small, but CO\(_2\) reacts with fluorine in the presence of CsF to give CF\(_2\) (OF \(_2\)). Kennedy and Cady have shown that the reaction of COF\(_2\) with fluorine is also catalyzed by CsF, HF, KAgF\(_4\) and CsCl. With these salts the CF\(_3\)O\(^-\) anion could not be formed as an intermediate. This would suggest that Lustig and coworkers vague proposal of a 'polar intermediate' may in fact be closer to the true mechanism than that involving formation of the trifluormethoxide anion.

A similar difference of opinion occurred over the mechanism for the chlorofluorination of sulphur tetrafluoride. This reaction occurs readily at room temperature in the presence of caesium fluoride. The generally accepted mechanism for
this reaction involves reaction between $\text{Cs}^+ \text{SF}_5^-$ and gaseous chlorine monofluoride.

\[ \text{SF}_4 \text{(g)} + \text{CsF} \text{(s)} \rightleftharpoons \text{Cs}^+ \text{SF}_5^- \text{(s)} \]

\[ \text{Cs}^+ \text{SF}_5^- \text{(s)} + \text{ClF} \text{(g)} \longrightarrow \text{SF}_5 \text{Cl} \text{(g)} + \text{CsF} \text{(s)} \]

This mechanism was shown to be incorrect by Kolta and coworkers in 1982. As a result of radiotracer studies involving ($^{36}\text{Cl}$) chlorine monofluoride and ($^{35}\text{S}$) sulphur tetrafluoride, they proposed that the mechanism could best be described by the following five equilibrium reactions.

\[ \text{SF}_4 \text{(g)} + \text{CsF} \text{(s)} \rightleftharpoons \text{CsF} \text{SF}_4 \text{(ads)} \]

\[ \text{CsF} \text{SF}_4 \text{(ads)} \rightleftharpoons \text{Cs}^+ \text{SF}_5^- \text{(s)} \]

\[ \text{ClF} \text{(g)} + \text{CsF} \text{(s)} \rightleftharpoons \text{CsF} \text{ClF} \text{(ads)} \]

\[ \text{CsF} \text{ClF} \text{(ads)} \rightleftharpoons \text{Cs}^+ \text{ClF}_2^- \text{(s)} \]

\[ \text{CsF} \text{ClF} \text{(ads)} + \text{CsF} \text{SF}_4 \text{(ads)} \rightleftharpoons \text{SF}_5 \text{Cl} \text{(g)} + 2\text{CsF} \text{(s)} \]

with CsF ClF (ads) and CsF SF$_4$ (ads) as the active species rather than Cs SF$_5$ (s) and ClF (g).

These results, together with those of Kennedy and Cady show that the mechanisms of reactions catalysed by ionic fluorides are not as straightforward as was first thought. They cannot simply be assumed to occur via formation of a fluoroanion.
This work was carried out in an attempt to identify the species present on the surface of a solid fluoride during reaction with a gaseous fluoride. The species were identified by using radiotracers and by infra-red spectroscopy. Comparison of the results obtained with those in the literature indicated that there are many similarities between the species involved in a reaction on the surface of the solid and the species involved in reaction within the bulk of the solid.
CHAPTER 2 EXPERIMENTAL

2.1 EQUIPMENT

Most of the reactants used in this work are either air or moisture sensitive. In order to ensure anhydrous and oxygen free conditions, all experimental work was performed in vacuo ($10^{-4}$ Torr) or in an inert atmosphere box ($H_2O < 10$ppm).

2.1.1 THE VACUUM SYSTEM

Several different vacuum lines were used during the course of this work. The basic system consisted of a Pyrex glass vacuum line which was pumped by means of a mercury diffusion pump, together with an oil sealed rotary pump. The pumps were protected from any volatile material in the line by waste traps which were cooled in liquid nitrogen.

The main components of the vacuum line were a manometer or pressure gauge (Heise) to measure the pressure of gas or vapour contained in the line, a vacustat which was used to measure the efficiency of the pumping system and a main manifold. The type of main manifold fitted depended on the operation being carried out. The simplest manifold consisted of outlets to which reaction vessels were attached by
means of cone and socket joints which were sealed with Kel-F grease. Other manifolds had reaction vessels and secondary manifolds connected directly to them. Reactions were carried out either in glass reaction vessels fitted with polytetrafluoroethylene (Rotaflo) stopcocks or in Monel metal pressure vessels (Hoke) fitted with Monel valves (Whitey). To ensure that as much as possible of the moisture adsorbed on the surface of the glass was removed, the glass vessels and line were flamed out with a gas/oxygen flame while the line was being pumped.

2.1.2 GAS UPTAKE APPARATUS

In order to follow manometrically the uptake of gas by a solid the apparatus shown in figure 2.1 was used. This consisted of a constant volume manometer, a small volume manifold, a bulb B to increase the volume of the manifold if necessary and a socket fitted with a Rotaflo stopcock onto which the sample bulb was attached. The volume of the system was accurately calibrated before use. Pressure changes were measured using a cathetometer.

The constant volume manometer is shown in more detail in figure 2.2. The mercury level was manipulated by applying air or vacuum to the reservoir by means of the two way stopcocks so that the mercury in the right hand limb was always brought to a reference mark before a measurement was taken.
Figure 2.1 Constant volume apparatus
Figure 2.2
Constant volume manometer
2.1.3 THE INERT ATMOSPHERE BOX

An argon atmosphere Lintott box ($H_2O < 10$ppm) was used when handling and storing all samples. Vessels were evacuated and in the case of glass vessels flamed out before being transferred to the box. The box contained a balance which allowed samples to be weighed in this dry atmosphere.

2.1.4 INFRA-RED SPECTROSCOPY

The IR work was performed on a Perkin Elmer 580 or 983 spectrometer. The spectra were obtained as Nujol and Fluorube mulls, between AgCl plates or in a gas IR cell equipped with AgCl windows. All mulls were prepared in the inert atmosphere box due to their sensitivity to moisture and air.

2.2 PREPARATION AND PURIFICATION OF REAGENTS

2.2.1 PURIFICATION OF ACETONITRILE

HPLC or spectroscopic grade MeCN was refluxed over anhydrous $AlCl_3$ for one hour before being distilled into a flask containing $K_MnO_4$ and $Li_2CO_3$ over which it was refluxed for 0.25 hours. The MeCN was distilled into another flask containing $KHSO_4$ over
which it was refluxed for one hour before being transferred to a flask containing CaH$_2$ and again refluxed for 1 hour. It was then distilled into another flask containing P$_2$O$_5$ and distilled for half an hour before being finally refluxed over a fresh sample of P$_2$O$_5$ for a further half hour. The MeCN was then transferred, without exposure, to atmospheric moisture, to vessels containing previously activated 3A molecular sieves. It was degassed in vacuo, allowed to stand at room temperature for 24 hours, then vacuum distilled onto fresh 3A sieves before being used.

2.2.2 PURIFICATION OF DI-ETHYL ETHER

Analar Et$_2$O was purified by adding small pieces of freshly cut sodium until no further reaction was observed. The Et$_2$O was then degassed in vacuo and allowed to stand over activated 3A molecular sieves for 24 hours. Before use the Et$_2$O was vacuum distilled onto fresh 3A molecular sieves.

2.2.3 PURIFICATION OF PYRIDINE

Analar pyridine was purified by degassing in vacuo then drying over activated 3A molecular sieves.
2.2.4 PURIFICATION OF AsF₅ AND BF₃

Arsenic pentafluoride (Ozark-Mahoning) and boron trifluoride (Matheson Inc) were purified by trap to trap distillation over NaF at -80°C and stored over NaF at -196°C. NaF removes any HF which may be present.

2.2.5 PURIFICATION OF CO₂

Carbon dioxide was obtained in the form of dry ice (Distillers Co.) In this form it contains a high proportion of water. The water was removed by first crushing the solid CO₂ followed by three trap to trap distillations over fresh P₂O₅ at -80°C. The CO₂ was then transferred into a large volume bulb containing P₂O₅ and left at room temperature for twelve hours before use.

2.2.6 PREPARATION AND PURIFICATION OF F₂CO

Carbonyl fluoride was prepared by the reaction of carbonyl chloride with sodium fluoride in acetonitrile.

In a typical preparation carbonyl chloride (3.0g, 30.4 m mol) was condensed onto sodium fluoride (16g 360 m mol) in acetonitrile (30 ml) and the reaction
mixture kept at 20°C for 36 hours in a stainless steel pressure vessel (300 ml). Fractionation of the volatile components gave carbonyl fluoride (1.9g 28.8m mol).

The carbonyl fluoride was purified by trap to trap distillation at -80°C and stored in a stainless steel pressure vessel until required to prevent reaction with glass to form silicon tetrafluoride.

2.2.7 PURIFICATION OF IF₅

Iodine pentfluoride was purified by trap to trap distillation over NaF followed by shaking at room temperature with Hg metal. The IF₅ was stored over a fresh sample of Hg at room temperature until required for use.

2.2.8 PREPARATION OF Li BF₄

Lithium tetrafluoroborate was prepared by the reaction of boron trifluoride with lithium fluoride (B.O.H.) in acetonitrile.

Boron trifluoride (5.71g 84m mol) was condensed onto lithium fluoride (2g 76.9m mol) in acetonitrile
(10 ml) and the reaction mixture was shaken at room temperature for 72 hours. Removal of the solvent and volatile material gave LiBF$_4$ (6.96g 7.4 mmol).

2.2.9 **PURIFICATION OF (NbF$_5$)$_4$**

Niobium pentafluoride (Fluorochem Ltd) was purified by sublimation using the apparatus shown in figure 2.3. The crude niobium pentafluoride was placed in flask A and heated using an oil bath to 70°C. Pure NbF$_5$ was trapped in the U tube by cooling it to -196°C in liquid nitrogen. When the sublimation process was complete the U tube was sealed off at points C1 and C2 and transferred to an inert atmosphere box where it was stored until required.

2.2.10 **PREPARATION AND PURIFICATION OF FNO**

Nitrosyl fluoride was prepared by the reaction of nitrogen dioxide (Matheson Inc) with caesium fluoride (BDH).

Nitrogen dioxide (4 m mol) was condensed onto caesium fluoride (10g 66m mol) and the vessel allowed to reach room temperature. After four days 3.6m mol of nitrosyl fluoride were produced.
Figure 2.3  NbF$_5$ sublimation apparatus
The rate of reaction could be increased in two ways. If the vessel containing the nitrogen dioxide and caesium fluoride was heated to 120°C the reaction was complete within three hours. If the caesium fluoride was pretreated with hexafluoroacetone (see chapt. 3) the reaction was complete within ten minutes.

2.2.11 PREPARATION AND PURIFICATION OF SF$_4^{63}$

Sulphur tetrafluoride was prepared by fluorination of elemental sulphur by iodine pentafluoride.

Purified iodine pentafluoride (45m mol) was condensed into a stainless steel pressure vessel containing elemental sulphur (7m mol). The vessel was then heated at 373K for 5 hours followed by 473K for 48 hours. After reaction the volatile material was removed at 195K and condensed into a similar vessel over NaF.

The SF$_4$ was purified by reaction with BF$_3$ at 195K forming the adduct SF$_3^+$$\cdot$BF$_4^-$. Unreacted material was removed by pumping at this temperature, and the adduct decomposed by adding the calculated quantity of dry diethyl ether at 195K.$^{24}$ The infra-red spectrum of the product showed no sign of any impurities.
2.2.12 PREPARATION OF β-UF₅

β-uranium pentafluoride was prepared by the reaction of purified uranium hexafluoride on iodine in iodine pentafluoride according to equation 2.1.

$$10 \text{UF}_6 + \text{I}_2 \rightarrow 10\text{UF}_5 + 2\text{IF}_5 \quad \text{Equation 2.1}$$

In a typical preparation I₂ (0.36m mol) and UF₆ (6m mol) in IF₅ (20m mol) were shaken at room temperature for 1 hour. Removal of the colourless volatile material gave uranium pentafluoride (0.35m mol).

Aluminium trifluoride (Ozark Mahoning 99.5%) was used as received. Caesium fluoride (BDH Optran grade) was used as received or treated with hexafluoroacetone as described in chapter 3.

2.3 RADIOCHEMICAL TECHNIQUES

Radiotracer methods are widely used for monitoring exchange reactions and for studying surface catalysed processes. Their main advantage is their sensitivity in detecting small numbers of atoms or molecules when these are radioactive.

Before 1934 only the heavy elements with naturally occurring radioactive isotopes could be used to follow the movement of atoms or molecules during reactions. Artificial radioactivity
was discovered by Curie and Joliot early in 1934. They discovered that aluminium foil which had been bombarded with \( \alpha \) particles gave off radiation after the bombardment had ceased (equation 2.2). Following this discovery many more radioisotopes were produced by other groups of workers using similar bombardment techniques.

\[
\begin{align*}
27\text{Al} + 4\text{He} & \rightarrow 30\text{P} + 1\text{n} \\
13 & \quad 2 & 15 & \quad 0
\end{align*}
\]

Because of the low neutron fluxes available at this time, only short-lived radioisotopes of low specific activity could normally be produced. Since 1945, the successful operation of nuclear reactors and the development of particle accelerators have made available high particle fluxes. Consequently radioisotopes, both short and long-lived, of nearly all the elements have become available. This has removed most of the restrictions on the systems which could be examined and exchange reactions have provided much information on a wide variety of topics, for example molecular structure, bond types and reaction kinetics.

2.3.1 **EXCHANGE REACTIONS**

An exchange reaction occurs when atoms of a given element interchange between two or more forms of this element. Exchange reactions can be observed by labelling one of the elements with a radioisotope and following the position of the isotope. The general equation for an isotopic exchange reaction
may be written:

$$AX + BX^* \equiv AX^* + BX$$

Where \(^*\) designates the distinguishable (radioactive or stable) isotope. The rate of disappearance of the isotopic species from an initially unlabelled reactant is described by a first order rate law regardless of the number of atomic species which participate, since there can be no change in the concentration of the reactants.\(^6\) It is possible therefore to carry out quantitative investigations of exchange reactions. Results can be expressed in terms of the fraction of activity exchanged \((f)\) where \((f)\) is defined by equation 2.3.\(^6\)

\(f=\frac{\text{fraction of activity in the initially unlabelled compound}}{\text{fraction of fluorine \((mg\text{-atom})\) in the initially unlabelled compound}}\)

\(f\) is determined experimentally using either equation 2.4 or 2.5

\[
f = \frac{A_1}{A_1 + A_2} \left( \frac{x_m}{x_m + y_m} \right)^{-1}
\]

\[
f = \frac{(A_0 - A_2) (x_m + y_m)}{A_0 x_m}
\]

\[
equation 2.4
\]

\[
equation 2.5
\]
where $A_1$ and $A_2$ counts $s^{-1}$ are the count rates, corrected for decay, after exchange between $m_1$ and $m_2$ mol of reactants ($1$ being inactive initially) containing respectively $x$ and $y$ F atoms. $A_0$ counts $s^{-1}$ is the corrected count rate of reactant $2$ before exchange.

Equations 2.4 and 2.5 should in theory give the same answer providing that the radiochemical balance is $>95\%$ that is $A_0 = A_1 + A_2$. In practice this is not always the case since there are three possible situations which can arise.

1. Fluorine exchange with no retention of the gas by the solid. In this case either equation may by used and the value of $f$ obtained indicates the degree to which exchange has occurred. $f = 0$ corresponds to no exchange and $f = 1$ corresponds to complete exchange, that is a random distribution of activity. This situation was observed in the reactions of SF$_3^{18}$F with AlF$_3$ and (NbF$_5$)$_4$ reported in chapter 5 of this work.

2. Retention of the gas by the solid with no fluorine exchange. In this case equation 2.4 would give a value of $f > 1$ and equation 2.5 would give a value of $f = 0$. Therefore as soon as uptake of gas occurs equation 2.4 becomes invalid and equation 2.5 must be used. This situation was
observed in the reactions of AsF$_4$ $^{18}$F, BF$_2$ $^{18}$F and SF$_3$ $^{18}$F with CsF reported in chapter 4 of this work.

3. Fluorine exchange and retention of gas by the solid. In this case equation 2.4 will give a value of $f > 1$. Since equation 2.5 depends on the specific count rate of the gas before and after reaction, a true measure of the fraction exchanged will be obtained if this equation is used. This situation was observed in the reaction of $^{18}$F FCO with CsF reported in chapter 4 and also in the reactions of AsF$_5$, BF$_3$ and SF$_4$ with Cs $^{18}$F at high temperature reported in chapter 2.

Equation 2.5 will give a true measure of the fraction exchanged whereas equation 2.4 will only give a true result if there is no uptake of gas. If an $f$ value of $>1$ is obtained when using equation 2.4 this suggests that uptake of gas has occurred and equation 2.5 must be used if an accurate $f$ value is required.

2.3.2 CHOICE OF ISOTOPE

In general the choice of isotope is determined by three factors. These are:
a) The availability of the isotope
b) The length of its half life
c) The ease of detection

The three radioisotopes used in this work are $^{14}$C, $^{18}$F and $^{35}$S, the longest lived radioactive isotopes of each element. All three are readily detected. $^{14}$C and $^{35}$S are $\beta^-$ emitters detectable using Geiger Müller counters with $\beta$ max 0.155 MeV and 0.167 MeV respectively, both also have long half lives ($^{14}$C $t_{1/2} = 5730$ yr, $^{35}$S $t_{1/2} = 87.4$ d).

$^{18}$F is a $\gamma$ emitter ($\gamma$ max = 0.51 MeV) and is detectable using a scintillation counter. Although $^{18}$F is the longest lived radioactive isotope of fluorine, its half life is only $109.72 \pm 0.06$ min. This introduces experimental problems that must be overcome. Due to the short half life no more than one working day is available for each experiment since after six half lives only 1-2% of the starting activity is left. All synthesis and purification must therefore be carried out as quickly as possible.

Figure 2.4 shows the kinetic relationship between incorporation and decay of fluorine - 18. The formation of the $^{18}$F labelled compound during the chemical reaction competes with the radioactive decay of $^{18}$F. Reaction times longer than t limit lead to less net activity in the product.
Figure 2.4

Kinetic relationship between incorporation and decay of $^{18}$F

1 = Product formation
2 = Decay curve of $^{18}$F
3 = Incorporation of $^{18}$F in the labelled product
When using radiotracers to study a particular system it is better if two different isotopes are used, since comparable results obtained from two different sets of tracer experiments are more conclusive than a single set of data obtained for one radioisotope.

The use of two different isotopes to study the same system helps in characterising the species involved and also in distinguishing the reaction processes which are occurring. For example, by using both $^{18}$F and $^{35}$S labelled SF$_4$ and $^{18}$F and $^{14}$C labelled COF$_2$, it is possible to determine whether growth of activity in the solid is due to fluorine exchange or uptake of the gas by the solid.

Fluorine -18 is an energetic $\gamma$-emitter which gives information about the overall bulk reaction as all activity present in the sample can be detected. Sulphur -35 and carbon -14 are both weak $\beta^+$-emitters. Due to absorption of the radioactivity by the solid only activity originating from the surface of the solid can be detected in systems involving these isotopes. Comparison of $^{18}$F results with those from $^{35}$S or $^{14}$C labelled samples allows the surface and bulk species to be differentiated.

In this work the results of reactions involving BF$_3$ and AsF$_5$ are based only on $^{18}$F radiotracer work and those of CO$_2$ on $^{14}$C work only as no other suitable isotopes were available.
COUNTING OF $^{14}$C AND $^{35}$S SAMPLES

2.4.1 GEIGER MULLER (G.M.) COUNTERS

Carbon-14 and sulphur-35 both decay by beta ($\beta^-$) emission.

A $\beta^-$ particle is an electron which is ejected from the nucleus. Emission of a beta particle leaves the mass number of the isotope unchanged since the number of nucleons present is unaltered, but the atomic number is increased by one.

Samples labelled with $^{14}$C and $^{35}$S were counted using a Geiger Muller tube. A Geiger Muller tube consists of an earthed cylindrical case filled with a gas, usually argon, together with a low concentration of an organic substance often alcohol or methane. A positively charged electrode is suspended along the centre of the tube. Radiation enters the tube through a thin mica window and interacts with the gas to produce an electrical pulse. The electrical pulses are recorded by an electronic scaler which produces an output which is proportional to the strength of the initial ionising radiation.

2.4.2 PLATEAU CURVE

In a GM. counter no counts are recorded until the applied potential is large enough to attract the free electrons to the anode. When this point known
as the Geiger threshold is reached (Vt) the count rate begins to rise rapidly until a plateau is reached where the count rate increases only very slowly with voltage. (figure 2.5).

The plateau is never flat due to the generation inside the counter of spurious discharges caused by secondary electron emission. This occurs when the positive ions produced in the initial ionisation reach the cathode and cause secondary electron emission from the surface. This secondary electron emission is usually suppressed by the addition of an organic quench gas such as CH₄. As the potential increases the quench gas cannot cope with the large number of spurious discharges and the count rate begins to rise rapidly until the counter begins to discharge.

Plateau regions were determined regularly for every Geiger Muller tube used by sweeping through the voltage region whilst monitoring the count obtained from a caesium-137 source. Figure 2.5 shows a typical plateau curve obtained. The working voltage was set in the middle of the plateau region.
Figure 2.5 G.M. Tube plateau curve

Voltage (Volts) vs. Count rate (counts min⁻¹)

- Voltage range: 300 V to 500 V
- Count rate curve shows a plateau for values above a certain voltage.
2.4.3 DEAD TIME

Immediately after the collection of electrons in a GM discharge a sheath of positive ions surrounds the central wire. These positive ions reduce the voltage gradient below the value necessary for ion multiplication, and the counter cannot record another event until the positive ions reach the cathode. As a result each pulse from the GM tube is followed by a period during which no particles can be detected. This insensitive period is known as the dead time of the counter, as in accurate counting experiments a correction is necessary for counts lost in such periods especially if the counting rate is high.

The true count rate \(N_t\) is related to the observed count rate \(N_0\) by the relation:

\[
N_t = \frac{N_0}{1 - N_0 \tau}
\]  

\textit{equation 2.6}

where \(\tau\) is the dead time.

2.4.4 DETERMINATION OF DEAD TIME

The dead times of the GM tubes used were determined by counting samples of Cs\(^{18}\)F over periods of three half lives.
The decay of a radioisotope is described by equation 2.7

\[ A_t = A_0 e^{-\lambda t} \]  

Equation 2.7

where \( \lambda \) = decay constant
\( A_t \) = Activity of sample at time \( t \)
\( A_0 \) = Activity of sample at time \( t = 0 \)

hence a plot of log \( A_t \) versus time should be a straight line with gradient \( -\lambda \) and intercept log \( e^a A_0 \). When a plot of log \( e^a (A_t) \) versus time was drawn a linear relationship was obtained for \( t \geq 200 \) min. At times \( t < 200 \) min a curve was obtained because at these times the count rate was high enough for the dead time to have a considerable effect.

The linear portion of the plot was extrapolated to time \( t = 0 \) using the known half life of \(^{18}F\) fluorine (109.72 ± 0.06 minutes). This line gave \( N_t \) the true count rate which is related to \( N_o \) the observed count rate \( N_o \) by the relation:

\[ N_t = \frac{N_o}{(1 - N_oT)} \]  

Equation 2.6

where \( T \) is the dead time.

This calculation was performed using the first twenty points on the graph and the mean of these
Figure 2.6
Log count rate of Cs$^{18}$ vs time
results was taken to be the dead time of the GM tube. Figure 2.6 shows both the experimentally observed line and the calculated true line.

2.5 COUNTING OF $^{18}$F-FLUORINE SAMPLES

2.5.1 SCINTILLATION COUNTERS

$^{18}$F fluorine decays by positron emission ($\beta^+$). A positron is a positively charged electron which is ejected from the nucleus following the transformation within the nucleus of a proton into a neutron. As is the case with $\beta^-$ emission, emission of a positron leaves the mass number of the isotope unchanged but in positron emission the atomic number decreases by one.

The emitted positrons interact with surrounding atoms in a manner very similar to that of an ordinary electron. When the positron has lost virtually all its initial kinetic energy, it combines with a negative electron and annihilation of both particles occurs. Annihilation of the positrons emitted by $^{18}$F fluorine results in the emission of $\gamma$ radiation ($\gamma_{\text{max}}$ 0.51MeV) $\gamma$ rays are high energy electromagnetic waves.

The $\gamma$ rays produced in the annihilation process are counted using a Tl/NaI scintillation counter. (Ekco electronics instruments). The scintillation counter
basically consists of a large NaI crystal, a
photomultiplier and an amplifier.

When ionising radiation passes through the NaI
light is emitted in a short pulse. The size of the
pulse is proportional to the energy given up by the
radiation to the scintillator. The light from the
scintillator liberates electrons at the photocathode
of the photomultiplier, the number being proportional
to the energy, electrons are accelerated by a dc
voltage to the first electrode where each electron
liberates another four or so. This is repeated down
the tube so that in a 10 stage tube there is a gain
of $4^{10}$. The resulting pulse is then fed to an
amplifier and then to a scaler where it is recorded.

To achieve maximum pulse height, the scintillator
crystal is surrounded by a reflector, and the space
between the crystal and the photomultiplier filled
with paraffin oil or silicone oil of high viscosity
to improve the light transmission.

Before use the scaler and scintillation counter were
calibrated using a standard caesium-137 $\gamma$ - source
and then with a sodium-22 source which emits $\gamma$ -rays
of the same energy as those emitted by $^{18}_F$ (0.51MeV).

In each case a $\gamma$ -ray spectrum was obtained by
monitoring the counts from the source while varying
Figure 2.7 $\gamma$-ray spectrum of $^{23}$Na

![Gamma-ray spectrum graph]

- **Y-axis:** Counts min$^{-1}$
- **X-axis:** Voltage Volts

- Voltage range: 0 to 500 Volts
- Count rate range: 1000 to 4000 counts min$^{-1}$
the applied voltage. The $\gamma$-ray spectrum obtained for the sodium-22 source is shown in figure 2.7. During experiments the scaler was set to count at the position of the $\gamma$-peak \( ^{+}5\% \).

2.5.2 DECAY CORRECTION

The disintegration of the nuclei of a radioactive material follows an exponential law

\[
N_t = N_0 e^{-\lambda t}
\]

\[\text{equation 2.8}\]

when

\[\begin{align*}
N_0 &= \text{Number of unstable atoms at time } t = 0 \\
N_t &= \text{Number of unstable atoms at time } t \\
\lambda &= \text{decay constant}
\end{align*}\]

The rate of decay is indicated by the half life of the isotope

\[T_{\frac{1}{2}} = \frac{0.693}{\lambda}
\]

\[\text{equation 2.9}\]

Since the half life of fluorine-18 is \((109.72^{+0.06}_{-0.06} \text{ minutes})\) the rate of decay is such that significant decay occurs within the time taken to carry out one experiment. This means that all experimental data obtained must be corrected for decay before being analysed. All results were corrected to the time of the last measurement taken using equation 2.8. All calculations were carried out by microcomputer.
Listings and explanations of all computer programmes are given in the appendix.

2.6 **BACKGROUND**

The count recorded in any radiochemical analysis includes a contribution from sources other than the sample. Background activity can be traced to the existence of minute quantities of radon isotopes in the atmosphere, to the materials used in construction of the laboratory, to cosmic radiation, and to the release of radioactive materials into the earth's atmosphere. In order to obtain a true count it is necessary to correct the total count for background.

\[ C_t = C_o - C_b \]  \hspace{1cm} \text{Equation 2.10}

where

- \( C_t \) = true count
- \( C_o \) = observed count
- \( C_b \) = background count

The level of background radiation can be reduced by shielding the counting equipment. The scintillation counter used for counting \(^{18}\text{F}\) samples is encased in lead for this reason. The \(^{14}\text{C}\) and \(^{35}\text{S}\) samples were counted in a glass reaction vessel which could not be shielded and consequently a higher background count was obtained in these experiments.
2.7 STATISTICAL ERRORS

The decay of a radioisotope is a completely random process and is therefore subject to fluctuation due to the statistical nature of the process. This means that if a source of constant activity is measured in such a way as to exclude all other errors in measurement, the number of disintegrations observed in successive periods of fixed duration will not be constant. The probability $W(m)$ of obtaining just $m$ disintegrations in time $t$ from $N_0$ original radioactive atoms is given by the binomial expression:

$$W(m) = \frac{N_0!}{(N_0-m)!m!} p^m (1 - p)^{N_0-m}$$  \hspace{1cm} \text{equation 2.11}

where $p$ is the probability of a disintegration occurring within the time of observation. From this expression it can be shown$^{73}$ that the expected standard deviation for radioactive disintegration $\sigma$ is given by:

$$\sigma = \sqrt{m e^{-\lambda t}}$$  \hspace{1cm} \text{equation 2.12}

In practice the observation time $t$ is short compared to the half life so $\lambda t$ is small. When this is so:

$$\sigma = \sqrt{m}$$  \hspace{1cm} \text{equation 2.13}

where $m$ is the number of counts obtained. In this work all errors quoted on radiochemical measurements are the combination
of the uncertainty in the physical measurements such as weight of sample and pressure of gas, and the uncertainty in the count obtained.

2.8 $^{14}$C AND $^{35}$S COUNTING APPARATUS

Reactions involving carbon-14 or sulphur-35 labelled species were monitored using the apparatus shown in figure 2.8. This consisted of two intercalibrated GM tubes contained in a calibrated evacuable glass vessel which allowed the surface radioactivity to be determined directly.\(^7\) In order to ensure an identical counting geometry for each GM tube care was taken to keep both tubes at the same height. A solid sample could be placed directly beneath either of the GM tubes by means of a movable glass sample boat. In order to test that only the GM tube with an active solid beneath it registered counts from the solid, the counts from both GM tubes were monitored with a 137-caesium source placed directly below one of the tubes. (Table 2.1).

The tube with the 137-caesium source under it gave a large count whereas the other tube gave only a background count.

