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C. Shen
(Ph.D. Thesis)

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Preparations and Characterizations of Novel Graphite-like Materials AND Some High Oxidation State Fluorine Chemistry

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Preparation and Characterization of Novel Graphite-like Materials AND
Some High Oxidation State Fluorine Chemistry

by

Ciping Shen

Abstract

Novel graphite-like materials, BCx (6>x≥3), have been prepared using
BCl3 and C6H6 at 800 °C - 1000 °C, and CxN (14>x≥5) have been synthesized
using C5H5N and Cl2 at 680 °C - 986 °C. Bulk and thin film characterization
techniques have been used to obtain information pertinent to the structure and
bonding in these solids.

A new 1st stage salt C8K(NH3)1.1 has been prepared by reacting C8K
with gaseous NH3 at 20 °C. The carbon sub-lattice is hexagonal: a = 2.47 Å, c =
6.47 Å. The smaller a parameter and lower conductivity compared to C8K are
attributed to the diminution of the electron transfer from K to the conduction band
as a consequence of the solvation of K by NH3.

A simplified liquid phase method for synthesizing Li-graphite intercalation
compounds has been developed. The synthesis of a novel lamellar mixed
conductor, Cx+Li2N+, has been attempted.

The stability and conductivity of (BN)3SO3F have been studied:
(BN)3SO3F has been shown to be metallic with a specific conductivity of 1.5
S·cm⁻¹. The relatively low conductivity compared to C8,3SO3F is attributed to
the low mobility of holes in the BN sheets.
F₂, in the presence of Lewis acids, oxidizes Xe to Xe(II) in the dark to produce XeF₆AsF₆ in WF₆ or anhydrous HF (AHF), or in liquid AsF₅ at -65 °C. However, O₂ is not oxidized by F₂/Lewis acid under similar conditions. Xenon solvated in AHF is oxidized by F₂ in the dark to form XeF₂ at 20 °C. The probable mechanistic and thermodynamic reasons for these observations are proposed.

O₂⁺ in AHF has been shown to be a very powerful oxidizer, able to oxidize IrF₆⁻ to IrF₆, Ag⁺ to Ag²⁺, and in basic AHF, Ag(II) to Ag(III) in AgF₄⁻. The oxidizing power of Ag²⁺ in AHF has been assessed thermodynamically, and shown to be comparable to that of O₂⁺ in AHF.

Two new AgF⁺ salts, AgFW₂O₂F₉ and "AgFWOF₅BF₃", have been synthesized. They have small, temperature-independent paramagnetism similar to that of known chain polymer (Ag-F)ₙ⁺ salts. The crystal structure of AgW₂O₂F₉ has been solved. Crystals of AgFW₂O₂F₉ and "AgFWOF₅BF₃" have been obtained.

The pseudo-trifluorides (AgF₂)₃MF₆ (M = As, Au, Sb, Pt) have been prepared and the crystal structure of (AgF₂)₃AsF₆ has been solved. These pseudo-trifluorides are isostructural. They are a new type of AgF⁺ salt, with a formulation of (AgF⁺)₂AgF₄⁻MF₆⁻.
To my wife, Lindsay,

A rose is a rose
more than a rose
in a lover’s hands
in the beloved’s eyes
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xx
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Chapter 1

General Introduction

1.1. General Introduction

This thesis has two parts. The first part, Chapter 2 through Chapter 6, deals with the preparations and characterizations of lamellar materials based on the graphite-like network. The second part, Chapter 7 to Chapter 10, deals with high oxidation state inorganic fluorine chemistry. Each chapter is written and organized as independent of the other chapters.

Chapters 2 and 3 describe the syntheses of nitrogen-containing and boron-containing graphites using low temperature synthetic routes, and their characterizations using various techniques. Chapter 4 describes a simplified liquid phase synthesis of lithium-graphite intercalation compounds and the attempts to synthesize a mixed conductor, $C_x^+Li_2N^-$. Chapter 5 describes the preparation of a new first stage K-NH$_3$-graphite intercalation compound, as well as the study of its structure and conductivity. Chapter 6 provides a transition to the second part of the thesis. A powerful oxidizer S$_2$O$_6$F$_2$ was used to prepare a BN intercalation compound, (BN)$_3$SO$_3$F. Its stability and conductivity are discussed.

In Chapter 7, the enhanced oxidizing power of fluorine in the presence of a Lewis acid is investigated. The mechanistic and thermodynamic aspects of these Lewis acid-assisted oxidations are discussed. Chapter 8 focuses on some of the oxidation chemistry of O$_2^+$ and Ag$^{2+}$. Their utility as powerful oxidizers in preparing other high oxidation state fluorine compounds is discussed. And the oxidizing power of solvated Ag$^{2+}$ in AHF is evaluated thermodynamically.
Chapter 9 describes the syntheses and characterizations of two new AgF+ salts containing complex oxyfluorotungstates as the counter anions. In Chapter 10, the syntheses and structural determinations of a new class of Ag compounds, pseudotrifluoride \((AgF_2)_3MF_6\), are discussed.