GM tube counting characteristics vary slightly from tube to tube so the two contained in the counting vessel were intercalibrated before use by recording the counts obtained from different pressures of radioactive gas. A set of results obtained using $^{35}$SF\(_4\) is illustrated in table 2.2.
Figure 2.8 $^{35}$S and C counting apparatus
### Table 2.1: Observed Count Rates

<table>
<thead>
<tr>
<th>POSITION OF $^{137}$Cs</th>
<th>TUBE 1 COUNTS s$^{-1}$</th>
<th>TUBE 2 COUNTS s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BACKGROUND</td>
<td>0.57</td>
<td>0.61</td>
</tr>
<tr>
<td>$^{137}$Cs under 1</td>
<td>85.23</td>
<td>0.65</td>
</tr>
<tr>
<td>$^{137}$Cs under 1</td>
<td>82.19</td>
<td>0.59</td>
</tr>
<tr>
<td>$^{137}$Cs under 1</td>
<td>83.36</td>
<td>0.62</td>
</tr>
<tr>
<td>$^{137}$Cs under 2</td>
<td>0.57</td>
<td>90.15</td>
</tr>
<tr>
<td>$^{137}$Cs under 2</td>
<td>0.59</td>
<td>89.79</td>
</tr>
<tr>
<td>$^{137}$Cs under 2</td>
<td>0.56</td>
<td>91.87</td>
</tr>
</tbody>
</table>

### Table 2.2: $^{35}$SF$_4$ Pressure vs Count Rate

<table>
<thead>
<tr>
<th>PRESSURE</th>
<th>COUNT RATE TUBE 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torr</td>
<td>COUNTS SEC 1</td>
</tr>
<tr>
<td>10 $^{+}$ 1</td>
<td>59.56 $^{+}$ 0.77</td>
</tr>
<tr>
<td>19 $^{+}$ 1</td>
<td>108.13 $^{+}$ 1.04</td>
</tr>
<tr>
<td>27 $^{+}$ 1</td>
<td>154.35 $^{+}$ 1.24</td>
</tr>
<tr>
<td>54 $^{+}$ 1</td>
<td>272.05 $^{+}$ 1.65</td>
</tr>
<tr>
<td>79 $^{+}$ 1</td>
<td>418.51 $^{+}$ 2.05</td>
</tr>
<tr>
<td>116 $^{+}$ 1</td>
<td>607.75 $^{+}$ 2.47</td>
</tr>
<tr>
<td>150 $^{+}$ 1</td>
<td>784.29 $^{+}$ 2.80</td>
</tr>
<tr>
<td>210 $^{+}$ 1</td>
<td>1090.81 $^{+}$ 3.30</td>
</tr>
<tr>
<td>302 $^{+}$ 1</td>
<td>1574.48 $^{+}$ 3.97</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PRESSURE</th>
<th>COUNT RATE TUBE 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torr</td>
<td>COUNTS SEC 1</td>
</tr>
<tr>
<td>10 $^{+}$ 1</td>
<td>59.63 $^{+}$ 0.77</td>
</tr>
<tr>
<td>19 $^{+}$ 1</td>
<td>109.76 $^{+}$ 1.05</td>
</tr>
<tr>
<td>27 $^{+}$ 1</td>
<td>158.52 $^{+}$ 1.26</td>
</tr>
<tr>
<td>54 $^{+}$ 1</td>
<td>276.03 $^{+}$ 1.66</td>
</tr>
<tr>
<td>79 $^{+}$ 1</td>
<td>425.16 $^{+}$ 2.06</td>
</tr>
<tr>
<td>116 $^{+}$ 1</td>
<td>616.57 $^{+}$ 2.48</td>
</tr>
<tr>
<td>150 $^{+}$ 1</td>
<td>796.76 $^{+}$ 2.82</td>
</tr>
<tr>
<td>210 $^{+}$ 1</td>
<td>1105.46 $^{+}$ 3.32</td>
</tr>
<tr>
<td>302 $^{+}$ 1</td>
<td>1593.51 $^{+}$ 3.99</td>
</tr>
</tbody>
</table>
A plot of pressure versus counts gives a straight line which passes through the origin as shown in figure 2.9.

The correlation factor for the two tubes was obtained by plotting the counts obtained from tube 1 against those obtained from tube 2. A straight line with gradient equal to the correlation factor was obtained (figure 2.10) typically 1.1 - 1.2.

Several different pairs of GM tubes were used in the course of this work. For each new pair, new plateau regions and correlation factor were determined.

Radiotracer experiments were carried out by first removing flask A from the counting vessel and loading it with an accurately weighed amount of the required solid in an inert atmosphere box. The flask was attached to the vacuum line and evacuated before being re-attached to the counting vessel which was then pumped for 30 minutes. After 30 minutes a measured pressure of radioactive gas was admitted to the counting cell and two 100 second counts taken. The average value of the counts obtained was taken as the activity of the gas before reaction. The radioactive gas was then removed from the counting vessel by condensing into Flask B. The flask containing the solid was then opened and the solid allowed to fall into the movable sample boat, which was then placed directly under one of the GM tubes. The GM tube which had the solid beneath it gave a count due to both the solid and the gas, whilst the other tube gave a count
Figure 2.9

$^{35}\text{SF}_4$ Count rate vs pressure

Count rate counts sec$^{-1}$

Pressure Torr
Figure 2.10
Count rate of G.M. tube 1 vs count rate of G.M. tube 2

Count rate (tube 1) counts sec$^{-1}$

Count rate (tube 2) counts sec$^{-1}$
due only to the gas. The reaction was followed by monitoring the counts from both tubes over a period of time. The difference in counts between the two GM tubes gave a measure of the activity present on the surface of the solid and the overall drop in gas phase counts gave a measure of the total uptake of gas by the bulk of the solid.

2.9 FLUORINE-18 COUNTING APPARATUS

Reactions involving fluorine-18 labelled species were monitored using the counting vessels shown in figure 2.11. Type 1 was used to count standard samples of gas and type 2 was used to follow the reaction between fluorine-18 labelled gas and a non active solid.

A weighed amount of the required solid was placed in one limb of the twin limbed flask in an inert atmosphere box. The flask was then transferred to the vacuum line and evacuated for 30 minutes. A measured pressure of \(^{18}\text{F}\) labelled gas was then admitted to the flask and the reaction followed by counting each limb alternately over a period of time. The limb containing the solid gave counts due to gas and solid, whilst the other limb gave counts due to gas alone. The difference between the two being a measure of the activity present in the solid. After reaction the radioactive gas was transferred from the twin limbed flask into a pre-weighed flask of type 1 and its specific count rate calculated. The specific count rate of the gas after reaction was then compared to the
specific count rate of a sample of the gas taken before reaction to determine whether the activity in the solid was due to $^{18}\text{F}$ exchange between the solid and the gas or to uptake of the gas by the solid.

Fluorine-18 labelled samples were counted using a well type scintillation counter. A well counter is less efficient at counting materials in the gas phase than those in either solid or liquid phases since only the material which is actually in the well of the counter is counted. In order to overcome this problem $\text{BF}_2^{18}\text{F}$ and $\text{AsF}_4^{18}\text{F}$ were counted as their adducts $^{75,76}$ with MeCN. $\text{SF}_4$ was counted as its adduct with pyridine $^{77}$ and $\text{COF}_2^{18}\text{F}$ was counted as a solid at $-196^\circ\text{C}$ by freezing in liquid nitrogen.

To test the validity of this method of counting, counting flasks were filled with varying amounts of labelled gas and the adducts formed. The samples were counted, a linear relationship between the amount of gas in the flask and count rate was obtained in each case. Figure 2.12 shows a plot of count rate vs amount of $\text{BF}_2^{18}\text{F}$.

2.10 PREPARATION OF RADIOCHEMICALLY LABELLED SPECIES

2.10.1 PREPARATION OF $\text{Cs}^{18}\text{F}$

Fluorine-18 was prepared in the Scottish Universities Research Reactor, East Kilbride using the irradiation
Figure 2.12

Count rate vs amount of $\text{BF}_2\text{EtO}_2^{18}$
This scheme requires $^{6}\text{Li}$ and $^{16}\text{O}$ to be intimately mixed. To achieve this $\text{Li}_2\text{CO}_3$ (BDH Analytical) is used as the target material.

$\text{Li}_2\text{CO}_3$ (2g) was irradiated with a neutron flux of $3 \times 10^{12}$ n cm$^{-2}$s$^{-1}$ for 30 minutes. The $^{18}\text{Li}$ produced in the irradiation was converted to $^{18}\text{H}$ by reaction with 50% $\text{H}_2\text{SO}_4$. The $^{18}\text{H}$ was distilled into a solution of Cs$\text{OH}$ at 0°C. The solution was then neutralised by addition of HF and evaporated to dryness on a hotplate to give Cs$^{18}\text{F}$ as a finely divided white powder. Before being used to label gaseous fluorides the Cs$^{18}\text{F}$ was further dried by heating at $120^\circ\text{C}$ under vacuum for 30 minutes.

Irradiation of 2g of lithium carbonate gave rise to a yield of $^{18}\text{F}$ of between 40 $\mu$Ci and 65 $\mu$Ci.

2.10.2 PREPARATION OF $^{18}\text{B}$, $^{18}\text{AsF}_5$, $^{18}\text{COF}_3$ AND $^{18}\text{SF}_3$

$^{18}\text{F}$ labelled boron trifluoride, arsenic pentfluoride and carbonyl fluoride were prepared by high temperature exchange with Cs$^{18}\text{F}$ in a Monel metal pressure vessel. Previous work has shown that Cs$^{18}\text{F}$ undergoes high temperature fluorine exchange more readily than any other Group 1 fluoride.

$^{18}\text{F}$ labelled sulphur tetrafluoride prepared by this method has a specific count rate which is too low,
so labelled SF$_4$ was prepared by first labelling BF$_3$ then forming its adduct with SF$_4^{26}$ and allowing the adduct to exchange at room temperature for twenty minutes before decomposing with measured amounts of dry diethyl ether.

Various reaction conditions were used in order to determine those which gave the greatest incorporation of $^{18}$F. The results of these experiments for each type of gas labelled are listed in tables 2.3 - 2.6.

From the results listed in table 2.3 it can be seen that increasing the temperature of reaction and pressure of gas increase the incorporation of $^{18}$F in BF$_3$. Table 2.4 lists the results of a series of experiments in which the Cs$^{18}$F was activated before use by reaction with hexafluoroacetone for 30 min then heating under vacuum at 120°C for 30 min. These results show that pretreatment with hexafluoroacetone has a much greater effect on the amount of $^{18}$F incorporated than increasing pressure or temperature. This is due to an increase in the surface area of the caesium fluoride caused by reaction with hexafluoroacetone (see chap 3) and hence a greater solid surface available for reaction with the BF$_3$.

Since pretreatment of the Cs$^{18}$F with hexafluoroacetone had such a marked effect on the incorporation of $^{18}$F
### TABLE 2.3

**BF$_3$ LABELLING**

**EFFECT OF TEMPERATURE AND PRESSURE ON $^{18}$F INCORPORATION**

<table>
<thead>
<tr>
<th>Pressure of BF$_3$ Torr</th>
<th>Temp $^\circ$C</th>
<th>Exchange Time min</th>
<th>Activity of Cs$^{18}$F</th>
<th>Counts in 100 sec Gas Phase m mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>510</td>
<td>85</td>
<td>60</td>
<td>30 $\mu$Ci</td>
<td>648</td>
</tr>
<tr>
<td>510</td>
<td>85</td>
<td>60</td>
<td>25 $\mu$Ci</td>
<td>616</td>
</tr>
<tr>
<td>510</td>
<td>100</td>
<td>60</td>
<td>30 $\mu$Ci</td>
<td>912</td>
</tr>
<tr>
<td>510</td>
<td>100</td>
<td>60</td>
<td>25 $\mu$Ci</td>
<td>750</td>
</tr>
<tr>
<td>760</td>
<td>125</td>
<td>60</td>
<td>30 $\mu$Ci</td>
<td>1028</td>
</tr>
<tr>
<td>760</td>
<td>125</td>
<td>60</td>
<td>30 $\mu$Ci</td>
<td>1358</td>
</tr>
</tbody>
</table>

### TABLE 2.4

**BF$_3$ LABELLING**

**EFFECT OF PRESSURE ON $^{18}$F INCORPORATION AFTER TREATMENT OF Cs$^{18}$F with (CF$_3$)$_2$CO**

<table>
<thead>
<tr>
<th>Pressure of BF$_3$ Torr</th>
<th>Temp $^\circ$C</th>
<th>Exchange Time min</th>
<th>Activity of Cs$^{18}$F</th>
<th>Counts in 100 sec Gas Phase m mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>760</td>
<td>125</td>
<td>60</td>
<td>45 $\mu$Ci</td>
<td>2467</td>
</tr>
<tr>
<td>760</td>
<td>125</td>
<td>60</td>
<td>35 $\mu$Ci</td>
<td>1906</td>
</tr>
<tr>
<td>1010</td>
<td>125</td>
<td>60</td>
<td>45 $\mu$Ci</td>
<td>3586</td>
</tr>
<tr>
<td>1010</td>
<td>125</td>
<td>60</td>
<td>55 $\mu$Ci</td>
<td>6690</td>
</tr>
<tr>
<td>1010</td>
<td>125</td>
<td>60</td>
<td>55 $\mu$Ci</td>
<td>5915</td>
</tr>
<tr>
<td>1010</td>
<td>125</td>
<td>60</td>
<td>55 $\mu$Ci</td>
<td>6203</td>
</tr>
</tbody>
</table>
in BF$_3$ the Cs$^{18}$F was treated in this way before determining optimum conditions for the labelling of AsF$_5$ and F$_2$CO. The results of these experiments are listed in tables 2.5 and 2.6. These results also show a dependence on temperature and pressure. Table 2.7 lists the optimum conditions for labelling each type of gas.

During the exchange reaction between Cs$^{18}$F and BF$_3$ approximately 6m mol of BF$_3$ were retained by the Cs$^{18}$F (6m mol). Infra red examination of the solid after reaction shows bands which can be assigned to BF$_4$.

This, together with the fact that increasing temperature and pressure increase incorporation of $^{18}$F, indicates that the exchange reaction occurs in two distinct stages. The first stage is adsorption of BF$_3$ and reaction to form BF$_4$ and then exchange between BF$_4$ and BF$_3$.

In the experiment involving AsF$_5$ and F$_2$CO uptake of gas was observed although to a lesser extent than that observed for BF$_3$. Infra red examination of the CsF after reaction indicated the presence of AsF$_6^-$ and COF$_3^-$ suggesting that $^{18}$F exchange occurs in the same way as in the CsF BF$_3$ system.
### TABLE 2.5

**AsF₅ LABELLING**

**EFFECT OF TEMPERATURE AND PRESSURE ON ¹⁸F INCORPORATION**

<table>
<thead>
<tr>
<th>Pressure of AsF₅ (Torr)</th>
<th>Temp °C</th>
<th>Exchange Time min</th>
<th>(CF₃)₂CO Pretreat</th>
<th>Activity of Cs ¹⁸F</th>
<th>Counts in 100 sec Gas Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>760</td>
<td>85</td>
<td>60</td>
<td>N</td>
<td>45 μCi</td>
<td>1356 m mol⁻¹</td>
</tr>
<tr>
<td>1010</td>
<td>125</td>
<td>60</td>
<td>N</td>
<td>35 μCi</td>
<td>1780</td>
</tr>
<tr>
<td>1010</td>
<td>125</td>
<td>60</td>
<td>Y</td>
<td>45 μCi</td>
<td>3471</td>
</tr>
<tr>
<td>1010</td>
<td>100</td>
<td>60</td>
<td>Y</td>
<td>40 μCi</td>
<td>3159</td>
</tr>
</tbody>
</table>

### TABLE 2.6

**F₂CO LABELLING**

**EFFECT OF TEMPERATURE AND PRESSURE ON ¹⁸F INCORPORATION**

<table>
<thead>
<tr>
<th>Pressure of F₂CO (Torr)</th>
<th>Temp °C</th>
<th>Exchange Time min</th>
<th>(CF₃)₂CO Treatment</th>
<th>Activity of Cs ¹⁸F</th>
<th>Counts in 100 sec Gas Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>760</td>
<td>100</td>
<td>60</td>
<td>N</td>
<td>65 μCi</td>
<td>5876 m mol⁻¹</td>
</tr>
<tr>
<td>1010</td>
<td>100</td>
<td>60</td>
<td>N</td>
<td>60 μCi</td>
<td>6499</td>
</tr>
<tr>
<td>1010</td>
<td>100</td>
<td>60</td>
<td>Y</td>
<td>65 μCi</td>
<td>11898</td>
</tr>
</tbody>
</table>

### TABLE 2.7

**OPTIMUM LABELLING CONDITIONS**

<table>
<thead>
<tr>
<th>Gas Type</th>
<th>Pressure Torr</th>
<th>Temp °C</th>
<th>Exchange Time</th>
<th>(CF₃)₂CO Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>AsF₅</td>
<td>1010</td>
<td>125</td>
<td>60 min</td>
<td>Y</td>
</tr>
<tr>
<td>BF₃</td>
<td>1010</td>
<td>100</td>
<td>60 min</td>
<td>Y</td>
</tr>
<tr>
<td>F₂CO</td>
<td>1010</td>
<td>100</td>
<td>60 min</td>
<td>Y</td>
</tr>
</tbody>
</table>
Several methods were tried in an attempt to produce nitrosyl fluoride of high enough specific count rate to be useful for exchange reactions.

The first method tried was that of Ratcliffe and Shreeve. NO$_2$ (2 mol) was condensed onto the Cs$^{18}$F in a stainless steel pressure vessel at -196°C and the vessel left at room temperature for 1 hour. Due to the short half life of $^{18}$F (110 minutes) this was the maximum time that could be allowed for reaction. Under these conditions very little $^{18}$FNO was produced.

In an effort to improve on this the caesium fluoride was pretreated with hexafluoroacetone before use by condensing into the vessel (CF$_3$)$_2$CO (10 mol). The vessel was left at room temperature for 30 min and then heated at 120°C for 30 min.

When this pretreated Cs$^{18}$F was treated with NO$_2$ the result was as in the previous attempt, a negligible yield of NO$^{18}$F.

In a second paper Ratcliffe and Shreeve state that reaction between CsF and NO$_2$ is complete in 15 minutes if the reaction is carried out at 300°C.
A third preparation was attempted in which the Cs$^{18}$F was first pretreated with hexafluoroacetone and the reaction with NO$_2$ carried out at 250$^0$C (the limit of the available heating coil). The amount of $^{18}$F NO produced in this reaction was too small to be of any use.

The main factor affecting the yield appears to be the small amount of Cs$^{18}$F produced by the reactor as the reaction of CsF with NOF requires CsF to be in excess. In view of this it was decided to add to the Cs$^{18}$F produced by the reactor 10g (65.8m mol) of hexafluoroacetone activated caesium fluoride, as activated caesium fluoride is known to react instantaneously with NO$_2$ and the addition of 10g of CsF would give the required excess.

This preparation resulted in a reasonable yield of NO$^{18}$F (2m mol) but with a very low specific count rate (3.5 count s$^{-1}$) which was too low to be of use in radiotracer experiments.

Attempts to label NOF by high temperature exchange with Cs$^{18}$F were also unsuccessful resulting in NO$^{18}$F of too low specific count rate to be of any use. As a result no further work with nitrosyl fluoride was carried out.
PREPARATION AND PURIFICATION OF $^{35}$SF$_4$

$^{35}$S labelled sulphur tetrafluoride was prepared from elemental sulphur and iodine pentfluoride according to equation 2.14

$$5S + 4IF_5 \rightarrow 5SF_4 + 2I_2$$  \hspace{1cm} \text{equation 2.14}

Rhombic ($^{35}$S) - sulphur (1 m Ci, specific activity 30 m Ci mg$^{-1}$, The Radiochemical Centre, Amersham) was dissolved in dry CS$_2$ and diluted by addition to a Monel metal pressure vessel containing inactive sulphur (7.0 m mol) also dissolved in CS$_2$. The CS$_2$ was removed under vacuum and purified iodine pentfluoride (44.8 m mol) added by vacuum distillation. The vessel was heated at 100°C for 12 hours followed by 200°C for 48 hours. After reaction the volatile material was removed at -80°C and condensed into another monel vessel containing predried sodium fluoride.

The $^{35}$SF$_4$ was purified by reaction with BF$_3$ at -80°C to form $^{35}$SF$_3$ $\cdot$ BF$_2$. Unreacted material was removed by pumping at this temperature. The adduct was decomposed by adding a calculated amount of dried diethyl ether at -80°C. The infrared spectrum of the $^{35}$SF$_4$ (table 2.8) contained no bands attributable to SF$_6$, SOF$_2$ or SiF$_4$. 
### TABLE 2.8

**INFRA RED SPECTRUM OF $^{35}$SF$_4$ (cm$^{-1}$)**

<table>
<thead>
<tr>
<th>This work</th>
<th>Literature SF$_4$</th>
<th>SF$_6$</th>
<th>SOF$_2$</th>
<th>SiF$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>887 s</td>
<td>892 $v_{A_1}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>860 s</td>
<td>867 $v_{B_1}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>730 vs</td>
<td>730 $v_{B_2}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>550 w</td>
<td>558 $v_{A_1}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>530 w</td>
<td>532 $v_{B_1}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>475 $v_{A_1}$</td>
<td></td>
<td></td>
<td>393</td>
</tr>
<tr>
<td></td>
<td>353 $v_{B_2}$</td>
<td></td>
<td></td>
<td>390</td>
</tr>
<tr>
<td></td>
<td>226 $v_{A_1}$</td>
<td></td>
<td></td>
<td>326</td>
</tr>
</tbody>
</table>
The $^{35}\text{SF}_4$ was diluted with inactive $\text{SF}_4$ (1:2 ratio) to give a working specific count rate of $258 \pm 3 \text{ counts s}^{-1} \text{ mol}^{-1}$. The $^{35}\text{S}$ count rate was determined using the counting vessel described in section 2.8 (figures 2.8). A linear count rate vs pressure relationship was obtained and is shown in figure 2.9.

2.10.5 PREPARATION AND PURIFICATION OF $\text{F}_2\text{^{14}CO}$

$^{14}\text{C}$ labelled carbonyl fluoride was prepared from carbonyl chloride and sodium fluoride.

$^{14}\text{C}$- carbonyl chloride (1m Ci, The Radiochemical Centre, Amersham) was supplied as a solution in toluene contained in a glass vial. The glass vial and a Monel metal pressure vessel were cooled to $-78^\circ\text{C}$ in solid $\text{CO}_2$. When cold the glass vial was cut open and the contents quickly transferred into the cooled metal vessel. The vial was rinsed with a small amount of toluene ($<10 \text{ ml}$) and the washings added to the metal vessel. The vessel was then degassed and the $\text{Cl}_2\text{^{14}CO}$ transferred to a second metal vessel at $-80^\circ\text{C}$ by vacuum distillation. Inactive $\text{Cl}_2\text{CO}$ (80m mol) was then added to dilute the radioactive sample.
Cl$_2^{14}$CO (30 m mol) and Cl$_2$CO (45 m mol) were condensed into a pressure vessel containing NaF; (41 g, 900 m mol) and 40 ml of acetonitrile. The vessel was then left at room temperature with occasional shaking for 36 hours.

$F_2^{14}$CO was removed at -80°C and purified by trap to trap distillation. The $F_2^{14}$CO had a specific count rate of 135 ± 2 counts s$^{-1}$m mol$^{-1}$. A linear count rate vs pressure relationship was obtained and is shown in figure 2.13.

2.10.6 **PURIFICATION OF $^{14}$CO$_2$**

$^{14}$CO$_2$ (2 m mol, 1 m Ci) which had been prepared by the addition of acid to Ba$^{14}$CO$_3$ was dried by three trap to trap distillations over fresh P$_2$O$_5$ at -80°C. It was then diluted with non radioactive CO$_2$ to give a specific activity of 2150 ± 5 counts s$^{-1}$ m mol$^{-1}$ before being transferred to a large volume storage bulb containing fresh P$_2$O$_5$ and left at room temperature for twelve hours before use. A linear count rate vs pressure relationship was obtained and is shown in figure 2.14.
Figure 2.13

Count rate of $F_2^{14}O$ vs pressure

Count rate counts/sec$^{-1}$

Pressure Torr
Figure 2.14
Count rate of $^{14}C_2O$ vs pressure

Count rate counts sec$^{-1}$

Pressure Torr
CHAPTER THREE
ACTIVATION OF CAESIUM FLUORIDE

INTRODUCTION

When caesium fluoride is used as a catalyst it is usually pretreated in some way. Methods of pretreatment range from simply heating and grinding in an inert atmosphere to formation and subsequent thermal decomposition of a chemical adduct. The caesium fluoride used in this work was pretreated by reaction with $(\text{CF}_3)_2\text{CO}$ in MeCN to form $\text{Cs}^+\text{OCF}(\text{CF}_3)_2^-$, and then decomposed by heating under vacuum to leave activated CsF. This activation process is known to increase the surface area and also to enhance the reactivity of the caesium fluoride. The effect of treating the caesium fluoride with $\text{F}_2\text{CO}$ in MeCN was also studied and the results compared with those of $(\text{CF}_3)_2\text{CO}$ activated CsF.

Before carrying out any radiotracer experiments with activated CsF the increase in surface area was determined using the $^8\text{Kr}$ B.E.T. method. Surface areas are normally measured by determining the amount of gas adsorbed at a given temperature as a function of pressure. When the surface area to be measured is small, that is below $5\text{m}^2\text{g}^{-1}$, the change in pressure cannot be measured accurately by conventional techniques. For these small areas krypton-85 is used as the adsorbate and the small changes in pressure can be
accurately determined. This is done by calibrating the pressure against the count rate of the krypton in counts sec\(^{-1}\).

3.1 EXPERIMENTAL

3.1.1 ACTIVATION OF CsF BY TREATMENT WITH \((\text{CF}_3)_2\text{CO}\)

Activated caesium fluoride was prepared according to the reaction scheme shown below using a variation of the method described by Redwood and Willis. \(^{84}\)

\[
\text{CsF}(s) + (\text{CF}_3)_2\text{CO}(g) \rightleftharpoons \text{Cs}^+(\text{solv}) + (\text{CF}_3)_2\text{FCO}^-(\text{solv})
\]

\[
\text{CsF}(s) + (\text{CF}_3)_2\text{CO}(g) \xrightarrow{\Delta} \text{Cs}^+ \text{OCF}(\text{CF}_3)_2^-(s)
\]

Caesium fluoride (4g, 26m mol, BDH Op tran grade) was ground in an inert atmosphere box and placed in a stainless steel pressure vessel (Hoke Inc.) together with four stainless steel ball bearings. The vessel was sealed and evacuated and hexafluoroacetone (30m mol), together with acetonitrile (5ml) added by vacuum distillation. The vessel was allowed to warm to room temperature and shaken for twelve hours. After twelve hours the acetonitrile and unreacted hexafluoroacetone were removed by vacuum distillation. The infra red spectrum of the product at this stage consisted of ten bands (Table 3.1). The results of a C and F analysis show that the product is \(\text{Cs OCF(CF}_3\}_2\).
**TABLE 3.1**

Infra red spectrum of Cs OCF (CF$_3$)$_2$ (cm$^{-1}$)

<table>
<thead>
<tr>
<th>Wavenumber</th>
<th>Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1450</td>
<td>m</td>
<td>ν CO</td>
</tr>
<tr>
<td>1350</td>
<td>w</td>
<td>ν CF</td>
</tr>
<tr>
<td>1250</td>
<td>s</td>
<td>ν CF</td>
</tr>
<tr>
<td>1210</td>
<td>s</td>
<td>ν CF</td>
</tr>
<tr>
<td>1150</td>
<td>s</td>
<td>ν CF</td>
</tr>
<tr>
<td>1100</td>
<td>s</td>
<td>ν CF</td>
</tr>
<tr>
<td>960</td>
<td>s</td>
<td>ν CC</td>
</tr>
<tr>
<td>780</td>
<td>w</td>
<td>ν CF</td>
</tr>
<tr>
<td>730</td>
<td>w</td>
<td>δ CF</td>
</tr>
<tr>
<td>630</td>
<td>w</td>
<td>δ CF</td>
</tr>
</tbody>
</table>

**TABLE 3.2**

Infra red spectrum of (CF$_3$)$_2$ CO (cm$^{-1}$)

<table>
<thead>
<tr>
<th>Wavenumber</th>
<th>Intensity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1805</td>
<td>m</td>
<td>ν CO</td>
</tr>
<tr>
<td>1340</td>
<td>sh</td>
<td>ν CF</td>
</tr>
<tr>
<td>1265</td>
<td>w</td>
<td>ν CF</td>
</tr>
<tr>
<td>1250</td>
<td>s</td>
<td>ν CF</td>
</tr>
<tr>
<td>970</td>
<td>s</td>
<td>ν CC</td>
</tr>
<tr>
<td>780</td>
<td>w</td>
<td>ν CC</td>
</tr>
<tr>
<td>720</td>
<td>sh</td>
<td>δ CF</td>
</tr>
<tr>
<td>640</td>
<td>w</td>
<td>δ CF</td>
</tr>
</tbody>
</table>
CsOCF (CF$_3$)$_2$ requires C 11.32%, F 41.82%

Found C 11.24%, F 41.54%

The vessel was heated under vacuum at 125°C for sixteen hours to decompose the adduct formed. After heating the CsF was transferred to an inert atmosphere box where it was ground in an agate mortar and pestle, and stored in a sealed glass vessel until required for use. After activation the caesium fluoride is an off white colour and resembles talc in appearance.

3.1.2 PREPARATION OF CsOCF$_3$

Caesium fluoride (2g, 13m mol) was ground in an inert atmosphere box and placed in a stainless steel pressure vessel equipped with a valve. Carbonyl fluoride (15 m mol) and acetonitrile (5ml) were added by vacuum distillation. The vessel was allowed to warm to room temperature and shaken for twelve hours. After twelve hours the acetonitrile and unreacted carbonyl fluoride were removed by vacuum distillation. The vessel was then transferred to an inert atmosphere box where the CsOCF$_3$ (13 m mol) produced was stored in a sealed glass vessel until required for use.
**TABLE 3.3**

Infra red spectrum (cm\(^{-1}\)) of solid Cs OCF\(_3\) Nujol Mull

<table>
<thead>
<tr>
<th>Present work</th>
<th>Literature(^{28})</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000 bw</td>
<td></td>
<td>(\nu_3 + \nu_1) (\text{HF}_2)(^{-}) 88</td>
</tr>
<tr>
<td>1825 w</td>
<td></td>
<td>(\nu_2 + \nu_1) (\text{HF}_2)(^{-})</td>
</tr>
<tr>
<td>1560 vs br</td>
<td>1560 vs br</td>
<td>(\nu_1) (A_1) \text{CO str}</td>
</tr>
<tr>
<td>1455 s</td>
<td>813 s</td>
<td>(\nu_3) (\text{CO}_2)(^{-}) 87</td>
</tr>
<tr>
<td>1230 s</td>
<td>595 mw</td>
<td>(\nu_2) (\text{HF}_2)</td>
</tr>
<tr>
<td>960 b vs</td>
<td>960 vs br</td>
<td>(\nu_4) (E) (\text{CF}_3) asym str</td>
</tr>
<tr>
<td>805 s</td>
<td>813 s</td>
<td>(\nu_2) (A_1) (\text{CF}_3) sym str</td>
</tr>
<tr>
<td>595 m</td>
<td>595 mw</td>
<td>(\nu_3) (A_1) \text{sym CF}_3) def</td>
</tr>
<tr>
<td>570 ms</td>
<td>574 ms</td>
<td>(\nu_5) E (\text{OCF}) def</td>
</tr>
<tr>
<td>420 w</td>
<td>423 w</td>
<td>(\nu_6) asym (\text{CF}_3)</td>
</tr>
</tbody>
</table>
The infra red spectrum of the trifluoromethoxide consisted of ten bands (table 3.3).

3.1.3 DECOMPOSITION OF Cs OCF₃

Cs OCF₃ (1g, 4.6m mol) was placed in a stainless steel pressure vessel equipped with a valve and heated under vacuum at 120°C for three hours. The vessel was allowed to cool and transferred to an inert atmosphere box. Infra red examination of the product showed that the trifluoromethoxide anion was no longer present.

3.1.4 SURFACE AREA DETERMINATION

Surface areas were determined by the B.E.T. method using the radio-isotope ⁸⁵ Kr as adsorbate. The apparatus was a modified version of that described by Aylmore and Jepson and consisted of a calibrated system connected to a standard vacuum line system. The calibrated section, constructed from Pyrex glass consisted of two sets of bulbs each with a mercury reservoir, a ⁸⁵ Kr storage bulb (B), a thin walled counting vessel (C) and the adsorbent sample bulb (S). This system is shown in figure 3.1.
Figure 3.1 B.E.T. Apparatus
The calibrated section was also connected to reservoirs containing $^{85}\text{Kr}$ ($t_\frac{1}{2} = 10.6\text{y}$, $\beta_{\text{max}} = 0.67\text{ MeV}$ Radiochemical Centre Amersham) and inactive Kr (BOC Ltd) and to a trap containing charcoal activated at 578 K in vacuo which was used to prepare diluted $^{85}\text{Kr}$ of a suitable working activity.

A calibration curve of $^{85}\text{Kr}$ count rate versus pressure was determined (Figure 3.2). Pressures were measured using a Pirani gauge and $^{85}\text{Kr}$ activities determined using a Geiger-Muller counter (Mullard 2P 1481) externally mounted immediately below the counting vessel C. The counting vessel was surrounded by lead to cut down the effect of background radiation. Twenty minutes were required for equilibrium to be attained after each pressure change. The count rates were reproducible, the time of counting being adjusted to give a total count of $\geq 10^4$, to minimise counting errors.

The sample bulb(S) was loaded with an accurately weighed sample (0.2 – 0.5g, 1.3 – 3.3m mol) of caesium fluoride in an inert atmosphere box, and degassed overnight. $^{85}\text{Kr}$ was admitted to the manifold and by filling the bulbs with mercury the volume of the system was changed thus altering the pressure, P. For every surface area determination a graph of volume versus temperature/pressure was drawn. This
Figure 3.2
Count rate of $^{85}$Kr vs pressure

Count rate counts sec$^{-1}$

Pressure Torr
gave a straight line which intercepted the y axis at a volume equal to the dead space of the apparatus. The sample bulb was then cooled to 77K in liquid nitrogen. A correction was made to take account of the effective volume of the apparatus when part of the system was cooled to 77K. The corrected volume versus temperature/pressure plot should be a line parallel to the room temperature line with an intercept equal to the dead space plus the temperature corrected volume. This was verified experimentally by carrying out an experiment with no CsF in the sample bulb.

With the bulb held at 77K a second volume versus temperature/pressure relationship was obtained. This was a straight line with the same intercept as the temperature corrected line but with a different gradient. The amount of $^{85}$Kr adsorbed was calculated by taking the difference in volume, $\Delta V$, between these two lines. The number of Kr molecules adsorbed $(n)$ is given by equation 3.1.

$$n = \frac{P \Delta V}{RT} \frac{N}{760 \times 10^3}$$  

Equation 3.1

Where $P$ = Pressure (Torr)

$\Delta V$ = Change in volume (ml)

$N$ = Avagadro number ($6.022 \times 10^{23}$)
\[ T = \text{Temperature at which the adsorption isotherm is determined, that is 77K} \]

\[ R = \text{Gas constant (0.082 l at mol}^{-1}\text{K}^{-1}) \]

The B.E.T. equation (equation 3.2) states that

\[
\frac{P}{n(R_0-P)} = \frac{1}{N_mC} + \frac{C-1}{N_mC} \frac{P}{P_0} \quad \text{Equation 3.2}
\]

where \( n \) = amount adsorbed at pressure \( P \)

\( P_0 \) = saturated vapour pressure of the gas at the adsorption temperature

\( C \) = constant for any particular gas/solid system

\( N_m \) = quantity of gas required to form a monolayer

Therefore a graph of \( \frac{P}{n(R_0-P)} \) versus \( \frac{P}{P_0} \) gives a straight line with gradient \( \frac{C-1}{N_mC} \) and intercept \( \frac{1}{N_mC} \).

Thus the surface area was calculated from equation 3.3.

\[
19.5 \times 10^{-20} \text{ m}^2 \quad \text{Equation 3.3}
\]

where \( 19.5 \times 10^{-20} \text{ m}^2 \) is the molecular area of Kr.

A typical calculation is shown in table 3.4 and in figures 3.3 and 3.4.

From figure 3.3

\[
\text{Gradient} = 0.7389 \times 10^{-18}
\]

\[
\frac{C-1}{N_mC} = 0.7389 \times 10^{-18}
\]
TABLE 3.4

SURFACE AREA DETERMINATION OF ACTIVATED CsF

<table>
<thead>
<tr>
<th>Volume (ml)</th>
<th>Counts (sec⁻¹)</th>
<th>Temp (°C)</th>
<th>Pressure (Tor)</th>
<th>T/P x 10⁻³ (°C Torr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>183.37</td>
<td>47.06</td>
<td>20.1</td>
<td>0.131</td>
<td>0.153</td>
</tr>
<tr>
<td>120.30</td>
<td>61.72</td>
<td>20.7</td>
<td>0.177</td>
<td>0.117</td>
</tr>
<tr>
<td>60.73</td>
<td>86.87</td>
<td>20.7</td>
<td>0.256</td>
<td>0.081</td>
</tr>
<tr>
<td>31.20</td>
<td>111.55</td>
<td>21.1</td>
<td>0.333</td>
<td>0.063</td>
</tr>
<tr>
<td>0.00</td>
<td>153.30</td>
<td>21.0</td>
<td>0.463</td>
<td>0.045</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Volume (ml)</th>
<th>Counts (sec⁻¹)</th>
<th>Temp (°C)</th>
<th>Pressure (Tor)</th>
<th>T/P x 10⁻³ (°C Torr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>183.37</td>
<td>37.15</td>
<td>21.4</td>
<td>0.100</td>
<td>0.214</td>
</tr>
<tr>
<td>120.30</td>
<td>45.32</td>
<td>21.6</td>
<td>0.126</td>
<td>0.171</td>
</tr>
<tr>
<td>60.73</td>
<td>60.48</td>
<td>21.7</td>
<td>0.173</td>
<td>0.125</td>
</tr>
<tr>
<td>31.20</td>
<td>71.97</td>
<td>22.2</td>
<td>0.209</td>
<td>0.106</td>
</tr>
<tr>
<td>0.00</td>
<td>89.77</td>
<td>22.0</td>
<td>0.265</td>
<td>0.083</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ΔV (ml)</th>
<th>n x 10⁻¹⁸</th>
<th>p⁰ - p</th>
<th>n(p⁰ - p) x 10⁻¹⁸</th>
<th>P/ n(p⁰ - p) x 10⁻¹⁸</th>
<th>P/P₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>62</td>
<td>0.773</td>
<td>2.390</td>
<td>1.847</td>
<td>0.054</td>
<td>0.040</td>
</tr>
<tr>
<td>53</td>
<td>0.833</td>
<td>2.364</td>
<td>1.969</td>
<td>0.064</td>
<td>0.051</td>
</tr>
<tr>
<td>43</td>
<td>0.827</td>
<td>2.317</td>
<td>2.148</td>
<td>0.080</td>
<td>0.069</td>
</tr>
<tr>
<td>39</td>
<td>1.016</td>
<td>2.881</td>
<td>2.317</td>
<td>0.090</td>
<td>0.084</td>
</tr>
<tr>
<td>34</td>
<td>1.123</td>
<td>2.225</td>
<td>2.499</td>
<td>0.106</td>
<td>0.106</td>
</tr>
</tbody>
</table>
Figure 3.3

Volume vs \( T/P \times 10^{-3} \)

1 Room temperature isotherm
2 Theoretical 77K isotherm
3 Experimental 77K isotherm
Figure 3.4

$\frac{P}{x(P^*-P)}$ vs $\frac{P}{P^*}$
Intercept = 0.0262 x 10^{-18}

\[
\frac{1}{N_m C} = 0.0262 \times 10^{-18}
\]

\[
N_m = \sqrt{\frac{C-1}{N_m C}} + \frac{1}{N_m C}
\]

\[
N_m = 1.307 \times 10^{18}
\]

The surface area = \(\frac{N_m \times \text{molecular area of Kr}}{\text{sample weight}}\)

\[
= \frac{1.307 \times 10^{18} \times 19.5 \times 10^{-20}}{0.0908}
\]

\[
= 2.808 \text{ m}^2 \text{ g}^{-1}
\]

3.2 RESULTS

3.2.1 THE \((CF_3)_2CO\) ACTIVATION PROCESS

The infra red spectrum of Cs(OCF (CF\(_3\))\(_2\)) consists of ten bands (Table 3.1). The band at 1450 cm\(^{-1}\) is assigned to the CO stretching mode by analogy with the frequencies in the ions CO\(_3^{2-}\) (1410 - 1450 cm\(^{-1}\)), HCOO\(^-\) and CH\(_3\)COO\(^-\) (near 1570 cm\(^{-1}\)) and CF\(_3\)COO\(^-\) (1700 cm\(^{-1}\)). Comparison of this frequency with the CO stretching frequency in \((CF_3)_2CO\) (table 3.2) shows a shift of approximately four hundred wave numbers, consistent with a change from a CO double bond to a CO single bond. This suggests that the
reaction of hexafluoroacetone with caesium fluoride results in the formation of an ionic product, not just a simple adduct.

The infra red spectrum of the heptafluoroisopropoxide after heating under vacuum at 125°C for 16 hours shows the same ten bands as those listed in table 3.1, indicating that complete decomposition does not occur as was previously thought. In an effort to quantify the amount of the anion remaining, fluorine and carbon analyses were carried out on a sample of the heptafluoroisopropoxide after heating. The results of these analyses are given below:

\[
\text{Cs(OCF} \text{(CF}_3\text{)}_2) \text{ requires C 11.32%, F 41.82%}
\]

\[
\text{Found after heating C 0.29%, F 12.44%}
\]

\[
\text{Mole ratio of carbon : fluorine before heating } = 1:2.33
\]

\[
\text{Mole ratio of carbon : fluorine after heating } = 1:27
\]

The results of the analyses after heating correspond to a solid comprising approximately 99.5% CsF and 0.5% Cs(OCF (CF\textsubscript{3})\textsubscript{2}). Thus all references in this work to activated caesium fluoride actually refer to a solid of this composition.
3.2.2 PREPARATION AND DECOMPOSITION OF CsOCF₃

The preparation of caesium trifluormethoxide by reaction of carbonyl fluoride with caesium fluoride in acetonitrile was first reported in 1965 by M E Redwood and C J Willis. The CsOCF₃ formed was reported to be crystalline and stable with respect to decomposition at room temperature. Its rate of decomposition at 80°C was reported to be very slow with less than 10% decomposition after 80 minutes. It has since been discovered that Cs OCF₃ can be completely decomposed by heating under vacuum at 120°C for three hours. The caesium fluoride which remained after reaction was similar in appearance to that obtained after treatment with hexafluoroacetone and had a similar B.E.T. surface area.

When Cs(OCF(CF₃)₂) is decomposed a small amount of the heptafluoroisopropoxide anion is retained. There is no evidence for the retention of any of the trifluoromethoxide anion when Cs OCF₃ is decomposed. With this in mind a sample of caesium fluoride was pretreated by formation and subsequent decomposition of Cs OCF₃, and its reactions with ¹⁸F labelled BF₃ were studied. The results obtained from these experiments were compared to those obtained from hexafluoroacetone pretreated caesium fluoride in an attempt to determine whether or not the small amount
of retained $\text{OCF(CF}_3\text{)}_2^-$ anion has any effect on the reactions (See Chapter 4 section 4.2.5).

The $\text{CF}_3\text{O}^-$ anion has $C_{3v}$ symmetry and has therefore six vibrational modes, $3 A_1$ and $3E$, all of which are infra red active. Assignment of all six modes has been accomplished by comparison with the vibrational spectrum of the isoelectronic ONF$_3^2\text{.}$ The infra red spectrum of the trifluoromethoxide prepared in section 3.1.2 contained ten bands. The IR spectrum of Cs OCF$_3$ prepared by Redwood and Willis $^84$ also showed more bands than expected for a simple CF$_3\text{O}^-$ anion of $C_{3v}$ symmetry. These extra bands are due to hydrolysis products, as Cs OCF$_3$ is readily hydrolysed to give HF, Cs HF$_2$ and H$_2$CO$_3$. The band at 1230 cm$^{-1}$ corresponds to the $\nu_2$ mode of HF$_2^-$. The bands at 1825 and 2000 cm$^{-1}$ correspond to the combination modes $\nu_2 + \nu_1$ and $\nu_3 + \nu_1$ of HF$_2^-$. The band at 1455 corresponds to the $\nu_3$ mode of the CO$_3^{2-}$ anion. $^87$

After decomposition by heating under vacuum for 3 hours at 120$^\circ$C the infra red spectrum contained no bands which could be assigned to the OCF$_3^-$ anion.

3.2.3 SURFACE AREA DETERMINATION OF CAESIUM FLUORIDE

When a gas is allowed to come into contact with the surface of a solid, the gas may be adsorbed by the
surface depending upon the experimental conditions. This adsorption is either chemical or physical in nature depending on the type of bond formed between the gas molecules, the adsorbate, and the solid surface, the adsorbent. Chemical adsorption involves the formation of chemical bonds between the adsorbate and the adsorbent. In consequence chemical adsorption is limited to the formation of a monolayer at the surface, and is limited to certain solid/gas systems, for example, hydrogen and transition metals. In contrast physical adsorption can, in principle occur between all gases and all solids provided the temperature is not considerably in excess of the boiling point of the adsorbate. Unlike chemical adsorption, in the physically adsorbed state, no chemical bonds are formed between the adsorbate and the adsorbent; forces similar to those responsible for the cohesive properties of liquids, for example van der Waals' forces are involved. Because of this, physical adsorption is not restricted to a monomolecular layer, multi layers may be built up on the surface.

The extent of coverage of the surface by the adsorbate is related to the pressure of the adsorbate gas. To determine the surface area of a sample it is necessary to determine when the adsorbed monolayer is complete.
The first important treatment of adsorption was developed by Langmuir. In his model, the surface of the solid was regarded as an array of adsorption sites. A state of dynamic equilibrium was postulated in which the rate at which molecules arriving from the gas phase and condensing on to bare sites is equal to the rate at which molecules evaporate from occupied sites.

The rate at which the gaseous species is adsorbed is proportional to the number of molecules colliding with the solid surface, which in turn is proportional to the partial pressure $p_a$, at a fixed temperature. The adsorption rate must also be proportional to the number of empty sites, assuming that the surface is energetically uniform. If the fraction of the sites covered is $\theta$, then $R_a$, the rate of adsorption per unit surface area may be written as:

$$R_a = K_a p_a (1 - \theta) \quad \text{Equation 3.4}$$

where $K_a$ is the rate constant for adsorption.

$R_a$, the rate of desorption of the adsorbed species, is proportional to the amount of adsorbate on the surface. Thus

$$R_d = K_d \theta \quad \text{Equation 3.5}$$

where $K_d$ is the rate constant for desorption.
At equilibrium, the rates of adsorption and desorption are equal and the extent of coverage at equilibrium, \( \theta_e \), may be obtained by equating \( R_a \) and \( R_d \) to give:

\[
\theta_e = \frac{K_{p_a}}{1 + K_{p_a}}, \quad \text{Equation 3.6}
\]

where \( K = \frac{k_a}{k_d} \)

Equation 3.6 is known as the Langmuir adsorption isotherm. In deriving this equation Langmuir assumed that adsorption was restricted to a monolayer.

The major difficulty to be overcome with physical adsorption is that, because of the close similarity with the liquefaction of gases, adsorbed monolayers are not complete before further adsorbed layers begin to form on top of the first layer.

By introducing a number of simplifying assumptions Brunauer, Emmett and Teller\(^2\) extended the Langmuir theory to cover multilayer physical adsorption.

When extended to the second layer, the Langmuir mechanism requires that the rate of condensation of molecules from the gas phase onto molecules already adsorbed in the first layer, shall be equal to the rate of evaporation from the second layer, that is

\[
a_2 p s_4 = b s_2 e^{-\frac{E_2}{RT}} \quad \text{Equation 3.7}
\]
and for the ith layer

\[ a_i p s_{i-1} = b_i s_i e^{-E_i/RT} \]  \quad \text{Equation 3.8}

where \( s_i \) is the surface area covered by \( i \) layers of
adsorbed molecules.

\( p \) is the pressure
\n\( E_i \) is the heat of adsorption of the \( i \)th layer

\( a_i, b_i \) are constants

The total surface area of the solid is given by

\[ A = \sum_{i=0}^{\infty} s_i \]  \quad \text{Equation 3.9}

and the total volume adsorbed is

\[ V = v_0 \sum_{i=0}^{\infty} s_i \]  \quad \text{Equation 3.10}

where \( v_0 \) is the volume of gas adsorbed on one square
centimetre of the adsorbent surface when it is
covered with a complete unimolecular layer of
adsorbed gas.

It follows that:

\[ \frac{V}{V_m} = \frac{V}{v_0} = \frac{\sum_{i=0}^{\infty} i s_i}{\sum_{i=0}^{\infty} s_i} \]  \quad \text{Equation 3.11}

where \( V_m \) is the volume of gas adsorbed when the entire
adsorbent surface is covered with a complete
unimolecular layer.
The summation indicated in equation 3.11 can be carried out by making the simplifying assumptions that the evaporation-condensation properties of the molecules in the second and higher adsorbed layers are the same as those of the liquid state. This allows \( s_1, s_2, \ldots, s_i \) to be expressed in terms of \( s_0 \).

\[
s_1 = Ys_0, \text{ where } Y = \left(\frac{a_i}{b_i}\right)e^{E_i/RT} \quad \text{Equation 3.12}
\]

\[
s_2 = Xs_1, \text{ where } X = \frac{p}{(g)e^{E/RT}} \quad \text{Equation 3.13}
\]

\[
S_3 = XS_2 = x^2s_1
\]

\[
s_i = xs_i = x^{i-1}s_1 = yx^{i-1}s_0 = cx^{i-1}s_0 \quad \text{Equation 3.14}
\]

where \( c = \frac{a_i}{b_i}e^{E_1 - E_L/RT} \),

\[
g = \frac{b_i}{a_i}
\]

\( E_L = \) heat of liquefaction

Substituting into equation 3.11 gives:

\[
\frac{v}{V_m} = \frac{cS_0}{s_0} \sum_{i=1}^{\infty} \frac{ix^i}{\left(1 + c \sum_{i=1}^{\infty} x^i\right)} \quad \text{Equation 3.15}
\]

The summation represented in the denominator is the sum of an infinite geometric progression.

\[
\sum_{i=1}^{\infty} x^i = \frac{x}{1-x} \quad \text{Equation 3.16}
\]
The summation in the denominator can be treated similarly:

\[ \sum_{i=1}^{\infty} i x^i = x \frac{d}{dx} \sum_{i=1}^{\infty} x^i = \frac{x}{(1-x)^2} \quad \text{Equation 3.17} \]

It follows therefore that:

\[ \frac{V}{V_m} = \frac{cx}{(1-x)(1-x + cx)} \quad \text{Equation 3.18} \]

At the saturation pressure of the gas, \( P_0 \), an infinite number of layers can build up on the adsorbent. To make \( v = \infty \), when \( p = p_0 \), \( x \) must be equal to unity. Thus from equation 3.13

\[ (P_0/g) e^{E_L/RT} = 1 \quad \text{and} \quad x = P/P_0 \]

Substituting into equation 3.18 gives the isotherm equation 3.19

\[ v = \frac{V_m c P}{(P_0-P) (1 + (c-1)(P/P_0))} \quad \text{Equation 3.19} \]

Equation 3.19 is the form of the B.E.T. equation used throughout this work.

The surface areas of the caesium fluoride samples were determined using the radio-isotope \( ^{85}\text{Kr} \) as adsorbate. The advantage of using a radioactive gas is that small changes in pressure can be determined relatively rapidly and with a high precision.
Three different types of caesium fluoride were examined:

**Type 1** CsF (B.D.H. Optran Grade) ground in an agate mortar and pestle in an inert atmosphere box.

**Type 2** CsF (B.D.H. Optran Grade) pretreated by reaction with \((\text{CF}_3)_2\text{CO}\) as described in section.

**Type 3** CsF (B.D.H. Optran Grade) pretreated by reaction with \(\text{F}_2\text{CO}\) as described in section.

Five surface area determinations were carried out on both hexafluoroacetone activated CsF and non activated CsF. Typical surface areas obtained were 0.25 m\(^2\) g\(^{-1}\) for non activated CsF and 2.55 m\(^2\) g\(^{-1}\) for activated CsF.

In these calculations the major source of error is graphical. If the error on each separate graph is calculated and the errors combined using the standard method for combination of errors, the error on the surface area determination of activated CsF is \(0.51\) m\(^2\) g\(^{-1}\).

A more satisfactory method than this is to carry out a number of surface area determinations and obtain the error limits by statistical analysis. Table 3.5 lists the results of five determinations on activated...
CsF. The mean value of these five results is 2.547. The standard deviation is 0.360. Hence by this method the surface area of activated CsF is $2.55 \pm 0.36 \text{ m}^2 \text{ g}^{-1}$. The disadvantage of this type of error calculation is that with such a small number of data points it cannot be assumed that the true value of the surface area agrees exactly with the mean of the results obtained, since further determinations would result in a different mean value. It is better therefore to determine an interval within which it is highly probable that the true value lies. This interval is called the reliability interval and the probability selected is called the reliability coefficient. The reliability interval $L$ is given by equation 3.20.

\[
L_{1,2} = \bar{X} \pm Kn R \quad \text{Equation 3.20}
\]

where $L_1$ = the lower limit of the reliability interval
$L_2$ = the upper limit of the reliability interval
$\bar{X}$ = the mean value
$Kn$ = the reliability coefficient
$R$ = the range of the results

For the given five results the reliability interval in which the true result lies with a probability of 95% is:

\[
2.55 \pm (0.51 \times 0.91)
= 2.55 \pm 0.46
\]
### TABLE 3.5

SURFACE AREA OF HEXAFLUOROACETONE ACTIVATED CsF

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Surface Area $m^2 g^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.076</td>
</tr>
<tr>
<td>2</td>
<td>2.355</td>
</tr>
<tr>
<td>3</td>
<td>2.807</td>
</tr>
<tr>
<td>4</td>
<td>2.986</td>
</tr>
<tr>
<td>5</td>
<td>2.511</td>
</tr>
</tbody>
</table>

### TABLE 3.6

SURFACE AREA OF NON ACTIVATED CsF

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Surface Area $m^2 g^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.310</td>
</tr>
<tr>
<td>2</td>
<td>0.249</td>
</tr>
<tr>
<td>3</td>
<td>0.272</td>
</tr>
<tr>
<td>4</td>
<td>0.224</td>
</tr>
<tr>
<td>5</td>
<td>0.192</td>
</tr>
</tbody>
</table>
Therefore it is 95% certain that the true value of the surface area of activated caesium fluoride lies in the range $3.01 - 2.09 \text{ m}^2 \text{g}^{-1}$.

Table 3.6 lists the results of five surface area determinations on non activated caesium fluoride. By applying equation 3.20 to these results, the reliability interval in which the true result lies with a probability of 95% is $0.31 - 0.19 \text{ m}^2 \text{g}^{-1}$.

Table 3.7 shows the results of three surface area determinations on caesium fluoride activated by formation and decomposition of CsOCF$_3$. For these three results the reliability interval in which the true result lies with a probability of 95% is $2.27 - 1.77 \text{ m}^2 \text{g}^{-1}$. The results of the surface area determinations on the three different types of CsF are summarised in table 3.8.

In an effort to reduce the error on each individual determination, the calculations were done using a programme written for the BBC microcomputer which employs linear regression analysis to obtain the line of best fit for each set of data. (Programme 1 in appendix)
TABLE 3.7

SURFACE AREA OF CsF ACTIVATED BY REACTION WITH F₂CO

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Surface Area m² g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.910</td>
</tr>
<tr>
<td>2</td>
<td>2.051</td>
</tr>
<tr>
<td>3</td>
<td>2.101</td>
</tr>
</tbody>
</table>

TABLE 3.8

SUMMARY OF SURFACE AREA RESULTS

<table>
<thead>
<tr>
<th>Type of CsF</th>
<th>Surface Area m² g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CF₃)₂CO activated CsF</td>
<td>3.01 - 2.09</td>
</tr>
<tr>
<td>F₂CO activated CsF</td>
<td>2.27 - 1.77</td>
</tr>
<tr>
<td>Non activated CsF</td>
<td>0.31 - 0.19</td>
</tr>
</tbody>
</table>
3.3 DISCUSSION

The surface areas of hexafluoroacetone activated caesium fluoride and non activated caesium fluoride have previously been determined by Kolta and coworkers\textsuperscript{83} using the apparatus described in section 3.1.4. The results obtained were much lower than those obtained in the present work. The values quoted are 0.04 m\(^2\) g\(^{-1}\) for non activated CsF and 0.41 m\(^2\) g\(^{-1}\) for hexafluoroacetone activated CsF.

This difference occurs because Kolta and coworkers used the vapour pressure of solid krypton in their calculations (P\(^0\) = 0.62 Torr at 77K) but if the solid is taken as the reference state the adsorption isotherm shows an unusually sharp upturn at the high pressure end. The usual practice, following Beebe,\textsuperscript{94} is therefore to take P\(^0\) as the saturation vapour pressure of the supercooled liquid. (P\(^0\) = 2.49 Torr at 77K). All B.E.T. surface area calculations in this work are based on the saturation vapour pressure of the supercooled liquid.

Pretreatment of caesium fluoride with hexafluoroacetone in acetonitrile produces marked changes in both the appearance of the CsF and in its physical properties. The pretreatment process results in a ten fold increase in surface area and produces an off white, finely divided solid which resembles talc.
The increase in surface area is too large to be due simply to a reduction in the CsF particle size. The two most likely explanations for this large increase in surface area are:

1. Disruption of the crystal structure by (CF$_3$)$_2$CO

2. Formation of a porous structure

CsF reacts with (CF$_3$)$_2$CO to produce Cs$^+$ (OCF(CF$_3$)$_2$)$^-$ as an ionic solid. Infra red examination of this product confirms that there is no free (CF$_3$)$_2$CO present, it is all converted to OCF(CF$_3$)$_2^-$ . To accommodate the large heptfluoroisopropoxide anion, the crystal lattice must undergo some form of expansion. After Cs(OCF(CF$_3$)$_2$) has been heated under vacuum, examination of the solid by infra red spectroscopy has shown that some OCF(CF$_3$)$_2^-$ is retained. Although the solid contains only 0.5% CsOCF(CF$_3$)$_2$ after heating this must prevent the CsF from returning to its original crystal structure, hence the surface area must increase.

When CsF reacts with F$_2$CO in acetonitrile CsOCF$_3$ is formed. When the trifluoromethoxide is heated under vacuum the solid is completely decomposed to leave only CsF. The surface area of this CsF is 1.91m$^2$g$^{-1}$ compared to 2.55m$^2$g$^{-1}$ for hexafluoroacetone activated CsF. This shows that the retained DCF (CF$_3$)$_2^-$ can only have a minor effect on the surface area of the CsF since treatment with F$_2$CO produces a similar effect with no trifluoromethoxide retained to affect the crystal structure.
Thermal decomposition reactions of the type shown below

\[
\text{Solid A} \rightarrow \text{Solid B + gas}
\]

are known to produce porous solids. For example the production of lime by calcination of limestone\textsuperscript{94} or chalk where the loss of a volatile component leads to the development of a pore system with its associated increased surface area. The decomposition of CsOCF(CF\textsubscript{3})\textsubscript{2} is a reaction of this type and it is therefore reasonable to assume that a porous solid is formed.

The pore systems of solids are of many different kinds. The individual pores may vary greatly both in size and in shape within a given solid, and between one solid and another. Pores are usually classified according to their average width as proposed by Dubinin.\textsuperscript{95} This classification is summarised in table 3.9.

In a micropore the interaction energy of the solid with a gas molecule is significantly higher than in a wider pore, owing to the proximity of the walls and the overlap of their potential fields. The amount adsorbed at a given relative pressure is correspondingly enhanced. If micropores are present in a sample the specific surface area derived by the B.E.T. procedure will be erroneously high.\textsuperscript{96}

This problem is encountered with hexafluoroacetone activated potassium fluoride. With activated KF it is impossible to obtain reproducible results from sample to sample.\textsuperscript{97}
**TABLE 3.9**

CLASSIFICATION OF PORES ACCORDING TO THEIR WIDTH

<table>
<thead>
<tr>
<th>Pore Type</th>
<th>Width</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micropores</td>
<td>Less than 20 Å</td>
</tr>
<tr>
<td>Mesopores</td>
<td>Between 20 and 500 Å</td>
</tr>
<tr>
<td>Macropores</td>
<td>Greater than 500 Å</td>
</tr>
</tbody>
</table>
The average value obtained is much greater than that obtained for caesium fluoride, $21.08 - 9.31 \text{m}^2 \text{g}^{-1}$ compared to $3.01 - 2.09 \text{m}^2 \text{g}^{-1}$.

In order to calculate the B.E.T. surface area it is necessary to plot three adsorption isotherms, one at room temperature, one at 77K and a theoretical 77K isotherm which should be parallel to the room temperature line and intercept the y axis at the volume equal to the dead space of the system when the sample bulb is immersed in liquid $N_2$. For normal B.E.T. behaviour the intercepts of the theoretical isotherm and that determined at 77K should be the same. The experimentally determined 77K isotherms of activated KF intercept the y axis at points much greater than the volume of the dead space of the system. This suggests that an initial uptake of gas has taken place at low relative pressure which is consistent with capillary condensation in a microporous solid.

Hexafluoroacetone pretreatment of potassium fluoride must therefore produce a solid which is almost wholly microporous whereas the same treatment of caesium fluoride produces a solid composed of larger pores.
CHAPTER FOUR
CHAPTER 4

REACTIONS OF GASEOUS LEWIS ACID FLUORIDES WITH CAESIUM FLUORIDE

INTRODUCTION

In order to test the appropriateness of molecular analogies in describing the interactions of gaseous Lewis acids with a solid Lewis base, the reactions between caesium fluoride and AsF$_5$, BF$_3$, CO$_2$, F$_2$CO and SF$_4$ were studied. The reactions were studied at room temperature using $^{18}$F labelled species, together with $^{14}$C and $^{35}$S labelled species where appropriate.

4.1 EXPERIMENTAL

$^{18}$F labelled species were prepared by high temperature exchange with reactor produced Cs$^{18}$F as described in section 2.10.2. $^{14}$CO$_2$, F$_2$$^{14}$CO and $^{35}$SF$_4$ were prepared as described in sections 2.10.6, 2.10.5, 2.10.4.

The reactions between the $^{18}$F labelled gases and caesium fluoride were followed using the types of reaction vessel shown in figure 2.11.

One limb of the vessel was loaded with a weighed amount of CsF (usually 0.50g 3.3mol) in an inert atmosphere box. The vessel was removed from the box, attached to the vacuum line and evacuated. Using the pressure gauge attached to the main manifold a measured pressure of the labelled gas
(usually 300 Torr, which is equivalent to 1.1m mol of gas in the reaction vessel) was admitted to the reaction vessel. The growth of activity in the solid was followed by counting each limb of the reaction vessel alternately and subtracting the counts obtained from the limb with no CsF from the counts obtained from the limb containing the CsF. Figure 4.1 shows a typical set of results for the reaction between AsF$^{18}_4$ and CsF. Line 1 shows the count rate due to the solid + gas, Line 2 shows the count rate due to the gas and line 3 shows the count rate due to the solid alone. All experimental results were corrected for radioactive decay and background counts using a programme written for the Dragon microcomputer. (Programme number 2 in appendix).

Experiments involving $^{14}$CO$_2$, $^{14}$CO and $^{35}$SF$_4$ were carried out in the reaction vessel shown in figure 2.8. Weighed amounts of CsF (usually 0.50 to 3.3m mol) were loaded into the sample tube A in an inert atmosphere box. The sample tube was then evacuated and connected to the counting vessel. The counting vessel was pumped out for ten minutes and then isolated from the pump. Bulb B containing a known amount of labelled gas was opened and the pressure allowed to equilibrate. Three counts were taken and the average of these taken as the count rate of the gas before reaction. The gas was recondensed into the storage bulb and the flask containing the CsF opened to allow the CsF to fall into one section of the movable glass boat. The section containing the CsF was placed directly below one of the GM tubes and the labelled gas re-admitted to the counting vessel. Counts were taken at five minute intervals.
Figure 4.1

Reaction of AsF$_4^+$ with CsF.

Solid count rate vs time
The count rates obtained were corrected for background, the dead time of the GM tubes and their intercalibration factor using a programme written for the BBC microcomputer (Programme number 6 in appendix).

Manometric measurements were carried out using the apparatus described in section 2.1.2. The sample bulb was loaded in an inert atmosphere box and evacuated for 15 minutes before admission of the gas. The gas was first admitted to the system with the sample bulb closed and a pressure measurement taken. The sample bulb was opened allowing the reaction to proceed. The amount of gas uptake was calculated from the total fall in gas pressure after applying a correction to take into account the volume change on opening the sample bulb.