In the appendix, new simple two-dimensional and three dimensional mnemonic diagrams for thermodynamic relationships are presented and the rationale behind these mnemonic diagrams is discussed.

1.2. General experimental

1.2.1. Vacuum lines and reactors

Vacuum lines were constructed with 1/4" o.d. stainless steel tubing, connected by cross or Tee Swagelok unions and SS-1KS4 Whitey valves (Oakland Valve and Fitting, Concord, CA). An Acco-Helicoid gauge (Con Val, Fremont, CA) with a range of 0 - 1500 torr \(\pm 0.25\%) was fixed to the vacuum line to monitor pressures. A Varian 801 thermocouple gauge was used for vacuum measurement in the range of 0 - 2000 mtorr. The volume of the vacuum line was calibrated with a known volume so that quantities of gases could be measured tensimetrically. The vacuum line was connected to a mechanical pump through a glass cold trap cooled to \(-196^\circ\)C. Fluorine or other reactive volatiles were evacuated through a scrubber of disposable soda-lime.

The reaction vessels used in the fluorine chemistry were usually constructed of 3/8" or 1/2" FEP tubing, Teflon tees, and Teflon valves with Kel-F stems. Since FEP tubing is somewhat porous, small molecules may permeate through the wall slowly. Therefore, when HF was not involved in the reactions, preference was given to vessels of Pyrex glass. Each consisted of a Pyrex tube joined to a J. Young glass valve with Teflon O-rings. A separate Teflon line
attached to the vacuum manifold was used for carrying out reactions. This was to avoid contact between reactive volatiles, especially fluoroacids such as AsF$_5$ in HF, and the metals of the vacuum system since metals react rapidly with such a mixture. The Teflon line consisted of 1/4'' FEP tubing, Teflon tees, and Teflon valves. The reactors were connected to the Teflon line via 1/4'' S-shaped FEP tubing. This S-shaped connection not only provided a great deal of flexibility in manipulating the reactor but also was useful in preventing any solid foreign substance from falling into the reactor. The reactors and the Teflon line were always passivated with F$_2$ before reactions.

For reactions involving fluorine at elevated temperatures, for pressures between 5 and 20 atm, Monel cans (100 or 250 ml) fitted with SS-1KS4 Whitey valves were used. A sand bath controlled by a Eurotherm 808 temperature controller was used for heating.

1.2.1.1. Dry-box

Air-sensitive materials were stored and manipulated in a Vacuum Atmospheres Corp. DRILAB (North Hollywood, CA) filled with a dry argon atmosphere. The DRILAB was regenerated routinely (usually every four weeks) and the atmosphere inside was monitored by a small incandescent light bulb with a hole in it. The light bulb usually lasted for about a week when the argon atmosphere was dry.

1.2.2. Reagents

Anhydrous HF (AHF) was often used as a solvent in the fluorine chemistry. AHF 98% (Matheson, Newark, CA) was usually dried over K$_2$NiF$_6$
(Ozark-Mahoning-Pennwalt, Tulsa, OK). $K_2NiF_6$ oxidizes water to ozone which was removed by successive "freeze-pump-thaw" cycles.

The following reagent gases were commonly used. $F_2$ (Matheson, Newark, CA) was used as received. $BF_3$ (Matheson, Newark, CA) and $AsF_5$ (Ozark-Mahoning-Penwalt, Tulsa, OK) were checked by IR spectroscopy, and when found to be free of major volatile impurities, were used as received. When $AsF_5$ was used in glass reactors, it was sometimes passed through a column of NaF to ensure that it would be free of HF.

1.2.3. Characterization

1.2.3.1. X-ray powder diffraction

Debye-Scherrer photographs were obtained on an Enraf-Nonius 590 X-ray generator using a General Electric Precision Powder camera (45 cm circumference, Straumanis loading) using Ni filtered Cu K$\alpha$ radiation. Powder samples were loaded into 0.3 or 0.5 mm glass or quartz capillaries (Charles Supper Co., Natick, MA). Quartz capillaries were used for all fluorine compounds. Air-sensitive materials were loaded into the capillaries inside the DRILAB and the openings of the capillaries were plugged with degassed Kel-F grease (Halocarbon Product Corp, SC). The capillaries were finally drawn down and sealed with a microflame.

Indexing of X-ray powder data was usually tried with the help of spreadsheet programs such as Microsoft Excel for Windows, and refinement was done with Excel when the structure was successfully indexed.