4.2 RESULTS OF REACTION OF SF\(_4\) WITH CsF

The reactions of both activated and non activated CsF with SF\(_4\) have been investigated using both \(^{18}\)F and \(^{35}\)S labelled SF\(_4\) and in the case of activated CsF by conventional manometric means.

The results of three experiments between SF\(_3\)\(^{18}\)F and non activated CsF are summarised in table 4.1. Figure 4.2 shows a plot of solid count rate versus time for one of these experiments. This shows that the solid count rate rises rapidly and then begins to level off until an equilibrium level is reached after 35 minutes. Calculation of the
TABLE 4.1

REACTION OF SF$_3^{18}$F WITH NON ACTIVATED CsF - SUMMARY OF RESULTS

<table>
<thead>
<tr>
<th>Amount of CsF g</th>
<th>Amount of SF$_3^{18}$F Torr m mol</th>
<th>Specific Count Rate of SF$_3^{18}$F Before Reaction counts min$^{-1}$ m mol$^{-1}$</th>
<th>Specific Count Rate of SF$_3^{18}$F After Reaction counts min$^{-1}$ m mol$^{-1}$</th>
<th>Solid Count Rate After Reaction counts min$^{-1}$</th>
<th>Uptake m mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50 $\pm$ 0.01</td>
<td>300 $\pm$ 2</td>
<td>4217 $\pm$ 65</td>
<td>4215 $\pm$ 65</td>
<td>181 $\pm$ 13</td>
<td>0.043 $\pm$ 0.003</td>
</tr>
<tr>
<td>3.29 $\pm$ 0.06</td>
<td>1.0 $\pm$ 65</td>
<td>3557 $\pm$ 60</td>
<td>3558 $\pm$ 60</td>
<td>142 $\pm$ 12</td>
<td>0.040 $\pm$ 0.0035</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2516 $\pm$ 50</td>
<td>2509 $\pm$ 50</td>
<td>97 $\pm$ 10</td>
<td>0.0385 $\pm$ 0.004</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2733 $\pm$ 52</td>
<td>2731 $\pm$ 52</td>
<td>127 $\pm$ 11</td>
<td>0.0465 $\pm$ 0.004</td>
</tr>
</tbody>
</table>
Figure 4.2

Reaction of $\text{SF}_3^{18\text{F}}$ with non-activated CsF

Solid count rate vs reaction time
specific count rate before and after reaction shows that there is no change. This means that the activity in the solid is due to uptake of gas and not $^{18}$F exchange. A sample of $\text{SF}_3^{18}$F counted separately had a specific count rate of 4217 $\pm$ 65 counts min$^{-1}$ m mol$^{-1}$ so a solid count rate of 181 $\pm$ 13 counts min$^{-1}$ is equivalent to an uptake of 0.043 m mol of $\text{SF}_3^{18}$F. The average uptake observed in the four experiments was 0.042 $\pm$ 0.004 m mol. The observed solid count rate in these experiments was very low. In order to ensure that a significant number of counts were recorded and to reduce the error on the count rate the counting period was extended to fifteen minutes. This procedure was used throughout this work whenever a low count rate was obtained.

Table 4.2 shows the infra red spectrum of the CsF after reaction, together with the infra red spectrum of CsSF$_5$ prepared by Christe and coworkers. Comparison of the two sets of data shows that the reaction between $\text{SF}_3^{18}$F and CsF has resulted in the formation of some CsSF$_5$.

In an attempt to distinguish between surface and bulk reactions an experiment was carried out using $^{35}$SF$_4$. The results from this reaction were inconclusive, with the surface count rate being barely detectable due to the low surface area of non activated CsF. For this reason the study of the reaction between $^{35}$SF$_4$ and non activated CsF was abandoned and all further experiments with $^{35}$SF$_4$ were carried out using activated CsF.
### TABLE 4.2

**INFRA RED SPECTRUM OF CsF AFTER REACTION WITH SF$_3^{18}$F**

<table>
<thead>
<tr>
<th>Activated CsF</th>
<th>Non Activated CsF</th>
<th>Literature CsSF$_5^{40}$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1250</td>
<td></td>
<td></td>
<td>CF str</td>
</tr>
<tr>
<td>1210</td>
<td></td>
<td></td>
<td>CF str</td>
</tr>
<tr>
<td>1150</td>
<td></td>
<td></td>
<td>CF str</td>
</tr>
<tr>
<td>1110</td>
<td></td>
<td></td>
<td>CF str</td>
</tr>
<tr>
<td>793 s</td>
<td>790</td>
<td>793s</td>
<td>$A_1 \nu_1$</td>
</tr>
<tr>
<td>590 vsbr</td>
<td>590</td>
<td>590 vsbr</td>
<td>$E \nu_1$</td>
</tr>
<tr>
<td>460 s</td>
<td>465</td>
<td>466 s</td>
<td>$A_1 \nu_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>430 sh</td>
<td>$E \nu_8$</td>
</tr>
</tbody>
</table>
The results of four reactions between $\text{SF}_3^{18}\text{F}$ and activated CsF are listed in table 4.3. Figure 4.3 shows a plot of solid count rate versus time for the first experiment. The solid count rate rises rapidly at first and then begins to level off until an equilibrium level of $1560 \pm 40$ counts $\text{min}^{-1}$ is reached after 35 minutes. There is no change in the specific count rate of the gas so this solid count rate is due to gas uptake. A sample of $\text{SF}_3^{18}\text{F}$ counted separately had a specific count rate of $5270 \pm 73$ counts $\text{min}^{-1} \text{m mol}^{-1}$ so the observed solid count rate is equivalent to an uptake of $0.296 \pm 0.006$ m mol. The average uptake observed in the four experiments is $0.296 \pm 0.009$ m mol. Infra red examination of the CsF after reaction showed bands due to $\text{SF}_5^-$. (Table 4.2)

The experiments listed in table 4.3 were all carried out using an initial pressure of 300 torr of $\text{SF}_3^{18}\text{F}$. The results of a further six experiments carried out using pressures of 50, 75, 100, 150, 200 and 250 Torr are listed in table 4.4.

These experiments show that uptake is independent of initial pressure over the range 100-300 Torr and corresponds to $0.09 \pm 0.02$ m mol (m mol CsF)$^{-1}$. In order to verify the results of the reactions involving varying pressures of $\text{SF}_3^{18}\text{F}$, a manometric study was carried out using the constant volume apparatus described in section 2.1.2. The results of this study shown in figure 4.4, confirm that the uptake of
### TABLE 4.3

**REACTION OF SF$_3^{18}$F WITH ACTIVATED CsF - SUMMARY OF RESULTS**

<table>
<thead>
<tr>
<th>Amount of CsF g</th>
<th>Amount of SF$_3^{18}$F m mol</th>
<th>Specific Count Rate of SF$_3^{18}$F Before Reaction m mol$^{-1}$ min$^{-1}$</th>
<th>Specific Count Rate of SF$_3^{18}$F After Reaction m mol$^{-1}$ min$^{-1}$</th>
<th>Solid Count Rate After Reaction m mol$^{-1}$ min$^{-1}$</th>
<th>Uptake m mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50 $\pm$ 0.01</td>
<td>300 $\pm$ 2</td>
<td>5270 $\pm$ 73</td>
<td>5270 $\pm$ 73</td>
<td>1560 $\pm$ 40</td>
<td>0.30 $\pm$ 0.006</td>
</tr>
<tr>
<td>3.29 $\pm$ 0.06</td>
<td>1.0 $\pm$ 0.01</td>
<td></td>
<td></td>
<td>1276 $\pm$ 36</td>
<td>0.31 $\pm$ 0.009</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4117 $\pm$ 64</td>
<td>4109 $\pm$ 64</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1967 $\pm$ 44</td>
<td>1961 $\pm$ 44</td>
<td>560 $\pm$ 24</td>
<td>0.285 $\pm$ 0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2516 $\pm$ 50</td>
<td>2514 $\pm$ 50</td>
<td>729 $\pm$ 27</td>
<td>0.29 $\pm$ 0.01</td>
</tr>
</tbody>
</table>
Figure 4.3

Reaction of SF$_3^\text{16}$F with activated CsF

Solid count rate vs reaction time
TABLE 4.4

VARIATION IN UPTAKE WITH INITIAL PRESSURE OF SF$_4$

RADIOCHEMICAL MEASUREMENTS

<table>
<thead>
<tr>
<th>Pressure of SF$_4$ Torr</th>
<th>Uptake m mol (m mol CsF)$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 $\pm$ 2</td>
<td>0.027 $\pm$ 0.003</td>
</tr>
<tr>
<td>75 $\pm$ 2</td>
<td>0.065 $\pm$ 0.005</td>
</tr>
<tr>
<td>100 $\pm$ 2</td>
<td>0.081 $\pm$ 0.006</td>
</tr>
<tr>
<td>150 $\pm$ 2</td>
<td>0.100 $\pm$ 0.007</td>
</tr>
<tr>
<td>200 $\pm$ 2</td>
<td>0.085 $\pm$ 0.007</td>
</tr>
<tr>
<td>250 $\pm$ 2</td>
<td>0.098 $\pm$ 0.007</td>
</tr>
<tr>
<td>300 $\pm$ 2</td>
<td>0.091 $\pm$ 0.007</td>
</tr>
</tbody>
</table>
Figure 4.4

Reaction of SF$_4$ with activated CsF

Amount adsorbed vs initial pressure

Uptake of SF$_4$, mmol(mmol(CsF))$^{-1}$

Initial pressure Torr
SF$_4$ by activated CsF is independent of initial pressure over the range 100-300 Torr. Infra red spectroscopic examination of the solid after reaction is consistent with the formation of CsSF$_5$. (Table 4.2)

The reaction between $^{35}$SF$_4$ and activated CsF was studied at 23 different pressures between 2 and 308 Torr. Figures 4.5, 4.6 and 4.7 are plots of solid count rate versus time at initial pressures of 52, 110 and 296 Torr. The solid count rate increases rapidly until an equilibrium level corresponding to a surface uptake of 0.010 m mol (m mol CsF)$^{-1}$ is reached after 10 minutes. A plot of the amount of $^{35}$SF$_4$ adsorbed on the surface of the CsF versus initial pressure (figure 4.8), shows that the amount of surface coverage is independent of the initial pressure at all pressures greater than 10 Torr. When the $^{35}$SF$_4$ is removed from the counting vessel 85% of the total surface counts are also removed. This means that the major surface species is weakly adsorbed with only 15% of the total surface count rate due to a permanently adsorbed species. Infra red examination of CsF after reaction with SF$_3^{18}$F shows that some CsSF$_5$ is formed hence it is reasonable to assume that the permanently adsorbed surface species is the SF$_5^-$ anion. If the permanently adsorbed species is assumed to be SF$_5^-$, the weakly adsorbed species is most likely to be adsorbed molecules of SF$_4$.

When $^{35}$SF$_4$ is readmitted to the counting vessel the observed solid count rate is 90% of the count rate observed during the
Figure 4.5

Reaction of $^{35}\text{SF}_4$ with activated CsF

Surface count rate vs reaction time

Initial pressure = 52 Torr

Specific count rate of $^{35}\text{SF}_4 = 1450$ counts sec$^{-1}$ mmol$^{-1}$
Figure 4.6
Reaction of $^{35}\text{SF}_4$ with activated CsF
Surface count rate vs reaction time

Initial pressure = 110 Torr
Specific count rate of $^{35}\text{SF}_4$ = 1450 counts sec$^{-1}$ mmol$^{-1}$
Figure 4.7

Reaction of $^{35}\text{SF}_4$ with activated CsF

Surface count rate vs reaction time

Initial pressure = 296 Torr

Specific count rate of $^{35}\text{SF}_4 = 853$ counts sec$^{-1}$ mmol$^{-1}$
Figure 4.8 Reaction of $^{35}\text{SF}_4$ with activated CsF

Amount of $^{35}\text{SF}_4$ adsorbed on surface of CsF vs initial pressure
first admission. The fall in gas phase counts is equivalent to 20% of the decrease observed during the first admission. After two further admissions of $^{35}\text{SF}_4$ no further fall in gas phase counts is observed. These results show that there is a slow build up of $\text{SF}_5^-$ on the surface of the CsF and that diffusion of $\text{SF}_4$ into the bulk of the solid is very slow.

The overall uptake of $^{35}\text{SF}_4$, calculated from the fall in gas phase counts is $0.10 \pm 0.02$ m mol (m mol CsF)$^{-1}$ which is the same as that calculated from the experiments involving $\text{SF}_3^{18}\text{F}$. The results of the reactions between $\text{SF}_4$ and activated CsF are summarised in table 4.5.

4.3 DISCUSSION OF $\text{SF}_4$ RESULTS

$\text{SF}_4$ reacts readily at room temperature with both activated and non activated CsF to form CsSF$_5$. Complete reaction does not occur with the amounts reacting being $0.10$ m mol (m mol CsF)$^{-1}$ for activated CsF and $0.013$ m mol (m mol CsF)$^{-1}$ for non activated. The ratio of uptakes is 10:1, the same as the ratio of the surface areas.

No fluorine exchange is observed in either reaction.

Due to the low level of uptake by non activated CsF $^{35}\text{SF}_4$ did not provide any useful information. With activated CsF, studies using $^{35}\text{SF}_4$ showed that there are two distinct
<table>
<thead>
<tr>
<th>Description</th>
<th>Uptake m mol (m mol CsF)$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall uptake calculated from both $^{35}$S and $^{18}$F experiments</td>
<td>$0.10 \pm 0.02$</td>
</tr>
<tr>
<td>Surface uptake</td>
<td>$0.0030 \pm 0.0005$</td>
</tr>
<tr>
<td>Amount permanently retained on surface</td>
<td>$0.00045 \pm 0.0001$</td>
</tr>
</tbody>
</table>

No fluorine exchange is observed at room temperature.
species present on the surface of the solid one which is weakly adsorbed and one which is permanently adsorbed. The major surface species is weakly adsorbed SF$_4$ with only 15% of the total surface activity due to permanently adsorbed SF$_4$. Since infra red studies have shown that SF$_5^-$ is the major bulk species the permanently adsorbed surface species is also assumed to be SF$_5^-$. Since the specific count rate of the adsorbed $^{35}$SF$_4$ and the surface area of the CsF are known it is possible to estimate the number of F$^-$ ions present in the sample, and to compare this with the number of $^{35}$SF$_4$ molecules adsorbed. This can be done as follows:

BET surface area of activated CsF = 3.011 - 2.09 m$^2$ g$^{-1}$

Weight of sample = 0.50g

Surface area of sample = 1.505 - 1.040 m$^2$

Length of unit cell edge = 6.008Å

Area of one face of unit cell = 36.096Å$^2$

Assuming a perfect surface composed of a regular geometric array of unit cell faces:

Number of unit cell faces required to cover surface = (2.88 - 4.17) x 10$^{18}$

Number of surface F$^-$ ions per unit cell = 2

(Figure 4.9 shows the unit cell of CsF)

Number of surface F$^-$ ions in sample = (5.77 - 8.34) x 10$^{18}$

Surface count rate corresponds to (5.99 - 2.13) x 10$^{18}$ molecules

Although there is good agreement between these two estimates, it does not rule out the possibilities that SF$_4$ is weakly
Figure 4.9  CsF unit cell

- = F
-  = Cs

Number of F ions per face is \((4 \times 1/4) + 1 = 2\)
adsorbed at sites other than $F^{-}$ or that multiple adsorption occurs since many assumptions have been made in arriving at these estimates. The main assumptions are:

1. The surface of the CsF has no defects and is composed of a regular array of unit cell faces.

2. The unit cell edge length of activated CsF is the same as that of non activated CsF.

3. All of the surface $F^{-}$ ions in the sample are equally available.

This comparison also does not take into account the small amount of the heptafluoroisopropoxide anion retained by the CsF after activation. When these facts are taken into account the number of $F^{-}$ ions calculated is probably an over estimate.

Figures 4.10, 4.11 and 4.12 show the species present on the surface of the CsF based on the assumption that adsorption takes place at $F^{-}$ sites. The structure of the $SF_{5}^{-}$ anion is shown in figure 4.10. $SF_{5}^{-}$ is assumed to be the permanently adsorbed species. There are two possibilities for the weakly adsorbed species, both of which have similar structures to the $SF_{5}^{-}$ anion. Figure 4.11 shows $SF_{4}$ adsorbed with the lone pair in an axial position and figure 4.12 shows the lone pair in an equatorial position. Since the structure of the $SF_{5}^{-}$ anion has been characterised as
Figure 4.10  \( \text{SF}_5^- \)

Figure 4.11  \( \text{SF}_4(\text{ads}) \)

Figure 4.12  \( \text{SF}_4(\text{ads}) \)
being \( \text{C}_{4\text{v}} \) as shown in figure 4.10 the weakly adsorbed species is most likely to have the structure shown in 4.11, with the lone pair in an axial position.

\( \text{SF}_5^- \) is the major bulk species and the minor surface species. The fact that no fluorine exchange is observed is due to the \( \text{SF}_5^- \) anion being co-ordinatively saturated. Since \( \text{SF}_5^- \) is only the minor surface species the absence of \( ^1\text{H} \text{F} \) exchange also indicates that in the weakly adsorbed state, the S-F bonds of the adsorbed \( \text{SF}_4^- \) retain their integrity. In other words at no time during the reaction do the four S-F bonds of the \( \text{SF}_4^- \) become equivalent to the bond between the S and the \( ^1\text{H} \text{F} \) ion on the surface.

4.4 RESULTS OF REACTION OF \( \text{F}_2\text{CO} \) WITH ACTIVATED \( \text{CsF} \)

The reaction between \( \text{F}_2\text{CO} \) and activated \( \text{CsF} \) was studied using both \( ^1\text{H} \text{F} \) and \( ^1\text{C} \text{C} \) labelled \( \text{F}_2\text{CO} \), which allowed differentiation between surface and bulk reactions, and by manometric methods. After each reaction the \( \text{CsF} \) was examined by infra red spectroscopy. Three experiments were carried out using \( \text{F}^{18}\text{FCO} \); the results are listed in table 4.6. Figure 4.1.3 is a plot of solid activity versus time for experiment 1. This shows that there is a rapid initial increase in solid activity over the first 30 minutes of the reaction followed by a second period in which the growth of solid activity is much slower. The specific count rate of the \( \text{F}^{18}\text{FCO} \) before reaction was 7139 ± 85 counts min\(^{-1}\) m mol\(^{-1}\) and the specific count rate of the \( \text{F}^{18}\text{FCO} \) after reaction was 5842 ± counts min\(^{-1}\) m mol\(^{-1}\).
### TABLE 4.6

**REACTION OF $^{18}$F CO WITH ACTIVATED CsF - SUMMARY OF RESULTS**

<table>
<thead>
<tr>
<th>Amount of CsF</th>
<th>Amount of $^{18}$F CO</th>
<th>Specific Count Rate of $^{18}$F CO Before Reaction</th>
<th>Specific Count Rate of $^{18}$F CO After Reaction</th>
<th>Fraction Exchanged</th>
<th>Uptake m mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>g</td>
<td>m mol</td>
<td>m mol⁻¹</td>
<td>m mol⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50 ± 0.01</td>
<td>300 ± 2</td>
<td>7139 ± 85</td>
<td>5927 ± 76</td>
<td>0.344</td>
<td>0.194 ± 0.002</td>
</tr>
<tr>
<td>3.29 ± 0.06</td>
<td>0.944 ± 0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>7139 ± 85</td>
<td>5919 ± 76</td>
<td>0.346</td>
<td>0.201 ± 0.002</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5130 ± 71</td>
<td>4370 ± 66</td>
<td>0.300</td>
<td>0.198 ± 0.002</td>
</tr>
</tbody>
</table>

Average uptake = 0.198 m mol
Figure 4.13

Reaction of $^{18}$FFCO with activated CsF

Solid count rate vs reaction time

Count rate counts min$^{-1}$

Reaction time min
indicating that $^{18}$F exchange had occurred. The amount of
gas recovered after the reaction was less than the starting
amount indicating that in addition to $^{18}$F exchange uptake of
gas had also occurred.

Using equation 2.5 the fraction of $^{18}$F exchanged was
calculated, and using this figure the count rate due to
gas uptake was calculated by subtracting the count rate due
to exchange from the count rate of the CsF after 2 hours.
The calculation is now shown in detail for experiment 1 in
table 4.6.

The fraction exchanged ($f$) is given by

$$f = \frac{(A_o - A_{\text{r}})(n_m + n_{m_{\text{r}}})}{A_{n_{m_{\text{1}}}} + A_{n_{m_{\text{2}}}}},$$

where $m$ (m mol) = quantity of a species with $n$ exchangeable
F atoms.

Subscripts 1 and 2 refer to the initially inactive and
active species respectively.

$$A = \text{count rate (counts s}^{-1}\text{)} \text{ after exchange}$$

$$A_o = \text{count rate of reactant 2 before exchange}$$

Weight of CsF = 0.28g = 1.842 m mol

Pressure of $^{18}$CO = 300 Torr = 0.944 m mol

Count rate of gas before reaction = 7139 counts min$^{-1}$ (m mol)$^{-1}$

Count rate of gas after reaction = 5927 counts min$^{-1}$ (m mol)$^{-1}$

$$f = \frac{(7139 - 5927)(1.842 + (2 \times 0.944))}{7139 \times 1.842} \approx 0.344$$
100% exchange would result from a statistical distribution of $^{18}$F among all the fluorine atoms present.

Total number of fluorine atoms = $1.842 + 1.888 = 3.73$ mg atoms

Specific count rate of gas = 7139 counts min$^{-1}$ (m mol)$^{-1}$

Amount of $F_2 CO = 0.944$ m mol

Count rate of $F_2 CO = 6739$ counts min$^{-1}$

For 100% exchange $3.73 = 6739$ counts min$^{-1}$

$1.0$ mg atom $= 1806$ counts min$^{-1}$

CsF contains $1.842$ mg atom F so for 100% exchange count rate of solid would be $1.842 \times 1806$ counts min$^{-1}$

$= 3326$ counts min$^{-1}$

Calculated level of exchange is $34.4\%$

so count rate of solid due to exchange is $\frac{34.4}{100} \times 3326$

$= 1144$ counts min$^{-1}$

The count rate of the solid after reaction is $2532$ counts min$^{-1}$

So count rate due to uptake of gas is $2532 - 1144$

$= 1388$ counts min$^{-1}$

The specific count rate of the $F_2 CO$ is $7139 + 85$ counts min$^{-1}$ m mol$^{-1}$ so a count rate of $1388$ counts min$^{-1}$ is equivalent to an uptake of $0.194 + 0.002$ m mol of $^{18}F$CO.

In each case the infra red spectrum of the solid after reaction shows bands due to the $F_3 CO^-$ anion (Table 4.7)

The reaction between $F_2^{14}CO$ and activated CsF was studied at
### TABLE 4.7

Infra red frequencies of CsDCF<sub>3</sub>

<table>
<thead>
<tr>
<th>This Work</th>
<th>Literature&lt;sup&gt;28&lt;/sup&gt;</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1560</td>
<td>1560</td>
<td>( \nu_1 A_1 \text{CO str} )</td>
</tr>
<tr>
<td>955</td>
<td>960</td>
<td>( \nu_4 E \text{CF}_3 \text{ asym str} )</td>
</tr>
<tr>
<td>810</td>
<td>813</td>
<td>( \nu_2 A_1 \text{CF}_3 \text{ sym str} )</td>
</tr>
<tr>
<td>590</td>
<td>595</td>
<td>( \nu_3 A_1 \text{ sym CF}_3 \text{ def} )</td>
</tr>
<tr>
<td>575</td>
<td>574</td>
<td>( \nu_5 E, \text{OCF def} )</td>
</tr>
<tr>
<td>420</td>
<td>423</td>
<td>( \nu_6 E, \text{ asym CF}_3 )</td>
</tr>
</tbody>
</table>
nine different pressures between 20 and 308 Torr. Surface count rates were measured directly and the overall drop in gas phase counts was used as a measure of the uptake of gas by the bulk solid. Each reaction was followed for 1 hour before removing the $F_2^{14}CO$ from the counting vessel to determine the count rate of the CsF surface in the absence of gas.

Plots of solid activity versus time at initial $F_2^{14}CO$ pressures of 20, 100 and 308 Torr are shown in figures 4.14, 4.15 and 4.16.

The surface reaction between $F_2^{14}CO$ and activated CsF is complete before the first count is taken and the surface count rate remains constant at $6.1 \pm 1.6$ counts sec$^{-1}$ throughout the experiment. The $F_2^{14}CO$ used had a specific count rate of 1000 counts sec$^{-1}$ m mol$^{-1}$, so a surface count rate of $6.1 \pm 1.6$ counts sec$^{-1}$ is equivalent to a surface uptake of $0.0061 \pm 0.0016$ m mol of $F_2^{14}CO$. This surface count rate is independent of initial $F_2^{14}CO$ pressure as shown by figure 4.17.

When the $F_2^{14}CO$ is removed from the counting vessel the surface count rate drops to barely above background level indicating that 95% of the surface activity is dependent upon there being a pressure of $F_2^{14}CO$ in the counting vessel with only a very small amount of the $F_2CO$ being permanently adsorbed. The uptake of gas by the bulk solid is also dependant on the initial pressure of $F_2^{14}CO$ in the vessel. In order to check this pressure dependance a series of
Figure 4·14

Reaction of $^{14}$CO with activated CsF

Solid count rate vs reaction time

Initial pressure =20 Torr
Figure 4.15

Reaction of $\text{F}_2\text{CO}$ with activated $\text{CsF}$

Solid count rate vs reaction time

Initial pressure = 100 Torr
Figure 4.16
Reaction of $\text{F}_2\text{CO}$ with activated CsF
Solid count rate vs reaction time

Initial pressure = 308 Torr
Figure 4.17
Reaction of $F_{2}^{18}O$ with activated CsF
Solid count rate vs initial pressure
experiments was carried out using the constant volume manometer described in section 2.12. Measurements were carried out at 10 different pressures. The results are shown in figure 4.18, together with the uptakes calculated from the drop in overall gas phase counts in the F$_2^{14}$CO experiments. The two sets of data show very good agreement thus indicating that the fall in gas phase counts gives a reliable measure of the uptake of gas by the solid. Figure 4.17 shows that the uptake of F$_2$CO by bulk CsF is totally dependant upon the initial pressure of F$_2$CO in the system. When the samples were re-weighed after the constant volume experiments the increase in weight in each case was less than half that required for the uptake of F$_2$CO indicated by the drop in pressure (Table 4.8). This shows that the removal of the F$_2$CO from the counting vessel must also remove more than half of the F$_2$CO adsorbed within the bulk of the solid. For example the drop in pressure at 300 Torr is equivalent to an uptake of 0.25 m mol of F$_2$CO per m mol of CsF whereas the increase in weight after reaction is equivalent to an uptake of 0.11 m mol of F$_2$CO per m mol CsF. Infra red examination of the CsF after reaction reveals the presence of the F$_3$CO$^-$ anion as was the case in the reaction of F$^{18}$FCO with CsF (Table 4.7).

4.5 DISCUSSION OF F$_2$CO RESULTS

The reaction between F$_2$CO and activated CsF is rapid at room temperature. More than one type of species is present
Figure 4.18

Reaction of F₂CO with activated CsF

Uptake of F₂CO vs initial pressure

\[ \text{Uptake of } F_2CO \text{ mmol} \]

\[ \text{Initial pressure Torr} \]

- Uptake from constant volume
- Uptake from \(^{14}C\) measurements

Amount of CsF = 2.0 mmol
<table>
<thead>
<tr>
<th>Initial Pressure Torr</th>
<th>Uptake Calculated from Fall in Pressure m mol (m mol CsF)$^{-1}$</th>
<th>Uptake Calculated From increase in weight of CsF m mol (m mol CsF)$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>0.0712 $^{+}$ 0.01</td>
<td>0.0270 $^{+}$ 0.005</td>
</tr>
<tr>
<td>50</td>
<td>0.106 $^{+}$ 0.01</td>
<td>0.048 $^{+}$ 0.005</td>
</tr>
<tr>
<td>74</td>
<td>0.119 $^{+}$ 0.01</td>
<td>0.052 $^{+}$ 0.005</td>
</tr>
<tr>
<td>100</td>
<td>0.142 $^{+}$ 0.01</td>
<td>0.067 $^{+}$ 0.005</td>
</tr>
<tr>
<td>150</td>
<td>0.161 $^{+}$ 0.01</td>
<td>0.081 $^{+}$ 0.005</td>
</tr>
<tr>
<td>180</td>
<td>0.175 $^{+}$ 0.01</td>
<td>0.086 $^{+}$ 0.005</td>
</tr>
<tr>
<td>200</td>
<td>0.191 $^{+}$ 0.01</td>
<td>0.094 $^{+}$ 0.094</td>
</tr>
<tr>
<td>228</td>
<td>0.220 $^{+}$ 0.01</td>
<td>0.102 $^{+}$ 0.005</td>
</tr>
<tr>
<td>250</td>
<td>0.232 $^{+}$ 0.01</td>
<td>0.110 $^{+}$ 0.005</td>
</tr>
<tr>
<td>304</td>
<td>0.253 $^{+}$ 0.01</td>
<td>0.121 $^{+}$ 0.005</td>
</tr>
</tbody>
</table>
on the surface of the solid and also within the bulk of the solid.

There are two surface species present one which is permanently adsorbed probably as $F_3CO^-$ on the basis of the infra red results, and one which is weakly adsorbed and can be pumped away. These same two species appear to be present in the bulk of the solid as well as on the surface because on removing the $F_2CO$ from the reaction vessel the amount of gas which is adsorbed by the CsF falls by more than 50%.

In the reaction between CsF and $F^{18}CO$ both uptake of gas and fluorine exchange are observed. There are two possible explanations for this fluorine exchange. The first is that the weakly adsorbed species is adsorbed in such a way as to make the fluorine from CsF equivalent to the two from $F_2CO$ and the second is equivalence between $F_3CO^-$ and $F_2CO$ (ads) is possible. It is probable that the weakly adsorbed $F_2CO$ molecules are adsorbed in such a way as to allow all the fluorines to become equivalent. The evidence for this comes from a matrix isolation study by B.S. Ault in which he reports the formation of an unusual complex from the reaction of formaldehyde with CsF in an argon matrix. This reaction did not give rise to the expected fluoride ion transfer and formation of the $CH_2FO^-$ anion. No C-F stretching mode was observed and the C = O stretching mode was shifted by only 50-60 cm$^{-1}$ compared with a shift of 400 cm$^{-1}$ when $F_3CO^-$ is formed from $F_2CO$. This suggests that the fluoride ion is interacting weakly with the carbon centre.
of the CH₂O but not actually forming a bond.

A similar type of reaction may occur between the weakly adsorbed F₂CO and the CsF to give the species shown in figure 4.19.

Figure 4.19

If this reaction occurs there may be a point at which all the fluorines become equivalent and exchange is possible.

The possibility of equivalence between F₃CO⁻ and F₂CO (ads) seems unlikely based on the findings of Redwood and Willis in 1965.²⁷ They reported that CsOCF₃ was stable with respect to decomposition at room temperature. The infra red and Raman study of the F₃CO⁻ ion by Christe and coworkers does however indicate that two or more resonance forms of the anion exist. This view is supported by a later matrix isolation study of CsOCF₃ by B. Ault.¹⁰⁰ In the infra red spectrum of CsOCF₃, there is a band at 960 cm⁻¹ which is assigned to the doubly degenerate CF₃ stretching mode. In the matrix isolation study the degeneracy of the band is lost and it appears as two separate bands at 919 cm⁻¹ and 1039 cm⁻¹. The other band positions also show slight differences from their expected
values. The CF$_3$ frequencies have decreased by 350 cm$^{-1}$ compared with CF$_4$. The CO stretch is at a lower frequency than expected for a double bond and higher than that of a single bond.

Further evidence for the existence of resonance structures is supplied by W B Farnham and coworkers$^{29}$ in their study of the crystal and molecular structure of $\left[\left(\text{CH}_3\right)_2\text{N}\right]_3\text{S}^+$ $\left[\text{F}_3\text{CO}^-\right]$. The X-ray single crystal diffraction analysis shows that the C-F bond lengths are exceptionally long (1.390 and 1.397 Å) and the C-O bond length is quite short (1.227Å) compared with the corresponding gas-phase experimental values for CF$_3$OR (R=F, CF$_3$). The C-O bond length is close to that for the C=O bond in CF$_2$=O. In addition the FCF bond angles are very small compared to those of CF$_3$OR.

Mulliken population analyses indicate that there is an additional charge of $-0.2e$ on each F in CF$_3$O$.^-$. This excess charge implies that each of the resonance structures b-d contribute approximately 20% to the bonding in CF$_3$O$^-$. while (a) contributes 40%.

Figure 4.20
The existence of these resonance forms provides a ready mechanism for the equivalence of $F_3\text{CO}^-$ and $F_2\text{CO} (\text{ads})$ as the proposed weakly adsorbed species can be readily envisaged as a precursor to these resonance species as shown in figure 4.21.

Therefore, based on the evidence presented the two possible explanations for fluorine exchange can be combined to provide an overall description of the ways fluorine exchange can occur.

In the weakly adsorbed state, the two fluorines from the $F_2\text{CO}$ become equivalent to the fluorine from CsF. When this occurs the structure of the adsorbed species is similar to the structure of the $F_3\text{CO}^-$ anion. This allows fluorine exchange to occur either between $F_2\text{CO} (\text{ads})$ and $F^-$ or between $F_3\text{CO}^-$ and $F_2\text{CO} (\text{ads})$.

4.6 RESULTS OF REACTION OF $\text{BF}_3$ WITH CsF

As there are no suitable radioisotopes of boron, the reaction between $\text{BF}_3$ and CsF was studied using $^{18}\text{F}$
labelled BF$_3$ alone. The results obtained are comparable with those from a conventional manometric study of this system carried out at the same time.

Four experiments involving BF$_2^{18}$F and non activated CsF were carried out. Their results are summarised in table 4.9. Figure 4.22 shows a plot of solid count rate versus time for experiment number 3. There is a rapid rise in solid count rate until an equilibrium level is reached after 30 minutes. There is no change in the specific count rate of the BF$_2^{18}$F before and after reaction so the increase in the solid count rate is due to uptake of BF$_2^{18}$F by the caesium fluoride. Since the specific count rate of the BF$_2^{18}$F is known for each experiment, the observed solid count rates can be converted to amounts of BF$_2^{18}$F adsorbed. The calculated amounts of adsorbed BF$_2^{18}$F are shown in table 4.9. The average uptake observed is $0.088 \pm 0.004$ m mol.

Treatment of caesium fluoride with non radioactive BF$_3$ before reaction with BF$_2^{18}$F prevents any uptake of the BF$_2^{18}$F. Table 4.10 shows the results of a reaction between BF$_2^{18}$F and non activated CsF treated with BF$_3$. The observed counts are very low because they are gas phase counts and material in the gas phase cannot be efficiently counted in a well scintillation counter.

If the caesium fluoride is first treated with BF$_2^{18}$F to produce a radioactive solid and then allowed to react
<table>
<thead>
<tr>
<th>Amount of CsF g m mol</th>
<th>Amount of BF$_2^{18}$F Torr m mol</th>
<th>Specific Count Rate of BF$_2^{18}$F Before Reaction counts min$^{-1}$ m mol$^{-1}$</th>
<th>Specific Count Rate of BF$_2^{18}$F After Reaction counts min$^{-1}$ m mol$^{-1}$</th>
<th>Solid Count Rate After Reaction counts min$^{-1}$</th>
<th>Uptake m mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50$^\pm$ 0.01</td>
<td>300$^\pm$ 2</td>
<td>14326$^\pm$ 120</td>
<td>14362$^\pm$ 120</td>
<td>1275$^\pm$ 36</td>
<td>0.089$^\pm$ 0.003</td>
</tr>
<tr>
<td>3.29$^\pm$ 0.06</td>
<td>1.00$^\pm$ 0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>9513$^\pm$ 97</td>
<td>9511$^\pm$ 97</td>
<td>894$^\pm$ 30</td>
<td>0.094$^\pm$ 0.003</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12118$^\pm$ 110</td>
<td>12115$^\pm$ 110</td>
<td>1030$^\pm$ 32</td>
<td>0.085$^\pm$ 0.003</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5316$^\pm$ 73</td>
<td>5313$^\pm$ 73</td>
<td>457$^\pm$ 21</td>
<td>0.086$^\pm$ 0.004</td>
</tr>
</tbody>
</table>
Figure 4.22

Reaction of BF$_2^{18}$ with non-activated CsF

Solid counts vs reaction time

![Graph showing solid counts vs reaction time for the reaction of BF$_2^{18}$ with non-activated CsF]
### TABLE 4.10

**RESULTS OF REACTION OF BF$_{2}^{18}$F WITH NON ACTIVATED CsF TREATED WITH BF$_{3}$**

<table>
<thead>
<tr>
<th>Time min</th>
<th>Solid + Gas counts min$^{-1}$</th>
<th>Gas Counts counts min$^{-1}$</th>
<th>Solid Counts counts min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>439</td>
<td>422</td>
<td>17</td>
</tr>
<tr>
<td>9</td>
<td>454</td>
<td>433</td>
<td>21</td>
</tr>
<tr>
<td>17</td>
<td>446</td>
<td>448</td>
<td>-2</td>
</tr>
<tr>
<td>25</td>
<td>412</td>
<td>425</td>
<td>-13</td>
</tr>
<tr>
<td>32</td>
<td>436</td>
<td>416</td>
<td>20</td>
</tr>
<tr>
<td>38</td>
<td>435</td>
<td>436</td>
<td>-1</td>
</tr>
<tr>
<td>43</td>
<td>456</td>
<td>420</td>
<td>36</td>
</tr>
<tr>
<td>52</td>
<td>407</td>
<td>437</td>
<td>-30</td>
</tr>
<tr>
<td>58</td>
<td>434</td>
<td>454</td>
<td>-20</td>
</tr>
<tr>
<td>64</td>
<td>424</td>
<td>402</td>
<td>22</td>
</tr>
<tr>
<td>72</td>
<td>456</td>
<td>433</td>
<td>23</td>
</tr>
</tbody>
</table>

Count rate of solid after reaction = 28 counts min$^{-1}$

Specific count rate of BF$_{2}^{18}$F before = 6870 counts min$^{-1}$ m mol$^{-1}$

Specific Count rate of BF$_{2}^{18}$F after = 6870 counts min$^{-1}$ m mol$^{-1}$
with non radioactive BF$_3$ no $^{18}$F exchange is observed. This also indicates that the adsorbed BF$_2^{18}$F molecules do not exchange with the gas phase BF$_3$ molecules. The results of this experiment are listed in table 4.11.

The results of four reactions between BF$_2^{18}$F and activated CsF are given in table 4.12. The results obtained are similar to those of the reaction between BF$_2^{18}$F and non activated CsF, with a rapid increase in the solid count rate which reached an equilibrium level after 30 minutes as shown in figure 4.23. The only difference is that with non activated CsF, only a small proportion of the BF$_2^{18}$F was taken up by the caesium fluoride whereas with activated caesium fluoride all of the gas present in the reaction flask is taken up by the solid.

In an effort to determine the total amount of BF$_3$ which would react with 0.50g of activated CsF two adsorption experiments were carried out using the constant volume apparatus described in section 2.1.2. 0.50g of activated CsF was loaded into a sample bulb and the line filled with BF$_3$ to a pressure of 300 Torr. The overall drop in pressure was measured after 45 minutes. After correction for the change in total volume on opening the sample bulb, the fall in BF$_3$ pressure was equivalent to uptakes of 3.21 $^{\pm}$ 0.10 m mol and 3.15 $^{\pm}$ 0.10 m mol of BF$_3$ by 3.28 $^{\pm}$ 0.06 m mol and 3.16 $^{\pm}$ 0.06 m mol of activated CsF respectively. These results show that activated CsF will react with BF$_3$ in a 1:1 mole ratio at room temperature.
TABLE 4.11

RESULTS OF REACTION OF BF$_3$ WITH NON ACTIVATED CsF TREATED WITH BF$_2^{18}$F

<table>
<thead>
<tr>
<th>Time min</th>
<th>Solid Counts</th>
<th>Gas Counts</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Counts min$^{-1}$</td>
<td>Counts min$^{-1}$</td>
</tr>
<tr>
<td>2</td>
<td>1584</td>
<td>4</td>
</tr>
<tr>
<td>7</td>
<td>1536</td>
<td>2</td>
</tr>
<tr>
<td>12</td>
<td>1597</td>
<td>5</td>
</tr>
<tr>
<td>17</td>
<td>1532</td>
<td>1</td>
</tr>
<tr>
<td>22</td>
<td>1527</td>
<td>0</td>
</tr>
<tr>
<td>27</td>
<td>1555</td>
<td>2</td>
</tr>
<tr>
<td>37</td>
<td>1598</td>
<td>4</td>
</tr>
<tr>
<td>45</td>
<td>1589</td>
<td>1</td>
</tr>
<tr>
<td>55</td>
<td>1581</td>
<td>1</td>
</tr>
<tr>
<td>65</td>
<td>1526</td>
<td>5</td>
</tr>
<tr>
<td>70</td>
<td>1544</td>
<td>7</td>
</tr>
</tbody>
</table>

Count rate of BF$_3$ after reaction = 34 counts min$^{-1}$

Specific count rate of BF$_2^{18}$F before = 16781 counts min$^{-1}$ m mol$^{-1}$

Specific count rate of BF$_2^{18}$F after reaction = 16781 counts min$^{-1}$ m mol$^{-1}$
<table>
<thead>
<tr>
<th>Amount of CsF</th>
<th>Amount of BF$_2$$^{18}$F</th>
<th>Specific Count Rate of BF$_2$$^{18}$F Before Reaction Counts min$^{-1}$ m mol$^{-1}$</th>
<th>Count Rate of BF$_2$$^{18}$F After Reaction Counts min$^{-1}$</th>
<th>Count Rate Of Solid After Reaction Counts min$^{-1}$</th>
<th>Uptake m mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50 ± 0.01</td>
<td>300 ± 2 1.0 ± 0.01</td>
<td>15003 ± 123</td>
<td>65 ± 8</td>
<td>14995 ± 120</td>
<td>1.00 ± 0.01</td>
</tr>
<tr>
<td>3.29 ± 0.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>12118 ± 110</td>
<td>51 ± 7</td>
<td>12056 ± 110</td>
<td>1.00 ± 0.01</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>6870 ± 83</td>
<td>43 ± 7</td>
<td>6869 ± 83</td>
<td>1.00 ± 0.01</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>16781 ± 130</td>
<td>81 ± 9</td>
<td>16750 ± 130</td>
<td>1.00 ± 0.01</td>
</tr>
</tbody>
</table>

**TABLE 4.12**

REACTION OF BF$_2$$^{18}$F WITH ACTIVATED CsF, SUMMARY OF RESULTS
Figure 4.23

Reaction of BF$^{18}_2$ with activated CsF

Solid count rate vs reaction time
Table 4.13 shows the results of an experiment in which a sample of activated CsF was treated with non radio-active BF$_3$ before reaction with BF$_2^{18}$F. After one hour there is no detectable solid count rate.

Table 4.14 shows the results of an experiment in which the activated CsF was treated first with BF$_2^{18}$F and then with non radioactive BF$_3$. In this case there is a barely detectable growth in the gas phase count rate. There is no detectable change in the specific count rate of the BF$_2^{18}$F before and after reaction.

In this work the caesium fluoride was activated by treatment with hexafluoroacetone in acetonitrile and subsequent thermal decomposition of the adduct formed as described in chapter 3 section 3.1.1. Subsequent examination of this activated caesium fluoride revealed that 0.5% of the heptafluoroisopropoxide anion is retained after decomposition. In an effort to determine whether or not the retained anion plays any part in the reactions of activated caesium fluoride, two samples of caesium fluoride were activated by other means. The first sample was activated by heating under vacuum at 250$^\circ$ for 8 hours followed by grinding in an agate mortar and pestle. The second sample was treated with F$_2$CO as described in chapter 3 sections 3.1.2 and 3.1.3.
TABLE 4.13

REACTION OF $\text{BF}_2^{18}\text{F}$ WITH ACTIVATED CsF TREATED WITH $\text{BF}_3$

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Solid + Gas Counts (counts min$^{-1}$)</th>
<th>Gas Counts (counts min$^{-1}$)</th>
<th>Solid Counts (counts min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>451</td>
<td>456</td>
<td>-5</td>
</tr>
<tr>
<td>5</td>
<td>447</td>
<td>441</td>
<td>6</td>
</tr>
<tr>
<td>10</td>
<td>463</td>
<td>455</td>
<td>8</td>
</tr>
<tr>
<td>15</td>
<td>431</td>
<td>437</td>
<td>-6</td>
</tr>
<tr>
<td>20</td>
<td>457</td>
<td>442</td>
<td>15</td>
</tr>
<tr>
<td>25</td>
<td>423</td>
<td>419</td>
<td>4</td>
</tr>
<tr>
<td>30</td>
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<td>437</td>
<td>-2</td>
</tr>
<tr>
<td>40</td>
<td>419</td>
<td>407</td>
<td>12</td>
</tr>
<tr>
<td>50</td>
<td>472</td>
<td>480</td>
<td>-8</td>
</tr>
<tr>
<td>60</td>
<td>414</td>
<td>404</td>
<td>10</td>
</tr>
</tbody>
</table>

Count rate of solid after reaction = 43 counts min$^{-1}$

Specific count rate of $\text{BF}_2^{18}\text{F}$ before = 6638 ± 81 counts min$^{-1}$ m mol$^{-1}$

Specific count rate of $\text{BF}_2^{18}\text{F}$ after reaction = 6632 ± 81 counts min$^{-1}$ m mol$^{-1}$
**TABLE 4.14**

**REACTION OF BF$_2$ WITH ACTIVATED CsF TREATED WITH BF$_2$$^{18}$F**

<table>
<thead>
<tr>
<th>Time min</th>
<th>Solid &amp; Gas Counts Counts min$^{-1}$</th>
<th>Gas Counts Counts min$^{-1}$</th>
<th>Solid Counts Counts min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21820</td>
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<td>21101</td>
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<td>21096</td>
</tr>
<tr>
<td>63</td>
<td>20958</td>
<td>9</td>
<td>20949</td>
</tr>
</tbody>
</table>

Count rate of gas after reaction = 67 counts min$^{-1}$

Specific count rate of BF$_2$$^{18}$F before = 6637 ± 81 counts min$^{-1}$ mmol$^{-1}$
The results of the reaction of $\text{BF}_2^{18}\text{F}$ with CsF activated by heating are shown in figure 4.24. As with hexafluoroacetone activated CsF there is a rapid initial increase in solid count rate and an equilibrium level is reached after 30 minutes. Unlike the reaction of $\text{BF}_2^{18}\text{F}$ with hexafluoroacetone activated CsF all of the $\text{BF}_2^{18}\text{F}$ does not react with the CsF. The maximum uptake of $\text{BF}_3$, measured using the constant volume apparatus, corresponds to 0.33 m mol of $\text{BF}_3$ to 1 m mol of CsF. With hexafluoroacetone activated CsF the maximum uptake is 1.1.

$\text{F}_2\text{CO}$ activated CsF reacts with $\text{BF}_2^{18}\text{F}$ in a similar manner, to the thermally activated CsF as shown by figure 4.25. This shows a rapid initial increase in solid count rate which reaches an equilibrium value after 30 minutes. All of the $\text{BF}_2^{18}\text{F}$ in the reaction vessel is taken up by the CsF. Measurements carried out using the constant volume apparatus show that the maximum uptake of $\text{BF}_3$ corresponds to 0.95 m mol of $\text{BF}_3$ to 1 m mol of CsF.

In addition to the reactions already described the reaction between $\text{BF}_2^{18}\text{F}$ and $\text{NF}_4\text{BF}_4$ was studied. Figure 4.26 shows a plot of solid count rate versus time for this reaction. The solid count rate increases rapidly until an equilibrium value is reached after approximately 20 minutes. The specific count rate of the $\text{BF}_2^{18}\text{F}$ before reaction was 20095 ± 141 counts min$^{-1}$ m mol$^{-1}$ and after reaction it had dropped to 18702 ± 136 counts min$^{-1}$ m mol$^{-1}$. This indicates
Figure 4.24
Reaction of $\text{BF}_2^\text{18}$ with CsF activated by heating
Solid count rate vs reaction time

Count rate counts min$^{-1}$

Reaction time min
Figure 4.25

Reaction of \( \text{BF}_2^+ \) with CsF activated by reaction with \( \text{F}_2\text{CO} \).

Solid count rate vs reaction time

![Graph showing count rate vs reaction time](image-url)
Figure 4.26

Reaction of $\text{BFF}_{2}^{18}$ with $\text{NF}_{4}\text{BF}_{4}$

Solid count rate vs reaction time

[Graph showing the relationship between count rate and reaction time]
that the increase in solid activity is due to F exchange between BF$_4^-$ and BF$_2^{18}$F. Using equation 2.4 and assuming that there is no exchange between BF$_2^{18}$F and NF$_4^+$ the fraction exchanged ($f$) is $0.087 - 0.001$. The fraction exchanged calculated from a second experiment is $0.080 + 0.001$.

The systems described so far have all been studied under heterogeneous conditions. Measureable $^{18}$F exchange was observed between BF$_2^{18}$F and NF$_4$BF$_4$. Fluorine exchange between BF$_3$ and BF$_4^-$ has previously been observed under homogeneous conditions.$^{102}$ To show that the experimental techniques described in this work can be used to observe exchange under similar conditions the reactions between BF$_2^{18}$F and Li BF$_4$ in MeCN and between BF$_2^{18}$F and CsBF$_4$ in MeCN were studied.

The results are given in tables 4.15 and 4.16 and show that complete exchange is observed in the BF$_2^{18}$F/Li BF$_4$ system and 21% exchange is observed in the BF$_2^{18}$F/Cs BF$_4$ system.

4.7 DISCUSSION OF BF$_3$ RESULTS

Both activated and non activated CsF react readily with BF$_3$ at room temperature with uptake of gas always being observed. There are three possible species which could result from the uptake of gas - 1) Adsorbed BF$_3$ molecules, 2) the BF$_4^-$ anion or 3) the B$_2$F$_7$ anion.
### TABLE 4.15

**REACTION OF BF$_2^{18}$F WITH Li BF$_4$ IN MeCN**

<table>
<thead>
<tr>
<th>Count rate of BF$_2^{18}$F before reaction</th>
<th>Amount of BF$_2^{18}$F</th>
<th>Reaction time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Count rate of BF$_2^{18}$F before reaction = 15966 counts min$^{-1}$
- Amount of BF$_2^{18}$F = 2.7 m mol
- Reaction time = 60 minutes
- Count rate of Li BF$_4$ after reaction = 9003 counts min$^{-1}$
- Amount of Li BF$_4$ = 2.65 m mol
- Count rate of BF$_2^{18}$F after reaction = 6856 counts min$^{-1}$
- Fraction exchanged = 1.02

### TABLE 4.16

**REACTION OF BF$_2^{18}$F WITH CsBF$_4$ IN MeCN**

<table>
<thead>
<tr>
<th>Count rate of BF$_2^{18}$F before reaction</th>
<th>Amount of BF$_2^{18}$F</th>
<th>Reaction time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Count rate of BF$_2^{18}$F before reaction = 17261 counts min$^{-1}$
- Amount of BF$_2^{18}$F = 2.0 m mol
- Reaction time = 60 minutes
- Count rate of Cs BF$_4$ after reaction = 2926 counts min$^{-1}$
- Amount of Cs BF$_4$ = 1.95 m mol
- Count rate of BF$_2^{18}$F after reaction = 14215 counts min$^{-1}$
- Fraction exchanged = 0.21
Many $\text{BF}_4^-$ salts are known and the tetrahedral structure of the anion has been well characterised spectroscopically (Figure 4.27)

![Figure 4.27](image1.png)

![Figure 4.28](image2.png)

The $\text{B}_2\text{F}_7^-$ anion which has the structure shown in figure 4.28 exists at low temperatures in solution and in the solid state with large cations such as $(\text{C}_2\text{H}_5)_3\text{NH}^+$ but readily dissociates to give $\text{BF}_3$ and $\text{BF}_4^-$. Infrared examination of both activated and non-activated caesium fluoride after reaction with $\text{BF}_2^{18}\text{F}$ always produces a similar spectrum. Two weak bands are observed between 520 and 540 cm$^{-1}$, a medium band at 770 cm$^{-1}$ and a strong band at 1060 cm$^{-1}$. With non activated CsF a weak broad band is observed in place of the two weak bands at 520 cm$^{-1}$ and 540 cm$^{-1}$ due to the small amount of $\text{BF}_3$ involved in the reaction. Table 4.17 lists the bands observed in the IR spectrum of CsF after reaction with $\text{BF}_3$ together with the literature values for $\text{BF}_3^{109}$, $\text{KBF}_4^{105}$ and $(\text{Bu})_4\text{NB}_2\text{F}_7^{106}$. Comparison of these data shows that the product of the reaction between CsF and $\text{BF}_3$ is CsBF$_4$. This is further supported by the results of the manometric studies previously described which show that $\text{BF}_3$ reacts...
TABLE 4.17 INFRA RED SPECTRUM OF CsF AFTER REACTION WITH BF$_{2}^{18}$F

<table>
<thead>
<tr>
<th>Solid after reaction</th>
<th>BF$_3$ 109 cm$^{-1}$</th>
<th>KBF$_4$ 105 cm$^{-1}$</th>
<th>(Bu)$_4$NB$_2$F$_7$ 106 cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(solution in CH$_2$Cl$_2$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1505 v3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1219</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1099</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1070 )</td>
<td>1078 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1063 ) vs br</td>
<td>1063 ) v3</td>
<td>1052</td>
</tr>
<tr>
<td></td>
<td>1040 )</td>
<td>1038 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1020</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>833</td>
<td></td>
</tr>
<tr>
<td></td>
<td>768</td>
<td>773 v$_2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>716 v2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>530</td>
<td>536 ) v4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>522</td>
<td>525 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>482 v4</td>
<td></td>
</tr>
</tbody>
</table>
with hexafluoroacetone activated CsF in a 1:1 mole ratio.

With non activated CsF there is a much smaller uptake of BF$_3$ with only 0.027 m mol of BF$_3$ reacting per m mol of CsF. The ratio of the amount of BF$_3$ reacting with non activated CsF to the amount reacting with activated CsF is approximately 1:40. The ratio of surface areas is 1:10. The large difference in uptakes is due to the amount of bulk reaction which occurs. In the reaction of activated caesium fluoride with BF$_2^{18}$F the bulk reaction is complete and CsBF$_4$ is formed.

If non activated CsF is treated with BF$_3$ no further adsorption of gas can take place. This means that adsorption of BF$_3$ by non activated CsF is restricted to a limited number of specific sites, all of which are filled during the first reaction with BF$_3$.

The results of the reactions of BF$_3$ with CsF activated by treatment with F$_2$CO and with thermally activated CsF are similar to those of its reactions with hexafluoroacetone activated CsF.

Pre-treatment of CsF by repeated heating and grinding results in CsF with a surface area of 1.20 ± 0.20 m$^2$ g$^{-1}$. BF$_3$ reacts with this CsF giving a maximum uptake of 0.33 m mol of BF$_3$ per m mol of CsF.
When CsF is activated by reaction with $F_2CO$ it has a surface area of $2.27 \times 1.77 \text{ m}^2\text{ g}^{-1}$. $BF_3$ reacts with this CsF giving a maximum uptake of $0.95 \text{ m mol}$ of $BF_3$ per m mol of CsF. When the differences in surface areas are taken into account the uptakes of gas by ($CF_3)_2CO$ activated CsF and $F_2CO$ activated CsF are comparable. The uptake of gas by thermally activated CsF is much smaller suggesting that chemical pre-treatment of CsF does more than simply increase its surface area. The results obtained suggest that chemical pre-treatment produces a solid with a more open structure perhaps porous as proposed in chapter 3. The comparable results obtained from the two different types of chemically activated CsF show that the small amount of heptfluoroisopropoxide ion retained after activation by hexafluoroacetone does not play any part in the reactions of CsF activated in this way.

$^{18}$F exchange is observed in the homogeneous systems $BF_3$/LiBF$_4$ in MeCN and $BF_3$/CsBF$_4$ in MeCN. Exchange is complete in the $BF_3$/LiBF$_4$ system but only 21% exchange is observed in the $BF_3$/CsBF$_4$ in MeCN which means that the $BF_3$/CsBF$_4$ system is not truly homogeneous.

When studying the heterogeneous systems, measurable $^{18}$F exchange is only observed in the reaction of $BF_2^{18}F$ with NF$_4$BF$_4$. There is also a barely detectable increase in the gas phase count rate in the reaction of $BF_3$ with CsBF$_3^{18}F$ prepared from hexafluoroacetone activated CsF.
These results suggest that $^{18}\text{F}$ exchange between BF$_3$ and BF$_4^-$ is very slow at room temperature, unless a solvent is present. The proposed mechanism for fluorine exchange in solution involves a slight initial dissociation of BF$_4^-$ to give BF$_3$ + F$^-$ followed by the formation of a fluorine bridged B$_2$F$_7^-$ ion as shown below. $^{102}$

\[
\begin{align*}
\text{i} & \quad \text{BF}_4^- & \rightleftharpoons & \quad \text{BF}_3 + \text{F}^- \\
\text{ii} & \quad \text{BF}_3 + \text{BF}_4^- & \rightarrow & \quad (\text{F}_3\text{B} \overset{\text{F}}{\equiv} \text{BF}_3)^- 
\end{align*}
\]

Complexation of BF$_3$ with the solvent is not directly involved in fluorine exchange.

The heterogeneous exchange reaction probably occurs via the same type of fluorine bridged intermediate. In view of this it is not surprising that fluorine exchange between CsBF$_4$ and BF$_3$ is not readily observed. The B$_2$F$_7^-$ ion has only been successfully isolated in the solid state with large cations. The salts formed readily dissociate to give BF$_3$ and BF$_4^-$. The critical factor in determining whether or not the B$_2$F$_7^-$ ion will be formed by reaction of BF$_3$ with the BF$_4^-$ ion is proposed to be the distance between the tetrafluoroborate anion and the centre of positive charge in the cation. $^{108a}$ When bulky cations are present the distance between the charged centres is increased to such an extent that the interaction of the cation and the tetrafluoroborate anion becomes relatively weak. The co-ordinating power of the tetrafluoroborate anion toward a nucleophile thus approaches
its maximum potential value and it is able to co-ordinate with a free boron trifluoride molecule. Since $\left[(\text{CH}_3\text{)}_4\text{N}^+\right)$ \(\text{BF}_4^-\) does not react with $\text{BF}_3^{108}$, $\text{CsBF}_4$ would not be expected to react to any great degree with $\text{BF}_3$ hence no $^{18}\text{F}$ exchange should be observed.

4.8 RESULTS OF REACTION OF $\text{AsF}_5$ WITH CsF

Due to the lack of a suitable As radiisotope only $^{18}\text{F}$ labelled $\text{AsF}_5$ was used to study the reaction of $\text{AsF}_5$ with CsF. The results of four reactions between $\text{AsF}_4^{18}\text{F}$ and non activated CsF are summarised in table 4.18. Figure 4.29 is a plot of solid count rate versus time for one of these experiments. This shows that there is a rapid rise in solid count rate until an equilibrium level is reached after 10 minutes. Comparison of the specific count rate of the $\text{AsF}_4^{18}\text{F}$ before and after reaction shows that within experimental error there is no change. This rules out $^{18}\text{F}$ exchange as the cause of the growth of the solid count rate. The increase in count rate must therefore be due to uptake of the gas by the solid. A sample of $\text{AsF}_4^{18}\text{F}$ counted separately had a specific count rate of $11398 \pm 107$ counts min$^{-1}$ m mol$^{-1}$ so the count rate of $5910 \pm 77$ counts min$^{-1}$ in the CsF is equivalent to the uptake of $0.52 \pm 0.007$ m mol of $\text{AsF}_4^{18}\text{F}$ in this experiment. The average uptake observed in the four experiments was $0.498 \pm 0.015$ m mol.
Table 4.18

REACTION OF AsF$_4^{18}$F WITH NON ACTIVATED CsF - SUMMARY OF RESULTS

<table>
<thead>
<tr>
<th>Amount of CsF g</th>
<th>Amount of AsF$_4^{18}$F Torr m mol</th>
<th>Specific Count Rate of AsF$_4^{18}$F Before Reaction Counts min$^{-1}$ m mol$^{-1}$</th>
<th>Specific Count Rate of AsF$_4^{18}$F After Reaction Counts min$^{-1}$ m mol$^{-1}$</th>
<th>Count Rate of solid Counts min$^{-1}$</th>
<th>Uptake m mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50 $^{+}0.01$</td>
<td>300 $^{+}2$</td>
<td>11396 $^{+}107$</td>
<td>11398 $^{+}107$</td>
<td>5910 $^{+}77$</td>
<td>0.520 $^{+}0.007$</td>
</tr>
<tr>
<td>3.29 $^{+}0.06$</td>
<td>1.0 $^{+}0.01$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>8932 $^{+}95$</td>
<td>8930 $^{+}95$</td>
<td>4377 $^{+}66$</td>
<td>0.490 $^{+}0.007$</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>10647 $^{+}103$</td>
<td>10647 $^{+}103$</td>
<td>5324 $^{+}73$</td>
<td>0.500 $^{+}0.007$</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>4236 $^{+}65$</td>
<td>4235 $^{+}65$</td>
<td>2033 $^{+}45$</td>
<td>0.480 $^{+}0.010$</td>
</tr>
</tbody>
</table>
Figure 4.29
Reaction of $\text{AsF}_4^-$ with non activated $\text{CsF}$
Solid count rate vs reaction time

Count rate counts sec$^-1$

Reaction time min
A sample of AsF$_4^{18}$F was allowed to react with CsF to produce a radioactive solid. The labelled gas was removed and replaced by 300 Torr of non radioactive AsF$_5$. After one hour the gas phase count rate was barely above background level showing that the AsF$_4^{18}$F adsorbed by the CsF does not exchange with the gas phase AsF$_5^{18}$F. The AsF$_4^{18}$F on the surface of the CsF must therefore be permanently adsorbed.

The same result is obtained if CsF is first allowed to react with non radioactive AsF$_5$ and then with AsF$_4^{18}$F. Table 4.19 shows the results of one such reaction. The observed count rates are very low because they are gas phase count rates, and the well scintillation counter used cannot count materials in the gas phase very efficiently. The count rate of the CsF after reaction is barely above background level thus confirming there is no exchange at room temperature between adsorbed AsF$_5$ and AsF$_5^{18}$F in the gas phase.

A similar series of experiments was carried out with AsF$_4^{18}$F and CsF activated by pretreatment with hexafluoroacetone. Table 4.20 shows the results of four reactions between AsF$_4^{18}$F and activated CsF.