1.2.3.2. Vibrational spectroscopy
IR spectra were obtained on a Nicolet 5DX FTIR spectrometer at a resolution of 2 cm⁻¹. Gaseous samples were collected in a Pyrex gas cell (path length = 10 cm) with either KBr or AgCl windows. In fluorine chemistry, a Monel gas cell with AgCl windows was employed. The pressures of sample collected were usually between 5 and 100 torr.

Raman spectra were typically collected using one of the lines of a Coherent I-200 Argon ion laser for excitation. The light was focused into the sample in 0.5 mm sealed quartz capillaries and the scattered light was analyzed using a Spex 1805 triple monochromator and a liquid nitrogen-cooled CCD detector from Photometrics. Typical system resolution was less than 4 cm⁻¹.

1.2.3.3. Magnetic measurements

Variable temperature magnetic susceptibility measurements were carried out on SQUID magnetometers (S.H.E. Corp and Quantum Dynamics). The sample containers consisted of two Kel-F capped cylinders, one fitting snugly inside the other. Several discs of radius equal to that of the larger cylinders were cut from a Teflon sheet and placed on the bottom of that cylinder to serve as a gasket. The sample container and a Kel-F packing plunger were passivated with F₂ prior to use. A known quantity of material was packed into the smaller Kel-F cylinder inside the DRILAB using the packing plunger. A small amount of degassed Kel-F grease was applied to the outside of the smaller cylinder. The two cylinders were then pressed together, sealed by the Kel-F grease. Measurements were made at 5 and 40 kG in the temperature range of 6 K to 280 K.
Chapter 2

Synthesis and Characterization of Nitrogen-containing Graphite

2.1. Introduction

Graphite is the most stable form of carbon. It has a characteristic layered structure as a consequence of the trigonally coordinated carbon atoms forming sheets that are held together by van der Waals forces. The carbon valence $p$ orbitals perpendicular to these sheets ($P_z$ orbitals) form the frontier orbitals of the graphite. These are of $\pi$ symmetry, the bonding orbitals constituting the valence band (VB) and the antibonding orbitals the conduction band (CB). In ordered hexagonal graphite (ABAB... ordering) half of the carbon atoms of a sheet are eclipsed by atoms in neighboring sheets, and this provides for a very weak bonding interaction between the sheets, which is also manifested in a very slight overlap of the upper VB with the lowest part of CB ($E_g = -0.04V$ band gap). The free carrier concentration is approximately $10^{-4}$ per atm at room temperature, which leads to the semi-metallic character of graphite.

Using the terminology of semiconductor doping, it is anticipated that if more electron-rich species are substituted for some of the carbon atoms in a sheet, the population of electrons in the conduction band would increase to provide an $n$ type material. On the other hand, if electron-deficient species are introduced for substitution, holes would be created in the valence band to generate $p$ type materials. In addition, if extensive substitution (by one or the other of these species) occurs the number of carriers would increase in proportion, as long as the band structures is not altered. In that case increased metallic character over that of graphite would be expected.
Doping of graphite by substitution of carbon atoms has been reviewed by Marinkovic and Hirai. Most previous attempts at doping graphite used either high-temperature chemical vapor co-deposition or physical vapor deposition in which the types and doses of dopants were strictly limited. Earlier researchers found that nitrogen substitution in graphites occurred only to a small degree when carried out at high temperatures (in excess of 2000 K).

In this experimental work, low-temperature synthetic routes have been devised to yield material which may be thermodynamically unstable. These materials are BC$_3$, BC$_2$N, C$_x$N$_5$, and PC$_x$. The principle of this low-temperature route is illustrated by the following two reactions:

\[
\text{CH}_4 \rightarrow \text{C}_{\text{gr}} + 2\text{H}_2 \hspace{1cm} (1) \\
\Delta G^o = +12.13 \text{ kcal/mol graphite}
\]

\[
\text{C}_6\text{H}_6 + 3\text{Cl}_2 \rightarrow 6\text{C}_{\text{gr}} + 6\text{HCl} \hspace{1cm} (2) \\
\Delta G^o = -27.92 \text{ kcal/mol graphite}
\]

Reaction 1 is the pyrolysis of methane, often used in high-temperature chemical vapor deposition of graphite. The standard free energy is quite unfavorable and a very high reaction temperature is required for the reaction to take place. Then the breaking of the C-H bond to make the less favorable H-H bonds is assisted by entropy. In reaction 2, the chlorine-assisted dehydrogenation of benzene is employed. The elimination of the thermodynamically very stable molecule HCl contributes to the very favorable standard free energy and the reaction temperature can be much lower. Additionally, the carbon is already in the
aromatic sp2 hybridized form. Thus graphite can be made at moderate temperatures, as can highly doped graphite.