The results are similar to those obtained with non activated CsF. The solid count rate increases rapidly over the first ten minutes of the reaction before reaching its equilibrium level. This rapid increase is shown in figure 4.30. This increasing solid count rate must be due to uptake of gas
TABLE 4.19

RESULTS OF REACTION OF $^{18}$F WITH NON ACTIVATED CsF PRETREATED WITH AsF$_5$

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Solid + Gas Counts min$^{-1}$</th>
<th>Gas Counts min$^{-1}$</th>
<th>Solid Counts min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1089</td>
<td>1137</td>
<td>-48</td>
</tr>
<tr>
<td>6</td>
<td>1151</td>
<td>1171</td>
<td>-20</td>
</tr>
<tr>
<td>11</td>
<td>1118</td>
<td>1162</td>
<td>-44</td>
</tr>
<tr>
<td>16</td>
<td>1170</td>
<td>1149</td>
<td>+21</td>
</tr>
<tr>
<td>21</td>
<td>1164</td>
<td>1171</td>
<td>+7</td>
</tr>
<tr>
<td>26</td>
<td>1177</td>
<td>1150</td>
<td>+27</td>
</tr>
<tr>
<td>31</td>
<td>1159</td>
<td>1163</td>
<td>-4</td>
</tr>
<tr>
<td>35</td>
<td>1146</td>
<td>1140</td>
<td>+8</td>
</tr>
<tr>
<td>45</td>
<td>1176</td>
<td>1148</td>
<td>+28</td>
</tr>
<tr>
<td>55</td>
<td>1193</td>
<td>1182</td>
<td>+11</td>
</tr>
</tbody>
</table>

Count rate of solid after reaction $= 134$ counts min$^{-1}$

Average background count $= 112$ counts min$^{-1}$

Specific count rate of AsF$_4^{18}$F $= 10647$ counts m mol$^{-1}$ min$^{-1}$
**TABLE 4.20**

**REACTION OF AsF₄⁺¹⁸F WITH ACTIVATED CsF - SUMMARY OF RESULTS**

<table>
<thead>
<tr>
<th>Amount of CsF</th>
<th>Amount of AsF₄⁺¹⁸F</th>
<th>Specific Count Rate of AsF₄⁺¹⁸F Before Reaction</th>
<th>Specific Count Rate of AsF₄⁺¹⁸F After Reaction</th>
<th>Count Rate of Solid After Reaction</th>
<th>Uptake m mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>g</td>
<td>m mol</td>
<td>Counts min⁻¹ m mol⁻¹</td>
<td>Counts min⁻¹ m mol⁻¹</td>
<td>Counts min⁻¹ m mol⁻¹</td>
<td>m mol</td>
</tr>
<tr>
<td>0.50 ± 0.01</td>
<td>300 ± 2</td>
<td>13587 ± 116</td>
<td>13587 ± 116</td>
<td>11538 ± 107</td>
<td>0.850 ± 0.007</td>
</tr>
<tr>
<td>3.29 ± 0.06</td>
<td>1.0 ± 0.01</td>
<td>7755 ± 68</td>
<td>7751 ± 68</td>
<td>6747 ± 82</td>
<td>0.870 ± 0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10647 ± 103</td>
<td>10647 ± 103</td>
<td>8837 ± 94</td>
<td>0.830 ± 0.009</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4236 ± 65</td>
<td>4235 ± 65</td>
<td>3722 ± 61</td>
<td>0.880 ± 0.014</td>
</tr>
</tbody>
</table>
Figure 4.30

Reaction of $\text{AsF}_4^{+}$ with activated CsF

Solid count rate vs reaction time

Count rate counts min$^{-1}$

Reaction time min
by the solid as there is no change in the specific count rate of the \(\text{AsF}_4^{18}\)F before and after reaction. The \(\text{AsF}_4^{18}\)F used in this experiment had a specific count rate of 13567 ± 116 counts min\(^{-1}\) m mol\(^{-1}\) so a solid count rate of 11538 ± 107 counts min\(^{-1}\) corresponds to an uptake of 0.850 ± 0.007 m mol of \(\text{AsF}_4^{18}\)F. The average uptake observed in the four experiments was 0.857 ± 0.020 m mol of \(\text{AsF}_4^{18}\)F.

Treatment of the activated CsF with \(\text{AsF}_5\) prior to reaction with \(\text{AsF}_4^{18}\)F has very little effect on the result obtained. There is still a rapid rise in solid count rate and the equilibrium level is reached after 10 minutes. The only difference observed is that the equilibrium count rate corresponds to an uptake of 0.777 ± 0.011 m mol of \(\text{AsF}_4^{18}\)F compared to 0.857 ± 0.020 m mol for activated CsF which had not been pretreated with \(\text{AsF}_5\). Figure 4.31 shows a plot of solid count rate versus time for this reaction.

During the reactions of \(\text{AsF}_4^{18}\)F and activated CsF the reaction vessel became very hot and some sintering of the CsF was observed.

4.9 DISCUSSION OF \(\text{AsF}_5\) RESULTS

The reaction of \(\text{AsF}_4^{18}\)F with both activated and non activated CsF results in the uptake of gas with no \(^{18}\)F exchange observed in either case. Similarly to the reaction of \(\text{BF}_2^{18}\)F with CsF there are three different species which could be present on the
Figure 4.31

Reaction of $\text{AsF}_4^{19}$ with activated CsF pretreated with $\text{AsF}_5$

Solid count rate vs reaction time

Count rate counts min$^{-1}$

Reaction time min
surface of the CsF, 1) an adsorbed molecule of AsF$_5$, 2) the AsF$_6^-$ anion or 3) the As$_2$F$_{11}^-$ anion. The AsF$_6^-$ anion has been well characterised spectroscopically$^{110}$ and many salts are known$^{111}$. The As$_2$F$_{11}^-$ anion has been identified in solution$^{112}$ and isolated as the tetraethylammonium and tetrabutylammonium salts.$^{113}$ Both salts lose AsF$_5$ at temperatures above 0°C. The release of AsF$_5$ is reversible and finely powdered solid Et$_4$NAsF$_6$ slowly absorbs gaseous AsF$_5$. No reaction has been observed between caesium hexafluoroarsenate and arsenic pentafluoride.$^{113}$ Figures 4.32 and 4.33 show the structures of the AsF$_6^-$ and As$_2$F$_{11}^-$ anions.

The infrared spectrum of the CsF after reaction with AsF$_4^{18}$F is shown in table 4.21, together with the literature values for AsF$_5$ gas, CsAsF$_6$ and Et$_4$NAs$_2$F$_{11}$. Although the infrared spectrum of the CsF only shows one band it is reasonable to assume that CsAsF$_6$ has been formed. The band at 700 cm$^{-1}$ is sharp and does not show any fine structure and there is no band in the 500 cm$^{-1}$ region which rules out the possibility of the As$_2$F$_{11}^-$ anion. The absence of any other bands rules out the possibility of the surface species being adsorbed molecules of AsF$_5$. 

![Figure 4.32](image)

![Figure 4.33](image)
### TABLE 4.21

**INFRA RED SPECTRUM OF CsF AFTER REACTION WITH AsF$_4^{18}F$**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Vibrational Mode</th>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsF</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CsAsF$_6$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AsF$_5$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Et$_4$NAs$_2$F</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- 800 $v_5E$
- 785 $v_3A_2$
- 700 s $v_3$
- 699 s $v_3F_{1u}$
- 392 m $v_4F_{1u}$
- 400 $v_4A_2$
- 366 $v_6E$
- 128 $v_7E$
- 500 ms
- 770-850 sbr
The ratio of the amount of $\text{AsF}_4^{18}\text{F}$ uptake by non activated CsF to the amount of uptake by activated CsF is 1:1.72. The ratio of surface areas is 1:10, so the uptake of $\text{AsF}_4^{18}\text{F}$ by activated CsF is much lower than expected. This is due to the high degree of sintering which occurs during the reaction which is highly exothermic. The sintering will reduce the available surface area and hence uptake of gas.

The uptake of $\text{AsF}_4^{18}\text{F}$ by non activated CsF can be prevented by treatment of the CsF with non radioactive $\text{AsF}_5$. This shows that adsorption of $\text{AsF}_5$ by CsF is limited to a set number of distinct sites which are quickly filled. Treating activated CsF in a similar way results in a slightly reduced uptake of $\text{AsF}_4^{18}\text{F}$. A possible explanation is that the heat given out during the reaction causes some of the large granules formed by sintering during the original reaction to break open and thus reveal a new surface for adsorption of gas.

4.10 RESULTS OF REACTION OF $\text{CO}_2$ WITH ACTIVATED CsF

The reaction of $\text{CO}_2$ with activated CsF was studied using $^{14}\text{C}$ labelled $\text{CO}_2$, by conventional manometric means, and by infra red spectroscopy.

The reaction between $^{14}\text{CO}_2$ and activated CsF was studied at nine different pressures between 25 and 300 Torr.
As $^{14}\text{C}$ is a soft $\beta$ emitter only surface activities could be measured directly. A measure of the bulk reaction was obtained from the drop in gas phase counts within the closed reaction system. Each reaction was followed for 1 hour. After 1 hour the $^{14}\text{CO}_2$ was removed from the counting vessel and the activity on the solid in the absence of gas was measured. Figures 4.34, 4.35 and 4.36 are plots of solid activity versus time at initial $^{14}\text{CO}_2$ pressures of 25, 150 and 300 Torr. These figures show that the reaction between $^{14}\text{CO}_2$ and CsF is complete within the period before the first count is taken. The surface count rate is independent of initial pressure as shown in figure 4.37. At all $^{14}\text{CO}_2$ pressures studied a constant surface count rate of $50.12 \pm 5.2$ was obtained. The $^{14}\text{CO}_2$ used had a specific count rate of $3325 \pm 15$ counts s$^{-1}$ m mol$^{-1}$ so this surface count rate is equivalent to an uptake of $0.015$ m mol of $^{14}\text{CO}_2$. When the $^{14}\text{CO}_2$ is removed from the counting vessel the surface count rate drops sharply to $8.58 \pm 2.2$ counts s$^{-1}$.

There seems to be no correlation between solid count rate retained after removal of the $^{14}\text{CO}_2$ and initial pressure of $^{14}\text{CO}_2$. This is illustrated by figure 4.38 which is a plot of solid count rate in the absence of gas versus initial $^{14}\text{CO}_2$ pressure.

Although the amount of CO$_2$ adsorbed on the surface of the CsF is independent of initial pressure, the total uptake of $^{14}\text{CO}_2$ calculated from the fall in gas phase counts is
Figure 4.34

Reaction of $^{13}$CO$_2$ with activated CsF

Solid count rate vs reaction time

Initial pressure of $^{13}$CO$_2$ = 5 Torr
Figure 4.35
Reaction of $^{14}$CO$_2$ with activated CsF
Solid count rate vs reaction time

Initial pressure = 150 Torr
Figure 4.36
Reaction of $^{14}$CO$_2$ with activated CsF
Solid count rate vs reaction time

Initial pressure = 300 Torr
Figure 4.37

Reaction of $^{14}$CO$_2$ with activated CsF

Solid count rate vs initial pressure

Initial pressure Torr
Figure 4.38
Reaction of $^{14}$CO$_2$ with activated CsF
Retained solid counts vs initial pressure
dependant on initial pressure. In the range of pressures studied the maximum uptake of 0.108 m mol of CO$_2$ occurred at 300 Torr the highest pressure studied. Figure 4.39 is a plot of total uptake of CO$_2$ versus initial CO$_2$ pressure. The results are summarised in table 4.22.

The experiments carried out with $^{14}$CO$_2$ indicated that the bulk uptake of CO$_2$ by activated CsF is pressure dependant. With this in mind the manometric studies were carried out using an initial pressure of 300 Torr, the maximum possible in this system.

Two experiments were carried out using 0.50g of activated CsF. Reductions in CO$_2$ pressure of 10.91 Torr and 12.12 Torr were observed. As the volume of the system is 156.689 cm$^3$ these pressure drops are equivalent to gas uptakes of 0.099 $^{+}$0.020 and 0.110 $^{+}$0.020 m mol. Infra red examination of the solid after reaction did not reveal any bands in addition to those due to activated CsF. In view of this it was decided to carry out the experiment in the presence of MeCN in an attempt to reproduce the results of Martineau and Milne.$^{30}$

A reaction vessel containing activated CsF (3.0 m mol), CO$_2$ (10.0 m mol) and MeCN (10 ml) together with six ball bearings was shaken for 12 hours before removal of the solvent. The white product obtained was ground in an agate mortar and pestle and its infra red spectrum recorded as a Nujol mull
Figure 4.39

Reaction of $^{14}\text{CO}_2$ with activated CsF

Bulk uptake of $\text{CO}_2$ vs initial pressure

Uptake of $^{14}\text{CO}_2$ (mmol mmol$^{-1}$ CsF$^{-1}$) vs Initial pressure (Torr)
<table>
<thead>
<tr>
<th>Summary of Results of $^{14}$CO$_2$ + CsF Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>Total uptake of CO$_2$</td>
</tr>
<tr>
<td>Surface uptake of CO$_2$</td>
</tr>
<tr>
<td>Amount retained by CsF</td>
</tr>
</tbody>
</table>
Figure 4.40

Reaction of CO$_2$ with activated CsF in MeCN

Infrared spectrum of reaction product
Figure 4.40 continued
between AgCl plates (Figure 4.40). The details of the infra red spectrum obtained are listed in Table 4.23, together with the infra red spectrum of the product obtained by Martineau and Milne in 1971.

4.11 DISCUSSION OF RESULTS

Since Martineau and Milne's claim to have prepared \( \text{Cs}_2 \text{CO}_2 \text{F}_2 \), there have been several unsuccessful attempts to reproduce their results. In 1979 Lawlor and Passmore reported no reaction between CsF and CO \(_2\) at pressures up to 110 atm. They also reported that CO \(_2\) would not react with Et\(_4\)NF unless water was present. On the basis of these results they proposed that Martineau and Milne had obtained the infra red spectrum of a hydrolysis product rather than of the reported \( \text{Cs}_2 \text{CO}_2 \text{F}_2 \). Further evidence for this view was provided by S J David and B S Ault who reported matrix isolation studies of the \( \text{CO}_2 \text{F}^2- \) and \( \text{CO}_2 \text{F}^- \) anions.

None of the infra red bands observed in these studies correspond to any of those observed by Martineau and Milne (Table 4.24). In view of this David and Ault also suggested that Martineau and Milne had obtained the infra red spectrum of a hydrolysis product.

The infra red spectrum of the solid prepared in this work contains all the bands observed by Martineau and Milne, together with several other bands (Table 4.23). Comparison of this spectrum with those of \( \text{CO}_3^2- \), \( \text{HCO}_3^- \) and \( \text{HF}_2^- \), the
<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Alpha</th>
<th>Beta</th>
<th>Description</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>2720</td>
<td>w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2020</td>
<td>w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1640</td>
<td>m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1625</td>
<td>m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1365</td>
<td>s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1350</td>
<td>s</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1310</td>
<td>m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1150</td>
<td>m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1010</td>
<td>w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>980</td>
<td>m</td>
<td></td>
<td>CO and CF (1008 wsh)</td>
<td></td>
</tr>
<tr>
<td>850</td>
<td>s</td>
<td></td>
<td>stretching (985 m)</td>
<td></td>
</tr>
<tr>
<td>670</td>
<td>s</td>
<td></td>
<td>vibrations (850 s)</td>
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</tr>
<tr>
<td>650</td>
<td>w</td>
<td></td>
<td>deformations (680 s) (656 wsh)</td>
<td></td>
</tr>
</tbody>
</table>
## TABLE 4.24

### COMPARISON OF INFRA RED SPECTRA (cm⁻¹)

<table>
<thead>
<tr>
<th>Ault¹¹⁵ CO₂F⁻</th>
<th>Ault³² and David CO₂F₂⁻</th>
<th>Martineau and Milne³⁰ CO₂F₂⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>1749 v₄, B₂</td>
<td>1382 C-O str</td>
<td>1008 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>985 ) CO AND CF</td>
</tr>
<tr>
<td></td>
<td></td>
<td>) stretches</td>
</tr>
<tr>
<td>1316 v₂, A₁</td>
<td></td>
<td>850 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>) C-F</td>
</tr>
<tr>
<td>883 v₁, A₁</td>
<td>930 C-F str</td>
<td>880 ) deformations</td>
</tr>
<tr>
<td></td>
<td></td>
<td>) 685</td>
</tr>
<tr>
<td></td>
<td>700 C-F dif</td>
<td>656</td>
</tr>
<tr>
<td></td>
<td>612 C-F def</td>
<td></td>
</tr>
</tbody>
</table>
likely hydrolysis products, shows that \( \text{Cs}_2\text{CO}_2\text{F}_2 \) has
definitely not been formed, as all of the observed bands
can be assigned to one of three hydrolysis products
(\text{Table 4.25}).

Although Martineau and Milne claim that the characteristic
bands for \( \text{CO}_3^{2-} \) and \( \text{HCO}_3^- \) do not appear in their spectrum,
the five bands observed could quite reasonably be assigned to
these ions as shown in \text{table 4.25}.
<table>
<thead>
<tr>
<th>THIS WORK</th>
<th>Na HF₂</th>
<th>Cs₂CO₃</th>
<th>KHCO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>2720</td>
<td>2755 v₃ + 2v₁</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2020</td>
<td>2100 v₃ + v₁</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1640</td>
<td></td>
<td></td>
<td>1648 v₂</td>
</tr>
<tr>
<td>1625</td>
<td></td>
<td></td>
<td>1626 C-O str</td>
</tr>
<tr>
<td>1365</td>
<td>1461 v₃, B₂</td>
<td></td>
<td>1368 v₃</td>
</tr>
<tr>
<td>1310</td>
<td>1319 v₃, A₁</td>
<td></td>
<td>C-O str</td>
</tr>
<tr>
<td>1150 vCF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1010</td>
<td>1018 v₁, A₁</td>
<td></td>
<td>975 v₅</td>
</tr>
<tr>
<td>980</td>
<td></td>
<td></td>
<td>C₂(OH) str</td>
</tr>
<tr>
<td>850</td>
<td>870 v₂, B₁</td>
<td></td>
<td>656 v₉</td>
</tr>
<tr>
<td>670</td>
<td>685 v₄, A₁</td>
<td></td>
<td>H Torsion</td>
</tr>
<tr>
<td>650</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In addition to their infra red evidence, Martineau and Milne supported their claim with caesium and fluorine analyses and by comparison of the x-ray powder photograph of their product with that of $\text{Cs}_2\text{BeF}_4$. However, these results are not conclusive since $\text{Cs}_2\text{CO}_3$ would also give a similar x-ray powder pattern to $\text{Cs}_2\text{BeF}_4$ and a mix of $\text{Cs}_2\text{CO}_3$ and HF would give similar analytical results to $\text{Cs}_2\text{CO}_2\text{F}_2$ as shown below:

\[
\begin{align*}
\text{Cs}_2\text{CO}_2\text{F}_2 & \text{ requires Cs 76.42\% F 10.92\%} \\
\text{Cs}_2\text{CO}_3 \ 2\text{HF} & \text{ requires Cs 72.67\% F 10.38\%}
\end{align*}
\]

The results obtained in this work therefore show that Martineau and Milne did not prepare $\text{Cs}_2\text{CO}_2\text{F}_2$. They reported the infra red spectrum of a hydrolysis product rather than $\text{Cs}_2\text{CO}_2\text{F}_2$.

In addition to the results previously discussed Martineau and Milne also reported that dry CsF shows no tendency to adsorb carbon dioxide. The results of studies using $^{14}\text{CO}_2$ and constant volume manometer measurements show this observation to be false. Caesium fluoride will adsorb $\text{CO}_2$ at room temperature if the caesium fluoride is activated by treatment with hexafluoroacetone before use. The amounts involved are very small, 0.033 m mol of $\text{CO}_2$ adsorbed per m mol of CsF, determined from both $^{14}\text{CO}_2$ and manometric measurements. The amount of $\text{CO}_2$ involved in the reaction is too small to be detected by infra red spectroscopy and can only be detected by
very accurate manometric work or by radiotracer techniques. This may explain why Martineau and Milne did not observe any uptake of CO$_2$ at room temperature. They also do not give any indication of how the CsF was treated before reaction. The fact that there have been several unsuccessful attempts to reproduce Martineau and Milne’s work suggests that the method of CsF pretreatment is critical. None of the other attempts have used hexafluoroacetone pretreatment with heating being the most common treatment. In this work the use of hexafluoroacetone treated CsF resulted in the reproduction of Martineau and Milnes results at the first attempt.

The use of $^{14}$CO$_2$ allows bulk and surface reactions to be differentiated. The results obtained show that surface adsorption accounts for only a small proportion of the total gas uptake. The amount of surface adsorption is independent of initial pressure over the range of pressures studied but the adsorption is not permanent. If the $^{14}$CO$_2$ is removed from the counting vessel 83% of the surface activity is also removed. This suggests that there are two distinct adsorbed species present on the surface of the CsF, one which is weakly adsorbed and can be removed by pumping and one which is permanently adsorbed. The permanently adsorbed species is most likely to be CO$_2$F$^-$ rather than CO$_2$F$_2$.
since David and Ault have shown that the CO$_2$F$_2^{2-}$ anion has limited stability even at low temperatures. If CO$_2$F$^-$ is assumed to be the permanently adsorbed species, the weakly adsorbed species is most likely to be a weakly adsorbed molecule of CO$_2$.

4.12 COMPARISON OF RESULTS

Both activated and non activated CsF react readily at room temperature with the Lewis acids studied. Experiments using two different isotopes have shown that the reaction occurs both in the bulk of the solid and on its surface. Two distinct species, one permanently adsorbed and one weakly adsorbed, have been identified on the surface of the CsF during reactions with CO$_2$, F$_2$CO and SF$_4$. Surface species could not be identified in the reactions of AsF$_5$ and BF$_3$ with CsF due to the lack of suitable radioisotopes.

In the reactions involving AsF$_5$, BF$_3$ and SF$_4$, uptake of gas occurs but there is no measurable $^{18}$F exchange. $^{18}$F exchange between BF$_3$ and CsBF$_4$ is observed in the presence of a solvent.

$^{18}$F exchange between SF$_3^{18}$F and caesium fluoride at 150°C and 50°C was reported by Fraser and coworkers in 1972.
who quoted fractions exchanged of 0.2 at 150°C and 0.018 at 50°C. In this study there is no mention of any of the SF$_3^{18}$F being retained by the CsF.

A later study of this system by the same workers published in 1978 reported $f$ values of $>1$ if the CsF was reground between each cycle of the pretreatment process. In this study it was suggested that a small quantity of SF$_4$ may be retained on the CsF surface. This together with the results reported in this thesis cast doubt upon the original results of Fraser and coworkers.

No $^{18}$F exchange was observed between Cs$^{18}$F and SF$_4$ at 50°C (section 2.10.2). Studies using $^{35}$SF$_4$ and infrared spectroscopy show that SF$_4$ is permanently adsorbed by the CsF. This means that the fraction exchanged of 0.018 at 50°C quoted by Fraser and coworkers is wrong. The activity observed in the CsF must have been due to uptake of SF$_3^{18}$F and not $^{18}$F exchange. The value quoted for 150°C is also an over estimate as again no allowance has been made for uptake of gas.

Studies carried out using $^{35}$SF$_4$ show that there are two distinct species present on the surface of the CsF during the reaction. A permanently adsorbed species which is presumed to be SF$_5^-$ and the major surface species which is weakly adsorbed SF$_4$. This confirms the findings of Kolta and coworkers in 1982 who proposed a weakly
adsorbed state of SF₄ as the active species in the CsF catalysed chlorofluorination of SF₄.

In the reaction of ^18^F FCO with activated CsF both ^18^F exchange and uptake of gas are observed. This reaction was studied by Fraser and coworkers in 1973. ^18^F exchange was observed at 15°C, 50°C and 150°C but as in the case of SF₃^18^F and CsF no allowance was made for the uptake of F₂CO by CsF. The fraction exchanged at 15°C (0.013) is much lower than that observed in this work (section 4.4). This difference is due to the different techniques used to activate the CsF before use. Fraser and coworkers activated their CsF by three cycles of pumping and heating in vacuo at 150°C for 3 hours. The work reported in this thesis used CsF activated by treatment with (CF₃)₂CO as described in chapter 3.

In all cases except with CO₂ the bulk reaction results in the formation of the anion of the Lewis acid. The reaction of BF₃ with activated CsF results in complete conversion of the CsF to CsBF₄. AsF₅ reacts with activated CsF to produce 30% CsAsF₆. The results of work involving repeated addition of AsF₅ to the same sample of CsF suggest that complete conversion to CsAsF₆ is possible if the solid is ground between each addition of gas.

The results reported in this chapter suggest that hexafluoroacetone activated CsF would be a useful
synthetic reagent. CsAsF$_6$, CsBF$_4$, CsOCF$_3$, and CsSF$_5$ are all formed at room temperature. CsBF$_4$ and CsAsF$_6$ are normally prepared by dissolving CsF or CsHF$_2$ in aqueous HF and passing AsF$_5$ or BF$_3$ through the solution until no further precipitate is formed. The preparation of CsOCF$_3$ from non activated CsF requires a solvent such as MeCN and the preparation of CsSF$_5$ normally requires a high temperature. The use of activated caesium fluoride would mean that these salts could be prepared at room temperature directly from a gas/solid reaction without the need for any solvents.

In the reaction of CO$_2$ with activated CsF the amount of gas adsorbed during the reaction is too small to be detected by infra red spectroscopy unless the reaction is carried out in the presence of a solvent. If the reaction is carried out in MeCN the infra red spectrum of the product indicates various hydrolysis products rather than the expected CsCOF$_2$ or Cs$_2$CO$_2$F$_2$.

All of the reactions studied are independent of initial gas pressure except those of CO$_2$ and F$_2$CO with activated CsF. The reaction of CO$_2$ with activated CsF shows a slight dependence on initial gas pressure whereas the uptake of gas in the reaction of F$_2$CO with CsF is directly related to the initial gas pressure. In the reaction of F$_2$CO with CsF there is more than one type of adsorbed species present in both the bulk of the solid and on its surface.
In all the systems studied surface coverage is independent of initial pressure at all pressures greater than 20 Torr and the amount adsorbed on the surface is the same, within experimental error, in each case. The number of molecules of gas adsorbed on the surface is of the same order of magnitude as the estimated number of surface F\(^-\) ions. This suggests that adsorption occurs at \(\text{F}^-\) sites. However, due to the many assumptions which have to be made in estimating the number of surface \(\text{F}^-\) ions, the possibility of adsorption at other sites or of multilayer adsorption cannot be ruled out.

Figure 4.41 shows a plot of uptake of gas versus time for the reaction of each of the Lewis acids studied with non activated caesium fluoride. Figure 4.42 shows a similar plot for the reactions with activated caesium fluoride. The amount of uptake of gas by non activated CsF is related to the Lewis acidity of the gas, that is the stronger the Lewis acid, the greater the uptake. The fluoride ion affinities of the various acids used are listed in table 4.26.

The order of uptake of gas by activated CsF is not so easily explained. Although AsF\(_5\) is a stronger Lewis acid than BF\(_3\), it reacts to a lesser extent. This may be due to the sintering which occurs during the reaction but it could also be due to the porosity of the activated CsF.
Figure 4.1

Uptake of Lewis acids by non activated CsF

Uptake (mmol CsF⁻¹) vs Time (min)

- AsF₅
- SF₅
- SF₄
Figure 4.42

Uptake of Lewis acids by activated CsF

Uptake (mmol (mmol CsF)$^{-1}$) vs Time (min)
<table>
<thead>
<tr>
<th>ACID</th>
<th>$\text{kJ mol}^{-1}$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>AsF$_5$</td>
<td>$-464 \pm 17$</td>
<td>22</td>
</tr>
<tr>
<td>BF$_3$</td>
<td>$-385 \pm 25$</td>
<td>22</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>$-138 \pm 12$</td>
<td>119</td>
</tr>
<tr>
<td>F$_2$CO</td>
<td>$-146 \pm 12$</td>
<td>119</td>
</tr>
<tr>
<td>SF$_4$</td>
<td>$-192$</td>
<td>17</td>
</tr>
</tbody>
</table>
In chapter 3 it was suggested that pretreatment of CsF with hexafluoroacetone produced a porous solid. The rate of reaction of a gas with a porous solid is given by equation 4.1.

\[ r = \frac{k_v}{\rho} \cdot C_g \cdot \eta \cdot W \]  

where \( k_v \) = reaction rate constant per unit volume of solid, \( \text{sec}^{-1} \)

\( C_g \) = gas phase concentration of adsorbent \( g^- \), \( \text{mol cm}^{-3} \)

\( \eta \) = effectiveness factor

\( \rho \) = particle density, \( \text{g cm}^{-3} \)

\( W \) = weight of sample, g

The effectiveness factor \( \eta \) represents the degree to which reaction occurs within the internal structure of a porous solid. A value of \( \eta = 1 \) indicates that the reaction occurs equally throughout the internal pore structure. Values of \( \eta \ll 1 \) indicate that the reaction occurs on the outside surface of individual particles, with the internal structure playing no part in the reaction due to strong pore diffusion resistances.

The effectiveness factor decreases with increasing particle size, increasing temperature or reaction rate, decreasing pore size and degree of product formation within the pore structure.

When the effectiveness factor is unity the reaction rate
and total adsorption capacity will be dictated by the chemical reactivity of the reactants. As the effectiveness factor decreases, chemical reactivity becomes less important, and other variables such as particle size, pore size and reactant structure become important. Therefore when comparing the results of a range of gases such as those discussed in this chapter, it is necessary to compare both effectiveness factors and reactivity.

No attempt was made to measure particle size or pore volume in this work. But since all the samples of activated CsF were treated in the same way and have B.E.T. surface areas within the range 2.08-3.01 m²/g it is reasonable to assume that there were no major differences in particle size or pore volume between samples.

The pore volume of a porous solid is usually measured by mercury porosimetry which involves forcing mercury into the pores under very high pressure. This method cannot be readily applied to hygroscopic solids and it is debatable whether or not the volume of mercury forced into the solid gives a true measure of the pore volume available for adsorption of gas.

Assuming no major differences in particle size or pore volume between samples, the effectiveness factor of each gas will depend on its shape. The Lewis acids used are
Figure 4.43
The structure of AsF$_5$

Figure 4.44
The structure of BF$_3$

Figure 4.45
The structure of CO$_2$

Figure 4.46
The structure of F$_2$CO

Figure 4.47
The structure of SF$_4$
drawn schematically in figures 4.43 to 4.47. Figure 4.43 shows that AsF$_5$ has a bulky trigonal bipyramid structure which will only fit into large pores. So despite the fact that it is the strongest Lewis acid, complete reaction with CsF would not be expected on the first admission of gas to the sample as AsF$_5$ will have a low effectiveness factor. BF$_3$ on the other hand is a planar molecule which will fit into a wider range of pores and so it will have a high effectiveness factor. The high effectiveness factor together with the strong Lewis acidity of BF$_3$ should result in complete reaction, as is observed experimentally.

F$_2$CO will have a high effectiveness factor but due to its weak Lewis acidity uptake will be low. Similarly for SF$_4$ which is also a weak Lewis acid and which will have a lower effectiveness factor than F$_2$CO.

From figure 4.45, CO$_2$ would be expected to have an effectiveness value very close to unity. The low level of uptake in this case is due to the fact that CO$_2$ is a very weak Lewis acid.

The order of gas uptake can therefore be rationalised if both Lewis acidity and molecular shape are taken into account, thus supporting the view proposed in chapter 3 that activation of CsF by (CF$_3$)$_2$CO produces a porous solid.
CHAPTER FIVE
CHAPTER 5

REACTIONS OF THE SOLID LEWIS ACIDS AlF₃ AND NbF₅ WITH SF₄

INTRODUCTION

Chapter 4 dealt with the reactions of gaseous Lewis acids with a solid Lewis base. In this chapter the reactions of the solid Lewis acids AlF₃ and NbF₅ with the Lewis base SF₄ are discussed. The reactions were studied at room temperature using both ¹⁸F and ³⁵S labelled SF₄ which allowed bulk and surface reactions to be differentiated. The reaction of AlF₃ with SF₄ was also studied by conventional manometric methods.

5.1 EXPERIMENTAL

SF₃¹⁸F and ³⁵SF₄ were prepared as described in chapter 2 sections 2.10.2 and 2.10.4. The reactions were followed using the techniques and apparatus outlined in chapter 4 section 4.1 and described in detail in chapter 2.

5.2 RESULTS OF REACTION OF SF₄ WITH AlF₃

The results of two reactions between SF₃¹⁸F and AlF₃ are summarised in table 5.1. Figure 5.1 shows a plot of surface count rate versus time for experiment 1 in table 5.1. There is a rapid initial rise in the solid count rate until an equilibrium level is reached after 25 minutes.
<table>
<thead>
<tr>
<th>Amount of AlF₃</th>
<th>Amount of SF₃¹⁸F</th>
<th>Specific Count Rate of SF₃¹⁸F Before Reaction</th>
<th>Specific Count Rate of SF₃¹⁸F After Reaction</th>
<th>FRACTION EXCHANGED</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50g</td>
<td>300 Torr 1.0 m mol</td>
<td>12326 ± 111 counts min⁻¹ m mol⁻¹</td>
<td>9274 ± 96 counts min⁻¹ m mol⁻¹</td>
<td>0.30</td>
</tr>
<tr>
<td>5.95 m mol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50g</td>
<td>300 Torr 1.0 m mol</td>
<td>5627 ± 75 counts min⁻¹ m mol⁻¹</td>
<td>4160 ± 64 counts min⁻¹ m mol⁻¹</td>
<td>0.31</td>
</tr>
<tr>
<td>5.95 m mol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE 5.1

REACTION OF SF₃¹⁸F WITH AlF₃ - SUMMARY OF RESULTS
Figure 5.1
Reaction of \( \text{SF}_3^\text{F} \) with \( \text{AlF}_3 \)
Solid count rate vs reaction time

![Graph showing the reaction rate over time. The graph illustrates a trend where the count rate increases with time, reaching a plateau around 30-40 minutes. Error bars indicate variability in the count rate at different times.](image)
The specific count rate of the SF$_3^{18}$F before reaction was $12326 \pm 111$ counts min$^{-1}$ m mol$^{-1}$; after reaction it had fallen to $9274 \pm 96$ counts min$^{-1}$ m mol$^{-1}$ indicating that $^{18}$F exchange had taken place. The fraction exchanged calculated using equation 2.4 is 0.30. Using equation 2.5 the fraction exchanged is also 0.30. The fact that identical values are obtained using these two different equations means that there is no uptake of gas with the increase in solid count rate due to $^{18}$F exchange alone. This is confirmed by the infra red spectrum of the AlF$_3$ after reaction which showed no sign of either SF$_3^+$ or AlF$_4^-$ ions. The fraction exchanged in experiment two was 0.31.

The reaction between $^{35}$SF$_4$ and AlF$_3$ was studied at 16 different pressures between 14 and 300 Torr. Each reaction was monitored for 1 hour before removal of the $^{35}$SF$_4$.

Figures 5.2, 5.3 and 5.4 are plots of solid count rate versus time at initial $^{35}$SF$_4$ pressures of 24, 150 and 300 Torr. These show that the reaction is complete within the five minutes before the first count is taken. The level of surface count rate is dependant on the initial pressure of $^{35}$SF$_4$ as shown by figure 5.5. The maximum count rate corresponds to a surface uptake of $0.22 \pm 0.02$ m mol of $^{35}$SF$_4$ from an initial pressure of 300 Torr.

For each pressure of $^{35}$SF$_4$ studied the drop in overall gas phase counts was equal to the growth in solid counts.
Figure 5.2

Reaction of $^{35}\text{SF}_4$ with $\text{AlF}_3$

Solid count rate vs reaction time

Initial pressure = 24 Torr
Figure 5.3

Reaction of $^{36}\text{SF}_4$ with $\text{AlF}_3$

Solid count rate vs reaction time

Initial pressure = 150 Torr
Figure 5.4

Reaction of $^{35}\text{SF}_4$ with AlF$_3$

Solid count rate vs reaction time

Initial pressure = 300 Torr
Figure 5.5

Reaction of $^{35}\text{SF}_4$ with AlF$_3$

Solid count rate vs initial pressure
Figure 5.6

Reaction of $\text{SF}_4$ with $\text{AlF}_3$

Uptake of $\text{SF}_4$ vs initial pressure

Uptake of $\text{SF}_4$, mmol (mmol AlF$_3$)$^{-1}$

Initial pressure Torr
This shows that the reaction between $^{35}\text{SF}_4$ and $\text{AlF}_3$ is limited to surface adsorption with no bulk adsorption occurring in contrast to the reaction between $^{35}\text{SF}_4$ and activated CsF where both surface adsorption and bulk adsorption are observed.

When the $^{35}\text{SF}_4$ is removed from the counting vessel all of the surface adsorbed $^{35}\text{SF}_4$ is removed with the solid count rate falling to background level. If $^{35}\text{SF}_4$ is readmitted to the counting vessel the surface count rate returns to its original level. Removal of the gas again results in the complete removal of the surface activity with no indication of the formation of any permanently adsorbed species similar to those observed in the reaction between $^{35}\text{SF}_4$ and activated CsF.

The uptake of $\text{SF}_4$ by $\text{AlF}_3$ was studied at nine different pressures between 50 and 300 Torr using the constant volume manometer system described in chapter 2 section 2.12. The results are shown in figure 5.6 together with the uptakes calculated from the fall in the gas count rate in the $^{35}\text{SF}_4$ experiments. The two sets of data show very good agreement and confirm that the reaction between $\text{AlF}_3$ and $\text{SF}_4$ is dependant upon the initial pressure of gas and that the reaction is limited to the surface of the $\text{AlF}_3$ since the uptake of gas is equal to the measured surface uptake.
Figure 5.6

Reaction of $\text{SF}_4$ with $\text{AlF}_3$

Uptake of $\text{SF}_4$ vs initial pressure

![Graph showing the uptake of $\text{SF}_4$ vs initial pressure. The x-axis represents initial pressure in Torr, and the y-axis represents the uptake of $\text{SF}_4$ in mmol/(mmol $\text{AlF}_3$)⁻¹. The graph shows a linear increase in uptake with increasing initial pressure.]
The surface area of AlF₃ was determined by the B.E.T. method using N₂ as adsorbate. A value of 22.3 ± 2.6 m² g⁻¹ was obtained.

5.3 RESULTS OF REACTION OF SF₄ WITH NbF₅

Two experiments involving SF₃¹⁸F and NbF₅ were carried out. The results are summarised in table 5.2. The count rate of the solid rises rapidly until an equilibrium level is reached after 50 minutes, as shown by figure 5.7. Comparison of the SF₃¹⁸F specific count rate before and after reaction shows that the increase in solid count rate is due to¹⁸F exchange. The specific count rate of the SF₃¹⁸F before reaction was 15768 ± 125 counts min⁻¹ m mol⁻¹. The specific count rate of the SF₃¹⁸F after reaction was 2762 ± 53 counts min⁻¹ m mol⁻¹. Using equations 2.4 and 2.5 the fractions exchanged are 1.065 and 1.061 respectively. Those calculated for experiment 2 are 1.00 and 0.99. Since both equations give the same value, no uptake of gas has occurred, the increase in solid count rate is due to ¹⁸F exchange. The infra red spectrum of the NbF₅ after reaction showed only bands due to NbF₅ (Table 5.3).

The reaction between ³⁵SF₄ and NbF₅ was studied at 10 different pressures between 25 and 300 Torr. Each reaction was followed for 90 minutes before removal of the ³⁵SF₄.
### Table 5.2

**Reaction of $\text{SF}_3^{18}\text{F}$ with $\text{NbF}_5$ - Summary of Results**

<table>
<thead>
<tr>
<th>Amount of $\text{NbF}_5$</th>
<th>Amount of $\text{SF}_3^{18}\text{F}$</th>
<th>Specific Count Rate of $\text{SF}_3^{18}\text{F}$ Before Reaction</th>
<th>Specific Count Rate of $\text{SF}_3^{18}\text{F}$ After Reaction</th>
<th>Fraction Exchanged</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50 g</td>
<td>300 Torr</td>
<td>$15768 \pm 125$ Counts min$^{-1}$ m mol$^{-1}$</td>
<td>$2762 \pm 53$ Counts min$^{-1}$ m mol$^{-1}$</td>
<td>1.06</td>
</tr>
<tr>
<td>2.66 m mol</td>
<td>1.0 m mol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.51 g</td>
<td>300 Torr</td>
<td>$9765 \pm 99$ Counts min$^{-1}$ m mol$^{-1}$</td>
<td>$2239 \pm 47$ Counts min$^{-1}$ m mol$^{-1}$</td>
<td>0.99</td>
</tr>
<tr>
<td>2.71 m mol</td>
<td>1.0 m mol</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.7

Reaction of $\text{SF}_3^\text{18} \text{F}$ with $\text{NbF}_5$

Solid count rate vs reaction time
<table>
<thead>
<tr>
<th>THIS WORK</th>
<th>LITERATURE NbF$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>742 s</td>
<td>125 734 vs 126 746 s</td>
</tr>
<tr>
<td>720 vs</td>
<td>721 vs</td>
</tr>
<tr>
<td>700 s</td>
<td>700 vs</td>
</tr>
<tr>
<td>688 s</td>
<td>692 sh</td>
</tr>
<tr>
<td>670 s</td>
<td>672 s</td>
</tr>
<tr>
<td>660 m</td>
<td>661 m 126 660 s</td>
</tr>
<tr>
<td>514 ms</td>
<td></td>
</tr>
<tr>
<td>490 sb</td>
<td>479 w 126 498 sb</td>
</tr>
<tr>
<td>378 vs</td>
<td></td>
</tr>
</tbody>
</table>
Figures 5.8, 5.9 and 5.10 are plots of solid count rate versus reaction time at initial pressures of 25, 125 and 305 Torr.

In each case there is a rise in solid count rate over the first 20 minutes followed by a decrease over the next 50 minutes. At low initial pressures of $^{35}$SF$_4$ the maximum surface count rate is very small. This surface count rate increases with initial $^{35}$SF$_4$ pressure until a constant level of 80-90 counts sec$^{-1}$ is attained at all pressure greater than 100 Torr. The solid count rates after 70 minutes are also equal at pressures greater than 100 Torr. During the reaction the glass vessel becomes coated with an off white solid.

When the $^{35}$SF$_4$ is removed from the counting vessel the solid counts fall to background level indicating that all of the $^{35}$SF$_4$ has been removed from the surface.

If the same pressure of $^{35}$SF$_4$ is readmitted to the counting vessel the surface count rate follows the same pattern as that previously described. The count rate rises for the first 20 minutes and then falls over the next 50 minutes.

On removal of the gas there is a very small surface count remaining. This surface count rate is only detectable by counting for periods of 10,000 seconds or more.
Figure 5.8
Reaction of $^{35}$SF$_4$ with NbF$_5$
Solid count rate vs reaction time

Initial pressure = 25 Torr
Figure 5.9
Reaction of $^{35}\text{SF}_4$ with NbF$_5$
Solid count rate vs reaction time

Initial pressure = 125 Torr
Figure 5.10

Reaction of \( \text{SF}_4 \) with \( \text{NbF}_5 \)

Solid count rate vs reaction time

Initial pressure = 305 Torr
The admission of a further sample of $^{35}\text{SF}_4$ to the counting vessel results in a slight increase in the count rate which remains after removal of the gas. The surface count rate increases from 0.16 counts sec$^{-1}$ to 0.26 counts sec$^{-1}$.

5.4 DISCUSSION OF RESULTS

Due to its volatility at room temperature no surface area or manometric measurements were carried out on NbF$_5$. Its reaction with SF$_4$ was studied using radiotracer techniques alone.

100% $^{18}\text{F}$ exchange is observed in the reaction of SF$_3^{18}\text{F}$ with NbF$_5$. Complete $^{18}\text{F}$ exchange was also observed in a study of the reaction of SF$_3^{18}\text{F}$ with TaF$_5$ carried out in conjunction with the work reported in this thesis.

The reaction of $^{35}\text{SF}_4$ with NbF$_5$ produces a rapid initial increase in surface count rate followed by a slow decrease. In addition to this the walls of the reaction vessel become coated with a white solid as the reaction progresses. The decrease in surface count rate is due to the formation of a volatile reaction product, hence the appearance of a white solid on the walls of the reaction vessel. When the gas is removed from the reaction vessel all of the surface activity is removed indicating that the surface species is weakly adsorbed. The transition from a weakly adsorbed species to a strongly adsorbed species must be very slow because longer reaction times ($t > 3$ hours) and repeated
addition of gas to the same sample result in barely
detectable levels of permanently retained $^{35}\text{SF}_4$. Similar
results were also obtained in the study of the reaction
between $\text{SF}_4$ and $\text{TaF}_5$ using $^{35}\text{SF}_4$, with an increase followed
by a fall in the surface count rate accompanied by the
formation of a white coating on the walls of the reaction
vessel. 97

Infra red spectroscopy does not provide any clues to the
identity of the adsorbed species. This is because the
species is weakly adsorbed and only present if there is
a pressure of $\text{SF}_4$ in the reaction vessel.

The adsorbed species can however be identified by comparison
of the results reported in this chapter with the literature
results of the reactions of $\text{SF}_4$ and $\text{SeF}_4$ with a range of
Lewis acids.

$\text{SF}_4$ reacts with $\text{BF}_3$, $\text{PF}_5$, $\text{AsF}_5$, $\text{SbF}_5$ and $\text{GeF}_4$ to form
compounds of the form $\text{SF}_3^+ \text{MF}_n^-$. In each case there is
evidence for fluorine bridging between the ions. 128

The crystal structures of $\text{SF}_3^+$, $\text{BF}_4^-$, and $\text{GeF}_6^{2-}$ have been determined and are shown in chapter 1 figures
1.2 and 1.8. Each structure shows evidence of fluorine
bridging with each sulphur atom making close contact with
one fluorine atom from each of three different anions.

$\text{SeF}_4$ is isostructural with $\text{SF}_4$ and has been shown to react
in a similar manner 129,130,23 with Lewis acids forming
compounds containing the SeF$_3^+$ cation. Spectroscopic studies of these compounds indicate that they are best regarded as ionic compounds of the type SeF$_3^+ MF^-_n$ and that the ions are held together by relatively strong fluorine bridges.$^{23}$

In 1970 Edwards and Jones published the results of the reaction between NbF$_5$ and SeF$_4$. In this study the room temperature reaction of SeF$_4$ with NbF$_5$ resulted in the formation of the adduct SeF$_4$ 2NbF$_5$ with SeF$_4$ NbF$_5$ as a minor product. A crystal structure determination shows that the molecular geometry of the adduct is consistent with the ionic formulation (SeF$_3$)$^+$ (Nb$_2$F$_{11}$)$^-$. The crystal structure is shown in figure 5.11. Although this ionic formulation gives a reasonable representation of the structure it does not completely describe the structure. The selenium atom is surrounded by three fluorine atoms at 1.66 ± 0.03 Å with F-Se-F angles 94.2 ± 0.4°, giving the expected C$_3v$ symmetry for the cation. In addition to these three fluorine atoms the three fluorine atoms from neighbouring Nb$_2$F$_{11}^-$ ions are almost equidistant from the selenium atom at 2.40, 2.42 and 2.47Å, and form cis bridges to niobium atoms. The large distances between the bridging atoms are compatible with the presence of the non bonding electron pair on selenium filling a seventh co-ordination position.

Edwards and Jones described the structure as being "derived largely from the ionic formulation (SeF$_3$)$^+$

"
Figure 5.11 The structure of $\text{Se}_{\frac{3}{2}}\text{Nb}_2\text{F}_{11}$
With some contribution from a covalently linked arrangement with Nb$_2$F$_{11}^-$ units cis bridged to distorted octahedral SeF$_6$ units. In view of the similarities in the reactions of SeF$_4$ and SF$_4$ with BF$_3$, PF$_5$, AsF$_5$ and SbF$_5$ it is reasonable to assume that the reaction of SF$_4$ with NbF$_5$ will result in the formation of (SF$_3^+$)(Nb$_2$F$_{11}^-$) similar to the (SeF$_3^+$)(Nb$_2$F$_{11}^-$) compound described by Edwards and Jones. The transfer of a fluoride ion from SF$_4$ to NbF$_5$ in the formation of the (SF$_3^+$)(Nb$_2$F$_{11}^-$) compound provides an acceptable mechanism for $^{18}$F exchange.

Although (SF$_3^+$)(Nb$_2$F$_{11}^-$) is the most likely product, the possibility of the formation of (SF$_3^+$(MF$_6^-$) or of polymeric anions of the form (Nb$_n$F$_{5n+1}^-$. similar to those observed in antimony pentafluoride systems cannot be ruled out.

The reaction of SF$_4$ with AlF$_3$ results in 30% $^{18}$F exchange. A similar result was obtained in a radiotracer study of the reaction of SF$_4$ with CrF$_3$ carried out in conjunction with the work reported in this thesis. In this study 20% $^{18}$F exchange was observed after 60 minutes and it was proposed that exchange occurred via a fluorine bridged donor-acceptor species between SF$_3^+$ and CrF$_4^-$. Similar fluorine bridged intermediates have been proposed in other reactions between Lewis acids and SF$_4$, as previously mentioned. It is therefore reasonable to assume that a similar species is involved in the reaction between SF$_4$ and AlF$_3$. 
Studies using $^{35}\text{SF}_4$ indicate that the reaction between $^{35}\text{SF}_4$ and $\text{AlF}_3$ is complete in less than five minutes. The reaction must be limited to the surface of the $\text{AlF}_3$ since the overall drop in gas phase counts is equivalent to the increase in surface counts. The extent of surface adsorption is dependant on the initial pressure of $^{35}\text{SF}_4$, indicating that saturation coverage of the solid surface was not achieved within the pressure range studied. This is due to the large B.E.T. surface area of the $\text{AlF}_3$ ($22.3 \pm 2.6 \text{ m}^2 \text{ g}^{-1}$) which is much larger than that of the $\text{CsF}$ used previously where surface saturation was observed at relatively low pressures. Removal of the gas from the counting vessel results in complete removal of the surface activity, so the surface species must be weakly adsorbed.

In the reaction of $^{35}\text{SF}_4$ with $\text{CrF}_3$, adsorption was limited to the surface of the solid and the equilibrium count rate was not reached until after 30 minutes. Removal of the gas resulted in complete removal of the surface count rate.

The results of a manometric study of the reaction between $\text{SF}_4$ and $\text{AlF}_3$ confirm that the reaction is dependant on initial pressure.

The formation of the $\text{SF}_3^+$ cation has been proposed in all of the reactions discussed in this chapter, however only 30% $^{18}\text{F}$ exchange was observed in the reaction of $\text{SF}_3^{18}\text{F}$
with AlF$_3$ and 20% in the reaction of SF$_3^{18}$F with CrF$_3$
compared to 100% exchange in the SF$_3^{18}$F/NbF$_5$ and SF$_3^{18}$F/
TaF$_5$ systems. The only difference observed between the
two sets of reactions was the formation of a volatile
reaction product in the reactions of NbF$_5$ and TaF$_5$.
The volatility of the reaction product must therefore
play a part in determining the amount of $^{18}$F exchange
observed. In other words $^{18}$F exchange in the SF$_4$/AlF$_3$
and SF$_4$/CrF$_3$ systems is limited to the surface of the
solid whereas $^{18}$F exchange in the SF$_4$/NbF$_5$ and SF$_4$/TaF$_5$
systems occurs both on the surface of the solid and to a
large extent in the gaseous phase.

The results described in this chapter show that simple
molecular analogies are very useful in describing the
surface reactions between a solid Lewis acid and a
gaseous Lewis base.
CHAPTER SIX
CHAPTER 6

THE INTERACTION OF SF₄ WITH β-UF₅

INTRODUCTION

The room temperature reaction between SF₄ and β-UF₅ has previously been studied by D K Sanyal and J M Winfield using both ¹⁸F and ³⁵S labelled SF₄. Due to problems with the recording equipment, reliable results were not obtained for the ³⁵S experiments. The work reported in this chapter was undertaken in an attempt to fill this void. All ¹⁸F results quoted are those of Sanyal and Winfield.

6.1 EXPERIMENTAL

β-UF₅ was prepared as described in chapter 2 section 2.2.12. The reaction between ³⁵SF₄ and β-UF₅ was followed using the techniques and apparatus described briefly in chapter 4 section 4.1 and in detail in chapter 2.

6.2 RESULTS

The reaction between ³⁵SF₄ and β-UF₅ was studied at ten different pressures between 23 and 398 Torr. Each reaction was followed for 1 hour before removal of the ³⁵SF₄.
Representative results are given in tables 6.1 and 6.2 and in figures 6.1, 6.2 and 6.3. Figures 6.1, 6.2 and 6.3 are plots of solid count rate versus time at initial $^{35}$SF$_4$ pressures of 23, 150 and 398 Torr. These plots show that the reaction is complete within the five minutes before the first count is taken. The surface count rate is dependent on the initial pressure of $^{35}$SF$_4$ at all pressures below 200 Torr. Above 200 Torr the surface count rate is independent of the initial pressure. The maximum surface count rate of $26 \pm 1$ counts sec$^{-1}$ corresponds to an uptake of $0.36 \pm 0.01$ m mol of $^{35}$SF$_4$. Surface count rates were accurately determined by extending the counting time to give total counts of $5 \times 10^3$ (see tables 6.1 and 6.2).

At each different pressure of $^{35}$SF$_4$ the drop in the overall gas count rate was approximately equal to the growth in the solid count rate. This shows that there is no bulk adsorption occurring with the reaction being limited to surface adsorption. Figure 6.4 shows a plot of the drop in gas count rate versus initial pressure and figure 6.5 shows a plot of surface count rate versus initial pressure.

When the $^{35}$SF$_4$ is removed from the counting vessel there is no change in the surface count rate. When $^{35}$SF$_4$ is readmitted to the counting vessel there is no increase in the surface count rate. Admission of non radioactive SF$_4$ does not affect the surface count rate.
TABLE 6.1

REACTION OF $^{35}$SF$_4$ WITH $\beta$-UF$_5$

<table>
<thead>
<tr>
<th>TIME (min)</th>
<th>SOLID &amp; GAS COUNTS COUNTS SEC$^{-1}$</th>
<th>GAS COUNTS COUNTS SEC$^{-1}$</th>
<th>SOLID COUNTS COUNTS SEC$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>37.33</td>
<td>28.12</td>
<td>9.21</td>
</tr>
<tr>
<td>10</td>
<td>37.93</td>
<td>28.56</td>
<td>9.37</td>
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<tr>
<td>20</td>
<td>36.60</td>
<td>28.03</td>
<td>8.57</td>
</tr>
<tr>
<td>30</td>
<td>38.77</td>
<td>29.01</td>
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<td>28.73</td>
<td>9.10</td>
</tr>
<tr>
<td>50</td>
<td>37.57</td>
<td>28.55</td>
<td>9.02</td>
</tr>
<tr>
<td>60</td>
<td>37.40</td>
<td>27.97</td>
<td>9.43</td>
</tr>
<tr>
<td>AVERAGE</td>
<td></td>
<td>28.42</td>
<td>9.21</td>
</tr>
</tbody>
</table>

Initial pressure of $^{35}$SF$_4$ = 56 Torr
Counting time = 200 seconds
Count rate of $^{35}$SF$_4$ before reaction = 38.04 counts sec$^{-1}$
Drop in count rate = 9.62 counts sec$^{-1}$
### TABLE 6.2

**REACTION OF $^{35}$SF$_4$ WITH $^{99}$UF$_5$**

<table>
<thead>
<tr>
<th>TIME MIN</th>
<th>SOLID + GAS COUNTS COUNTS SEC$^{-1}$</th>
<th>GAS COUNTS COUNTS SEC$^{-1}$</th>
<th>SOLID COUNTS COUNTS SEC$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>208.14</td>
<td>179.79</td>
<td>28.35</td>
</tr>
<tr>
<td>10</td>
<td>207.34</td>
<td>178.35</td>
<td>28.99</td>
</tr>
<tr>
<td>20</td>
<td>208.78</td>
<td>179.95</td>
<td>28.38</td>
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<tr>
<td>30</td>
<td>207.61</td>
<td>178.99</td>
<td>28.62</td>
</tr>
<tr>
<td>40</td>
<td>208.84</td>
<td>179.33</td>
<td>29.51</td>
</tr>
<tr>
<td>50</td>
<td>208.43</td>
<td>179.89</td>
<td>28.54</td>
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<tr>
<td>60</td>
<td>207.37</td>
<td>179.49</td>
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</tr>
<tr>
<td>AVERAGE</td>
<td></td>
<td>179.39</td>
<td>28.67</td>
</tr>
</tbody>
</table>

**Initial pressure of $^{35}$SF$_4$ = 305 Torr**

**Count time = 100 seconds**

**Count rate of $^{35}$SF$_4$ before reaction = 208.69 counts sec$^{-1}$**

**Drop in count rate = 29.29 counts sec$^{-1}$**
Figure 6.1

Reaction of $^{35}\text{SF}_4$ with $\beta\text{-UF}_5$

Solid count rate vs reaction time

Initial pressure = 23 Torr
Figure 6.2
Reaction of $\text{SF}_4$ with $\beta$-UF$_5$
Solid count rate vs reaction time

Initial pressure = 150 Torr
Figure 6.3
Reaction of $^{35}$SF$_4$ with $\beta$-UF$_5$
Solid count rate vs reaction time

Initial pressure = 398 Torr
Figure 6.4 Reaction of $^{35}\text{SF}_4$ with $\beta-\text{UF}_5$
Drop in gas phase count rate vs initial pressure
Figure 6.5 Reaction of $\text{SF}_4$ with $\beta-\text{UF}_5$

Surface count rate vs initial pressure
6.3 DISCUSSION OF RESULTS

Solid $\beta$-UF$_5$ is polymeric and contains eight co-ordinate uranium. The symmetry of UF$_5$ as an isolated molecule is not known but is believed to be $C_{4v}$.

Uranium pentafluoride behaves as a Lewis acid with fluoride ion donors such as ammonium or alkali metal fluorides forming ionic derivatives $M^+ UF_5^-$ ($M = NH_4, Li, Na, K, Rb$ and Cs). With the strong Lewis acids SbF$_5$, AsF$_5$, NbF$_5$ and TaF$_5$ it forms fluorine bridged adducts in which ionic formulations play a minor part in the bonding. Uranium pentafluoride can therefore behave as a Lewis acid or as a Lewis base.

There is some disagreement over the reaction of $\beta$-UF$_5$ with SF$_4$. In 1984 Sanyal and Winfield published the results of a radiotracer study of the reactions of BF$_3$, PF$_5$ and SF$_4$ with $\beta$-UF$_5$. Fluorine - 18 exchange was observed in each case, together with retention of a small amount of the gas by the $\beta$-UF$_5$. In view of these similarities in the reactions of the three fluorides it was proposed that SF$_4$ was acting as a Lewis acid in the reaction with $\beta$-UF$_5$. Holloway and coworkers published the results of the reaction of SF$_4$ with $\beta$-UF$_5$ in HF in the same year. Based on spectroscopic evidence they proposed that SF$_4$ was acting as a Lewis base. Since neither of these papers provides conclusive evidence it is necessary to look for
similarities between both papers and the work reported in this chapter before attempting to reach a conclusion.

The reaction between SF$_4$ and $\beta$-UF$_5$ is rapid and restricted to the surface of the solid. The adsorbed species is permanently adsorbed and is unaffected by removal of the $^{35}$SF$_4$.

Experiments carried out using SF$_3^{18}$F show that approximately 70% $^{18}$F exchange is observed after two hours (Table 6.3).

By comparison with the results of the reactions discussed in chapter 4, the formation of a permanently adsorbed species suggests that the SF$_5^-$ anion has been formed. Further evidence for this comes from a radiotracer study of the reactions of $\beta$-UF$_5$ with SF$_4$ and the Lewis acids BF$_3$ and PF$_5$ by Sanyal and Winfield. They showed that small amounts of the Lewis acids were retained by the $\beta$-UF$_5$. Since SF$_4$ was also retained they proposed that it must be acting as a Lewis acid. However, the $^{18}$F experiments carried out in chapter 4 showed that no $^{18}$F exchange was observed in systems where SF$_5^-$ was formed. Sanyal and Winfield have demonstrated that 70% $^{18}$F exchange is observed after two hours. The observation of $^{18}$F exchange suggests that the adsorbed species is SF$_3^+$ by comparison with the results of the reactions between SF$_4$ and NbF$_5$ and AlF$_3$ discussed in chapter 5. The formation of the SF$_3^+$ cation was also proposed by Holloway and coworkers who studied the reaction of SF$_4$.
### TABLE 6.3

RESULTS OF REACTION OF SF$_3^{18}$F WITH PF$_5^{134}$

<table>
<thead>
<tr>
<th>AMOUNT OF $\beta$-UF$_5$ m mol</th>
<th>AMOUNT OF SF$_3^{18}$F m mol</th>
<th>REACTION TIME min</th>
<th>FRACTION EXCHANGED</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.52</td>
<td>1.62</td>
<td>120</td>
<td>0.72</td>
</tr>
<tr>
<td>0.66</td>
<td>2.75</td>
<td>100</td>
<td>0.67</td>
</tr>
</tbody>
</table>
with β-UF₅ in HF. Their results indicated that an adduct of composition 3UF₅SF₄ was formed.

Raman and infra red studies of the adduct were carried out both in HF solution and in the solid state. The x-ray powder photograph of the adduct was also recorded. The x-ray powder photograph showed that the adduct was a well-defined crystalline compound which did not contain UF₅⁻.

Holloway and coworkers interpretation of the spectroscopic data was based on the formation of SF₃⁺ and UF₆⁻ ions as shown in table 6.4. Table 6.5 lists the infra red spectrum of the SF₃⁺ ion in four different compounds. Comparison of the two sets of data shows that SF₃⁺ and UF₆⁻ are indeed the most likely products of this reaction. As this reaction was carried out in HF the results are not directly applicable to the heterogeneous reaction of SF₄ and β-UF₅ since SF₄ is known to be a weak base in HF,¹²⁸ ionizing to give SF₃⁺ and HF₂⁻. The infra red spectrum of Holloway and coworkers contains a number of additional bands, suggesting the presence of fluorine bridged species. Holloway and coworkers do in fact say that the reaction of SF₄ with β-UF₅ in HF yields "an adduct of composition 3UF₅SF₄ in which both ionic and fluorine bridged species are present."

As already mentioned SF₄ reacts with a number of Lewis acids to form fluorine bridged adducts which are essentially non-ionic. It is therefore necessary to consider the possibility that the heterogeneous reaction of SF₄ with β-UF₅ results in
<table>
<thead>
<tr>
<th>Solid</th>
<th>HF (soln)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.r</td>
<td>Raman</td>
<td>(SF₃)⁺</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>962 m</td>
<td>962 w</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>952 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>947 ) wbr</td>
</tr>
<tr>
<td></td>
<td></td>
<td>940 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>934 )</td>
</tr>
<tr>
<td>907 m</td>
<td>906 m</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>894 m</td>
</tr>
<tr>
<td></td>
<td></td>
<td>885 m</td>
</tr>
<tr>
<td>629 m</td>
<td>623 s</td>
<td>627 m</td>
</tr>
<tr>
<td>592 s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>566 s</td>
<td>556 vw</td>
<td></td>
</tr>
<tr>
<td>542 sh</td>
<td>540 s*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>535 vw</td>
<td>533 )</td>
</tr>
<tr>
<td></td>
<td>523 vw</td>
<td>530 ) s*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>525 )</td>
</tr>
<tr>
<td>509 s</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>470 w</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>455 vw*</td>
</tr>
<tr>
<td>216 w</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* - Bands assigned to SF₄
TABLE 6.5

VIBRATIONAL SPECTRUM OF THE SF$_3^+$ ION cm$^{-1}$

<table>
<thead>
<tr>
<th>SF$_3$.BF$_4$</th>
<th>SF$_3$.PF$_6$</th>
<th>SF$_3$.AsF$_5$</th>
<th>SF$_3$.SbF$_6$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>939</td>
<td>954</td>
<td>945</td>
<td>943</td>
<td>$v_1(A_1)$</td>
</tr>
<tr>
<td>529</td>
<td>531</td>
<td>530</td>
<td>529</td>
<td>$v_2(A)$</td>
</tr>
<tr>
<td>913</td>
<td>929</td>
<td>926</td>
<td>928</td>
<td>$v_3(E)$</td>
</tr>
<tr>
<td>414</td>
<td>408</td>
<td>411</td>
<td>411</td>
<td>$v_4(E)$</td>
</tr>
</tbody>
</table>
a non ionic fluorine bridged species. Adsorption of SF$_4$ to form two fluorine bridges, as shown in figure 6.6 would result in a seven co-ordinate sulphur species, with the lone pair occupying the seventh co-ordination position.

![Figure 6.6](image)

The structure of this species is similar to that of the SF$_3^+$ cation in SF$_3$ BF$_4$ and GeF$_5$ (SF$_3$)$_2$ (see figures 1.2 and 1.8) and the SeF$_3^+$ cation in SeF$_3$ Nb$_2$F$_{11}$ (figure 5.11). In each case the S (or Se) forms three fluorine bridges to neighbouring anions to give seven co-ordinate sulphur. A species of this type would allow $^{18}$F exchange and could be strongly adsorbed thus agreeing with the results of Sanyal and Winfield. In the presence of HF an ionic species as found by Holloway and coworkers would be more likely. It therefore seems most likely that the heterogeneous reaction of SF$_4$ with $\beta$-UF results in a fluorine bridged species, not an ionic species as previously proposed.
CHAPTER SEVEN
CHAPTER 7

CONCLUSIONS

Activation of CsF by treatment with hexafluoroacetone in MeCN causes a tenfold increase in its B.E.T. surface area. This large increase in surface area is due to the formation of a porous solid. CsF treated in this way is a useful synthetic reagent as it reacts readily at room temperature with a range of Lewis acids to form the Cs salt of the Lewis acid. Preparations of this type normally require solvents or high reaction temperatures and long reaction times.

Experiments carried out to determine the best conditions for labelling gaseous Lewis acid fluorides from reactor produced Cs$^{18}$F show that considerable uptake of gas occurs. This suggests that the mechanism of $^{18}$F exchange between Cs$^{18}$F and gaseous Lewis acids involves more than one step. The first step is adsorption of the acid by the caesium fluoride followed by formation of the anion of the acid. Exchange then occurs between the anion and the Lewis acid rather than between the fluoride ion and the Lewis acid. Further evidence for this is provided by the effect of hexafluoroacetone pretreatment of the Cs$^{18}$F before exchange. Pretreatment of the Cs$^{18}$F results in increased uptake of gas and anion formation. Therefore the observation of increased $^{18}$F exchange coupled with an increase in anion formation supports the view that exchange occurs between the anion of the Lewis acid and the Lewis acid itself.
Radiotracer studies of the reactions of gaseous Lewis acids with CsF and of solid Lewis acids with SF₄ have shown that surface adsorption always occurs, and in many systems additional bulk reactions occur.

The reactions of gaseous Lewis acids with activated CsF result in detectable bulk reaction but no ¹⁸F exchange is observed except in the reaction of F¹⁸FCO with activated CsF. In the reactions of CO₂ and SF₄ with activated CsF two distinct surface species have been identified, one which is strongly adsorbed and one which is weakly adsorbed. The permanently adsorbed species are proposed to be CO₂F⁻ and SF₅⁻ respectively and in each case the weakly adsorbed species is proposed to be an adsorbed molecule of gas.

The reaction between F₂CO and activated CsF results in the observation of two distinct species, both on the surface and in the bulk of the solid. The two species are proposed to be the CF₃O⁻ anion and weakly adsorbed F₂CO. ¹⁸F exchange is observed in this system. ¹⁸F exchange is observed in the reactions of SF₄ with the solid Lewis acids AlF₃ and NbF₅. In experiments using ³⁵SF₄ bulk reaction is observed, together with a single weakly adsorbed surface species which can be removed by pumping. This weakly adsorbed species is proposed to be SF₃⁺.

The reaction of PUF₅ with SF₄ is restricted to the surface of the solid. ¹⁸F exchange is observed and the surface species,
proposed to be F-bridged SF$_4$ molecules, is permanently adsorbed.

All of the reactions studied follow a general trend. The first step in all reactions is the formation of a surface adsorbed species which acts as a precursor for a Lewis acid base reaction. $^{18}$F exchange is observed at room temperature when the species formed is co-ordinatively unsaturated. If a co-ordinatively saturated species is formed no fluorine exchange will be observed unless formation of complex ions containing bridging fluorines is possible.

Although the CF$_3$O$^-$ anion is formed in the reaction of F$_2$CO with activated CsF, $^{16}$F exchange is observed. In this case the reaction is complicated by the presence of both strongly and weakly adsorbed species on the surface and in the bulk of the solid.

By combining all of the aforementioned results it is possible to derive a general model to describe room temperature heterogeneous Lewis acid base reactions between binary fluorides as shown below.

\[
\begin{array}{c}
\text{XF}_n(g) \rightarrow \text{XF}_n(\text{ads}) \\
\downarrow \\
\text{XF}^+(n-1) \quad \text{XF}^-(n+1) \\
\end{array}
\]

$^{18}$F exchange observed \quad No $^{18}$F exchange
The work presented in this thesis shows that radiotracer techniques can produce results which are comparable to those obtained by conventional techniques such as manometry. It also demonstrates that identical results can be obtained from two different radioisotopes using two different counting techniques. This shows that the counting techniques and apparatus used in this study are valid for this type of work.

The original aim of this work was to investigate the usefulness of molecular analogies in describing the reactions which occur at metal halide surfaces. The results presented in this thesis show that molecular analogies are certainly very useful in describing the reactions which occur between binary fluorides, having given rise to a general model which can be used to describe these reactions.

In view of this it seems highly likely that molecular analogies could be similarly applied to all surface reactions of metal halides, not just those of binary fluorides.
This appendix contains programme listings of all the computer programmes written specifically for this work. Each listing is accompanied by a brief explanation of the way in which the programme operates.
PROGRAMME 1 "B.E.T.S.A"

This programme was written for the BBC microcomputer and is used to calculate the B.E.T. surface areas of samples. The programme operates via a number of procedures (subroutines). The operation of each procedure is now explained.

PROC Background : Calculates the average background count.
PROC Input : Enters and stores experimental data
PROC Count : Corrects room temperature counts for background and calculates count rate in counts sec⁻¹.
PROC Temp : Converts °C to K
PROC Pressure : Converts count rate to equivalent pressure of ⁸⁵Kr using calibration data.
PROC Presstemp : Calculates T/P
PROC Linefit : Calculates best fitting straight line in a plot of volume versus T/P using linear regression. The calculated gradient and intercept are stored as C3 and M1 in line 180.

PROC Counts, PROC Temp, PROC Pressure, PROC Presstemp and PROC linefit are repeated in lines 190 - 230 for the 77K results.

The intercept and gradient are stored as C2 and M2 in line 240.

PROC Deltavol : Calculates the theoretical low temperature isotherm and then calculates the difference in volume between the theoretical and experimental isotherms at each point.
PROC Calc : Calculates $P/n (P_0 - P) \times 10^{18}$ and $P/P_0$

PROC Linefit is then used to calculate the best fitting straight line in a plot of $P/n (P_0 - P) \times 10^{18}$ versus $P/P_0$

PROC Calc SA : Calculate the surface area using the gradient and intercept calculated in PROC Calc.

PROC Results : Prints out the results

All variables are defined in chapter 3 section 3.1.4.
REM KRYPTON SURFACE AREA PROGRAMME JULY 85

CLS: PRINTTAB(10, 1):"KRYPTON SURFACE AREA."

DIM V(8), V1(8), T(8), C(8), C1(8), CB(6), TP(12), TP1(12), P(12)
P1(12), Y1(8), Y2(8), H(8), G(8), Y(8)

40 PRINT" Calibration date 6/9/83"
50 PRINT" NEW CALIBRATION (Y/N)"; A$ = GET$
60 IF A$ = "Y" THEN PROCRecal ELSE 90
70 END

80 FOR I = 1 TO B%/2: V(I) = 0: C(I) = 0: T(I) = 0: TP(I) = 0: NEXT
90 PROCBackground

100 PROCInput

110 PROCCounts

120 PROCTemp

130 PROCPressure

140 PROCPresstemp

150 PROCLinefit

160 FOR I = 1 TO B%/2: V(I) = 0: C(I) = 0: T(I) = 0: TP(I) = 0: NEXT
180 C3 = IT: M1 = M: R1 = R

190 PROCCounts

200 PROCTemp

210 PROCPressure

220 PROCPresstemp

230 PROCLinefit

240 C2 = IT: M2 = M: R2 = R

250 PROCDeitavol

260 PROCCalc

270 VDU2
280 FOR I=1 TO B%2
290 PRINT G(I),H(I)
300 NEXT
310 VDU3
320 FOR I=1 TO B%2:TP(I)=G(I):V(I)=H(I):NEXT
330 PROCLinefit
340 PROCCalcSA
350 PROCResults
360 END
370 DEFPROCBackground
380 CLS:INPUT"NUMBER OF BACKGROUND COUNTS (MAX.OF 6)";A%
390 PRINT"INPUT BACKGROUND READINGS"
400 B=0
410 FOR I=1 TO A%:INPUT CB(I)
420 B=CB(I)+B:NEXT
430 B=B/A%
440 PRINT "B=";B
450 ENDPROC
460 DEFPRCRECAL
470 CLS:PRINT"TO RECALIBRATE USE RECAL PROGRAMME TO ";
480 PRINT"OBTAIN GRADIENT(M) AND INTERCEPT(C) OF ";
490 PRINT"NEW CALIBRATION CURVE."
500 PRINT"SUBSTITUTE THESE VALUES FOR THOSE STORED ";
510 PRINT"IN LINE 850."
520 PRINT"CALIBRATION DATE IS STORED IN LINE 40."
530 PRINT"AFTER CHANGING M,C AND DATE SAVE PROGRAMME ON TAPE."
540 ENDPROC
550 DEFPROCInput
CLS: INPUT ' "NUMBER OF READINGS (MAX. OF 10) " '; B%

INPUT ' "SAMPLE WEIGHT " '; W

INPUT ' " COUNT TIME (SECONDS) " '; T%

INPUT ' " D.S.T. VOLUME DIFFERENTIAL " '; VD

CLS: PRINTTAB(10,1) " ROOM TEMPERATURE RUN. "

PRINT ' " INPUT VOLUME, COUNTS, TEMPERATURE "'

FOR I = 1 TO B%/2: INPUT V(I), C(I), T(I): NEXT

PRINT ' " ANY MISTAKES ( Y/N ) " '; A$ = GET$

IF A$ <> "Y" THEN 680

PRINT ' " INPUT DATA NUMBER, V, C, T " '; INPUT I, V(I), C(I), T(I)

PRINT ' " ANY MORE MISTAKES ( Y/N ) " '; A$ = GET$

IF A$ = "Y" THEN 650 ELSE 680

CLS: PRINTTAB(10,1) " LOW TEMPERATURE RUN. "

PRINT ' " INPUT VOLUME, COUNTS, TEMPERATURE "'

FOR I = 1 TO B%/2: INPUT V1(I), C1(I), T1(I): NEXT

PRINT ' " ANY MISTAKES ( Y/N ) " '; A$ = GET$

IF A$ <> "Y" THEN 760

PRINT ' " INPUT DATA NUMBER, V1, C1, T1 " '; INPUT I, V1(I), C1(I), T1(I)

PRINT ' " ANY MORE MISTAKES ( Y/N ) " '; A$ = GET$

IF A$ = "Y" THEN 730 ELSE 760

ENDPROC

DEFPROC Counts

FOR I = 1 TO B%/2: C(I) = (C(I) - B) / T%: NEXT

ENDPROC

DEFPROC Temp

FOR I = 1 TO B%/2: T(I) = T(I) + 273: NEXT

ENDPROC

DEFPROC Pressure
840 LOCAL M, C
850 C = 7.1638E-3; M = 3.1933E-3
860 FOR I = 1 TO B%/2: P(I) = M*C(I) + C: NEXT
870 ENDPROC
880 DEFPROC PressTemp
890 FOR I = 1 TO B%/2: TP(I) = T(I)/P(I): NEXT
900 ENDPROC
910 DEFPROC Linefit
920 XX = 0; YY = 0; XY = 0; sumX = 0; sumY = 0; sumXY = 0; sumYY = 0; sumXX = 0
930 LOCAL MEANX, MEANY
940 M = 0; C = 0; IT = 0
950 FOR I = 1 TO B%/2
960 sumX = sumX + TP(I): sumY = sumY + V(I): NEXT
970 MEANX = sumX/(B%/2): MEANY = sumY/(B%/2)
980 FOR I = 1 TO B%/2
990 sumXX = sumXX + TP(I)*TP(I): sumYY = sumYY + V(I)*V(I)
1000 sumXY = sumXY + TP(I)*V(I)
1010 XX = XX + (TP(I) - MEANX)*(TP(I) - MEANX): YY = YY + (V(I) - MEANY)*(V(I) - MEANY);
2500 XY = XY + (TP(I) - MEANX)*(V(I) - MEANY)
1020 NEXT
1030 M = ((B%/2)*sumXY-sumX*sumY)/((B%/2)*sumXX-sumX*sumX)
1040 IT = (sumY*sumXX-sumX*sumXY)/((B%/2)*sumXX-sumX*sumX)
1050 R = XY/SQR(XX*YY)
1060 ENDPROC
1070 DEFPROC DeltaVd
1080 FOR I = 1 TO B%/2
1090 C1 = C3 - VD
1100 Y1(I) = M1*TP(I) + C1
1110 Y2(I)=M2*TP(I)+C2
1120 Y(I)=Y1(I)-Y2(I)
1130 NEXT
1140 ENDPREGC
1150 DEFPROCCalc
1160 FOR I=1 TO B%/2
1170 H(I)=P(I)/((Y(I)*P(I)*0.12468)*(2.49-P(I)))
1180 G(I)=P(I)/2.49
1190 NEXT
1200 ENDPREGC
1210 DEFPROCCalcSA
1220 SA=1/M+IT
1230 SA=SA*0.195/W
1240 ENDPREGC
1250 DEFPROCCResults
1260 CLS:VDU2:PRINT'TAB(11,1)"ROOM TEMPERATURE RUN."
1270 @%=&2040C
1280 PRINT"GRADIENT=";M1
1290 PRINT"INTERCEPT=";C3
1300 PRINT"CORRELATION COEFFICIENT=";R1
1310 VDU3
1320 PRINT""""PRESS 'C' TO CONTINUE";REPEAT UNTIL GET$="C"
1330 CLS:VDU2:PRINT'TAB(11,1)"LOW TEMPERATURE RUN."
1340 PRINT"GRADIENT=";M2
1350 PRINT"INTERCEPT=";C2
1360 PRINT"CORRELATION COEFFICIENT=";R2
1370 VDU3
1380 PRINT""""PRESS 'C' TO CONTINUE";REPEAT UNTIL GET$="C"
CLS:VDU2:PRINTTAB(14,1)"SURFACE AREA."
PRINT"GRADIENT=";M
PRINT"INTERCEPT=";IT
PRINT"CORRELATION COEFFICIENT=";R
VDU3
PRINT"PRESS 'C' TO CONTINUE":REPEAT UNTIL GET$="C"
CLS:VDU2:PRINTTAB(8,4)"SURFACE AREA=";SA
VDU3
PRINTTAB(15,19)"'E' TO END":REPEAT UNTIL GET$="E"
CLS:PRINTTAB(15,10)"END OF RUN"
@%=&10
ENDPROC
PROGRAMME 2 "F.18"

Written for the Dragon Microcomputer

This programme corrects for the decay of $^{18}$F. Counts are corrected down to the latest time so that artificially high count rates are not produced.

The operation of the programme is as follows:

Lines 10-180 : Input of data
Lines 200 - 260 : Calculation based on equation 2.8
Lines 280 - 540 : Print out of results both on screen and printer
10 CLS: DIM A(20), B(20), C(20), D(20), T(20)
20 PRINT "FLUORINE 18 DECAY PROGRAMME"
30 PRINT
40 PRINT "INPUT NUMBER OF DATA PAIRS (MAX OF 20 )"
50 INPUT N
60 PRINT "AVERAGE NUMBER OF BACKGROUND COUNTS"
70 INPUT G
80 E = (LOG(2))/110
90 PRINT "INPUT A, T(MINUTES)"
100 FOR I = 1 TO N
110 INPUT A(I), T(I)
120 NEXT
130 PRINT
140 PRINT "ANY MISTAKES Y/N": INPUT C$
150 IF C$ < "Y" THEN 200
160 PRINT "DATA NO., A, T": INPUT I, A(I), T(I)
170 PRINT "ANY MORE MISTAKES Y/N": INPUT D$
180 IF D$ < "Y" THEN 200
190 GOTO 160
200 FOR I = 1 TO N
210 A(I) = A(I) - G
220 B(I) = T(I) * -E
230 C(I) = EXP(B(I))
240 D(I) = C(I) * A(I)
250 U(I) = INT(D(I) + 0.5)
260 NEXT
270 CLS
290 IF N>10 GOTO 310
300 IF N<10 GOTO 410
310 FOR I=1 TO 10
320 PRINT D(I)
330 NEXT
340 PRINT "PRESS ENTER TO CONTINUE": INPUT A$ 
350 IF A$="K" THEN 520 360 CLS
360 CLS
370 FOR I=11 TO N
380 PRINT D(I)
390 NEXT
400 GOTO 440
410 FOR I=1 TO N
420 PRINT D(I)
430 NEXT
440 PRINT
450 PRINT #2,"CORRECTED ACTIVITIES"
460 FOR I=1 TO N
470 PRINT #2,D(I)
480 NEXT
490 PRINT "ANOTHER RUN Y/N": INPUT B$ 
500 IF B$="Y" THEN RUN ELSE 510
510 PRINT
520 PRINT "END OF CALCULATION"
530 END
PROGRAMME 3 "F.18 PLOT"

Written for the Dragon microcomputer

This programme corrects the observed counts for decay of $^{18}_F$ and then produces a plot of solid counts versus reaction time on the monitor. The operation of the programme is as follows:

- Lines 10 - 400: Correction of Gas + solid counts for decay, using method described for programme 2.
- Lines 420 - 720: Correction of Gas phase counts for decay.
- Lines 730 - 760: Calculation of corrected solid counts.
- Lines 770 - 890: Print out of solid counts on screen only.
- Lines 900 - 970: Input of adsorption times.
- Lines 1040 - 1060: Scales points to fit computers graphic screen.
- Lines 1070 - 1110: Converts experimental points to points on graphic screen.
- Line 1130: Sets up graphic screen
- Lines 1140 - 1220: Plots axes.
- Lines 1230 - 1270: Plots points, drawing a circle round each point.
- Lines 1280 - 1320: Joins points.
PROGRAMME 3  F.18.PLOT

10 DIM A(15),B(15),C(15),D(15),T(15)
20 DIM A1(15),B1(15),C1(15),D1(15),T1(15),X(15),Y(15)
30 CLS
40 PRINT" F.18.PLOT"
50 PRINT"NUMBER OF DATA PAIRS (MAXIMUM OF 30)"
60 INPUT P
70 PRINT"AV.NO. OF BACKGROUND COUNTS"
80 INPUT G

90 E=(LOG(2))/110
100 CLS
110 PRINT"INPUT DECAY TIME(MINUTES),ACTIVITY(GAS+SOLID)"
120 FOR I=1 TO P/2
130 INPUT T(I),A(I)
140 NEXT I
150 PRINT"ANY MISTAKES Y/N":INPUT A$
160 IF A$<"Y"THEN 200
170 PRINT"INPUT DATA NUMBER,TIME,ACTIVITY":INPUT I,T(I),A(I)
180 PRINT"MORE MISTAKES Y/N":INPUT A$
190 IF A$<"N" THEN 170
200 FOR I=1 TO P/2
210 A(I)=A(I)-G
220 B(I)=T(I)*-E
230 C(I)=EXP(B(I))
240 D(I)=C(I)*A(I)
250 D(I)=INT(D(I))
260 NEXT I
270 CLS
280 PRINT"CORRECTED ACTIVITIES(GAS+SOLID)"
290 FOR I=1 TO 10
300 PRINT D(I)
310 NEXT I
320 PRINT "TYPE C TO CONTINUE"
330 A$=INKEY$
340 IF INKEY$<>"C" GOTO 340
350 FOR I=11 TO P/2
360 PRINT D(I)
370 NEXT I
380 PRINT "TYPE C TO CONTINUE"
390 A$=INKEY$
400 IF INKEY$<>"C" GOTO 400
410 CLS
420 PRINT "INPUT DECAY TIME (MINUTES), GAS PHASE COUNTS"
430 FOR I=1 TO P/2
440 INPUT T1(I), A1(I)
450 NEXT I
460 PRINT "ANY MISTAKES Y/N": INPUT A$
470 IF A$="Y" THEN 510
480 PRINT "INPUT DATA NUMBER, TIME, ACTIVITY": INPUT I, T1(I), A1(I)
490 PRINT "ANY MORE MISTAKES Y/N": INPUT A$
500 IF A$="N" THEN 480
510 FOR I=1 TO P/2
520 A1(I)=A1(I)-G
530 B1(I)=T1(I)*E
540 C1(I)=EXP(B1(I))
550 D1(I)=C1(I)*A1(I)
560 D1(I)=INT(D1(I))
570 NEXT I
580 CLS
590 PRINT "CORRECTED ACTIVITIES (GAS PHASE)"
600 FOR I = 1 TO 10
610 PRINT D1(I)
620 NEXT I
630 PRINT "TYPE C TO CONTINUE"
640 A$ = INKEY$
650 IF INKEY$ <> "C" GOTO 650
660 FOR I = 11 TO P/2
670 PRINT D(I)
680 NEXT I
690 PRINT "TYPE C TO CONTINUE"
700 A$ = INKEY$
710 IF INKEY$ <> "C" GOTO 710
720 CLS
730 FOR A = 1 TO P/2
740 Y(A) = D(A) - D1(A)
750 NEXT A
760 PRINT "CORRECTED SOLID COUNTS"
770 FOR A = 1 TO 10
780 PRINT Y(A)
790 NEXT A
800 PRINT "TYPE C TO CONTINUE"
810 A$ = INKEY$
820 IF INKEY$ <> "C" GOTO 820
830 FOR A = 11 TO P/2
840 PRINT Y(A)
850 NEXT A
860 PRINT"TYPE C TO CONTINUE"
870 A$=INKEY$
880 IF INKEY$<"C" GOTO 880
890 CLS
900 PRINT"INPUT ADS TIMES"
910 FOR A=1 TO P/2: INPUT X(A)
920 NEXT A
930 PRINT"ANY MISTAKES Y/N": INPUT A$
940 IF A$<"Y" THEN 980
950 PRINT"INPUT DATA NUMBER,TIME": INPUT A, X(A)
960 PRINT"ANY MORE MISTAKES Y/N": INPUT A$
970 IF A$<"N" THEN 950
980 REM**LINE GRAPH**
990 CLS
1000 PRINT"PRESS E TO END PROGRAMME AFTER THE GRAPH IS DRAWN"
1010 A$=INKEY$
1020 PRINT"TYPE C TO CONTINUE"
1030 IF INKEY$<"C" THEN GOTO 1030
1040 REM**SCALE**
1050 S=S+1
1060 FOR A=1 TO P/2: IF Y(A)/S>148 THEN 1050 ELSE NEXT A
1070 REM**CONVERSION OF XkY TO GRID COORDINATES**
1080 FOR D=1 TO P/2
1090 X(D)=(3*X(D))+20
1100 Y(D)=178-(Y(D)/S)
1110 NEXT D
1120 CLS
1130 PMODE 4,1:PCLS:SCREEN 1,0
1140 REM**DRAW AXES**
1150 LINE(20,10)-(20,178),PSET
1160 FOR F = 10 TO 178 STEP 4
1170 LINE(15,F)-(20,F),PSET
1180 NEXT F
1190 LINE(20,178)-(245,178),PSET
1200 FOR G = 20 TO 245 STEP 15
1210 LINE(G,183)-(G,178),PSET
1220 NEXT G
1230 REM**PLOT POINTS**
1240 FOR D = 1 TO P/2
1250 PSET(X(D),Y(D)),1
1260 CIRCLE(X(D),Y(D)),1
1270 NEXT D
1280 REM**JOIN POINTS**
1290 LINE(20,178)-(X(1),Y(1)),PSET
1300 FOR D = 1 TO (P/2)-1
1310 LINE(X(D),Y(D))-(X(D+1),Y(D+1)),PSET
1320 NEXT D
1330 A$=INKEY$
1340 IF INKEY$<"E" THEN GOTO 1340
1350 PRINT"ANOTHER RUN Y/N": INPUT A$
1360 IF A$="Y" THEN RUN ELSE 1370
1370 PRINT"END OF PROGRAMME"
1380 END
PROGRAMME 4 "F.E.X."

Written for the Dragon microcomputer

This programme calculates the fraction of $^{18}_{}F$ exchanged between a $^{18}_{}F$ labelled gas and a solid metal fluoride using equations 2.4 and 2.5. The programme operates as follows:

Lines 40 - 100 Calculation of the number of m moles of gas.

Lines 140 - 210 Calculation of the number of m moles of solid.

Lines 230 - 360 Calculation of fractions exchanged

Lines 360 - 400 Print out of results on screen.

$F_1$ is the fraction exchanged calculated using equation 2.5

$F_2$ is the fraction exchanged calculated using equation 2.4
PROGRAMME 4 F.EX.

10 CLS
20 PRINT"PROGRAMME TO CALCULATE FRACTION EXCHANGED BETWEEN F18 LABELED GAS AND A METAL FLUORIDE"
30 PRINT
40 PRINT"P(TORR), VOL, T": INPUT P, V, T
50 CLS
60 T=T+273
70 P=P/760
80 R=82.053
90 N=(P*V)/(R*T)
100 M2=N*1000
110 PRINT
120 PRINT M2;"MMOL OF GAS"
130 PRINT
140 PRINT"WEIGHT OF SOLID": INPUT W
150 CLS
160 PRINT
170 PRINT"MOL.WT.OF SOLID": INPUT MW
180 CLS
190 M1=(W/MW)*1000
200 PRINT
210 PRINT M1;"MMOL OF SOLID"
220 PRINT
230 PRINT"ACTIVITY OF GAS BEFORE REACTION ": INPUT AO
240 PRINT
250 PRINT"ACTIVITY OF GAS AFTER REACTION": INPUT AT
260 CLS
270 PRINT
280 PRINT "ACTIVITY OF SOLID AFTER REACTION": INPUT A1
290 PRINT
300 PRINT "NO. OF F ATOMS IN SOLID": INPUT N1
310 PRINT
320 PRINT "NO. OF F ATOMS IN GAS": INPUT N2
330 PRINT
340 F1 = (AO - AT) * ((N1 * M1) + (N2 * M2)) / (N1 * M1 * AO)
360 CLS
370 PRINT
380 PRINT "FRACTION EXCHANGED (F1) ="; F1
390 PRINT "FRACTION EXCHANGED (F2) ="; F2
400 PRINT "ANOTHER RUN Y/N": INPUT A$;
410 IF A$ = "Y" THEN 430 ELSE RUN
420 PRINT
430 CLS: PRINT "END OF CALCULATION"
440 END
PROGRAMME 5 "D.T.C."

Written for the Dragon microcomputer

This programme is used to calculate the dead time of a GM tube. The method of obtaining the data required for this calculation is described in chapter 2 section 2.4.4.

The programme operates as follows:

Lines 10 - 110  Input of data
Lines 120 - 140  Calculation of dead time using equation 2.6.
Lines 150 - 180  Print out of dead time on printer
PRUGRAI1HE 5 D1C

10 DIM C(20), CC(20)

20 CLS: PRINT "DEAD TIME CORRECTION PROGRAMME"

30 PRINT: INPUT "NUMBER OF BACKGROUND COUNTS"; N

40 PRINT: PRINT "ENTER BACKGROUND COUNTS"

50 FOR I = 1 TO N: INPUT B(I)

60 CB = CB + B(I): NEXT: CB = CB / N

70 PRINT: PRINT "ENTER NUMBER OF COUNTS": INPUT M

80 PRINT: PRINT "COUNT TIME": INPUT T

90 PRINT: PRINT "DEAD TIME": INPUT DT

100 PRINT "INPUT COUNTS"

110 FOR I = 1 TO M: INPUT C(I)

120 NEXT

130 PRINT "ANY MISTAKES Y/N": INPUT A$

140 IF A$ <> "Y" THEN 180

150 PRINT "ENTER COUNT NUMBER, COUNT": INPUT I, C(I)

160 PRINT "ANY MORE MISTAKES Y/N": INPUT A$

170 IF A$ = "Y" THEN 150

180 FOR I = 1 TO M

190 C(I) = C(I) - CB: C(I) = C(I) / T

200 CC(I) = C(I) / (1 - DT * C(I))

210 NEXT

220 CLS: PRINT: PRINT "ENTER TUBE CORRELATION FACTOR"

230 PRINT "ENTER 1 IF NOT REQUIRED"

240 INPUT CF

250 FOR I = 1 TO M

260 CC(I) = CC(I) * CF

270 CC(I) = INT(CC(I) * 100 + 0.5) / 100
280 NEXT
290 PRINT -2"COUNTS","CORRECTED COUNTS"
300 FOR I=1 TO N
310 PRINT -2,C(I),CC(I)
320 NEXT
330 PRINT"ANOTHER RUN Y/N":INPUT BS
340 IF BS="Y" THEN RUN ELSE 350
350 CLS:PRINT"END OF CALCULATION"
360 END
PROGRAMME 6 "DT.CR."

Written for the BBC microcomputer

This programme is used to correct observed counts for the dead time of the Geiger Muller tubes and to take account of the correlation factor of the tubes. The programme operates as follows:

- Lines 10 - 60: Calculation of average background count
- Lines 70 - 170: Input of data
- Lines 180 - 280: Calculation using equation 2.6
- Lines 290 - 320: Print out of results on printer
PROGRAMME 6 D1.CK.

10 DIM TB20), AO(20), AT(20)
20 CLS: PRINT "DEAD TIME CALCULATION PROGRAMME"
30 PRINT: INPUT "NUMBER OF DATA PAIRS"; N
40 PRINT: PRINT "ENTER OBSERVED ACTIVITY, TRUE ACTIVITY"
50 FOR I = 1 TO N
60 INPUT AO(I), AT(I): NEXT
70 PRINT "ANY MISTAKES Y/N"; INPUT AS
80 IF AS <> "Y" THEN 120
90 PRINT: INPUT "ENTER PAIR NUMBER, OBSERVED ACTIVITY, TRUE ACTIVITY"
"; I, AO(I), AT(I)
100 PRINT "ANY MORE MISTAKES Y/N"; INPUT AS
110 IF AS = "Y" THEN 90
120 FOR I = 1 TO N
130 T(I) = (AT(I) - AO(I)) / (AT(I) * AO(I))
140 NEXT
150 VDU1: PRINT "DEAD TIME"
160 FOR I = 1 TO N
170 PRINT "T"; ; T(I)
180 NEXT
190 PRINT "ANOTHER RUN Y/N"; INPUT AS
200 IF AS = "Y" THEN RUN ELSE 210
210 CLS: PRINT "END OF CALCULATION"
220 END
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