BC3, a metallic material, is synthesized via the interaction of BCl3 and benzene (also see Chapter 3); and BC2N, a semiconductor, is synthesized via the interaction of BCl3 and CH3CN. In both reactions, the thermodynamically stable molecule HCl is eliminated. These novel graphite-like materials have unique physical and chemical properties and could have potential applications in batteries, photo energy conversion and microelectronics.

For the electron-rich substituents, the most likely candidate to substitute for carbon in the sheets is the next neighbor nitrogen since, in its sp2 hybridized form, it exhibits comparably good π orbital overlap with carbon as exemplified by the aromatic carbon-nitrogen heterocycles such as pyridine. A single nitrogen atom can contribute one more electron to the π system than a carbon atom. Because of the relatively high thermodynamic stability and large entropy terms for species such as (CN)2 and N2, low reaction temperatures were judged to be essential for minimizing the elimination of such species. The starting materials, pyridine and chlorine, were chosen in order to meet these requirements. Pyridine was chosen because it already contains a nitrogen in an aromatic sp2 hybridized form. Both enthalpy and entropy help to drive this reaction since small, thermodynamically very stable HCl molecules are liberated. The ideal reaction is then:

\[ C_5H_5N(g) + \frac{5}{2}Cl_2(g) \rightarrow C_5N + 5 \text{HCl} \]  

(3)

The reaction products have been characterized by elemental analysis, X-ray powder diffraction, X-ray photoelectron spectroscopy (XPS), Electron energy
loss spectrometry (EELS), density, and conductivity measurements. The chemical vapor deposition process was also followed by IR spectroscopy.

Work on phosphorus-containing graphite, PC\textsubscript{X}, will also be discussed briefly.

2.2. Experimental:

2.2.1. Chemical vapor deposition (CVD)

Novel graphites in this work have been grown with a chemical vapor deposition technique. A schematic of the CVD apparatus is shown in Figure 2.1. The validity of reaction (3) was investigated in the temperature range of 680-1000 °C. Because of its good thermal conductivity, helium was used as a carrier gas. The flow rates through each reagent bubbler were accurately controlled using a Brooks model 5878 mass flow control system. The reagent supplies were used in liquid form and appropriate slush baths were used to regulate their temperatures and therefore their vapor pressures. The combination of vapor pressure and helium flow rate determined how much of each reactant would be carried into the hot reaction zone of the oven at any given time. Typical working conditions involved gas vapor pressures and flow rates on the order of 4 Torr and 20 sccm, respectively. The pyridine (Fisher Scientific P368-500) was dried with molecular sieves(4A) then distilled in the presence of anhydrous CaCl\textsubscript{2}. The chlorine was used as purchased (Matheson Gas Products, research grade-99.96% purity). Reaction conditions were chosen such that chlorine in the reaction zone was present in approximately a two-fold excess of that required for equation (3).

The entire apparatus was thoroughly dried by baking the quartz reactor at 150 °C in a vacuum prior to reaction. The entire apparatus was then pumped
down to a vacuum of 10⁻³ torr before beginning each reaction. Several quartz substrates (approximately 1.7x0.7x0.1 cm) were placed in the center of the reaction tube in order to obtain good thin film samples for conductivity and XPS analyses. (The glassy nature of the quartz substrate was not expected to assist in single crystal growth but suitably inert single crystal substrates were not available). Materials scraped from the reactor wall were used for the analytical, density, and diffraction measurements.

2.2.2. Study of the CVD process by gas phase IR spectroscopy

By coupling an IR gas cell (KBr window, 10 cm path length) to the exit of the CVD apparatus, IR spectroscopy was used to identify gaseous byproducts of the reaction and the gaseous species in the hot zone.

The extent of self-decomposition of pyridine was examined through the reaction temperature range by examining the gaseous species produced by flowing pyridine (with helium but without chlorine) through the hot zone of the reactor. The gas phase IR spectroscopy was also used to study the interaction of pyridine and chlorine at various reaction temperatures. A similar IR study was performed to check the extent to which the amount of chlorine dictates the concentrations of reaction byproducts in the reaction. At 946°C where pyridine is extensively pyrolyzed, both reactants were flowed through the reaction zone and an IR spectrum was taken of their resulting gaseous products. The amount of chlorine was varied from much less to much more than the corresponding pyridine concentration as required by equation (3).

2.2.3. Density measurement
The densities of the CₓN materials were measured using a floatation method. A small amount of powdered sample was suspended in a mixture of chloroform and bromoform. A known amount of the resulting solution was then weighed and a density for the solution and correspondingly the suspended product, was obtained. As a control experiment, the density of SP-1 graphite was measured using this method. The obtained value, 2.28 g/cm³, compares very well with the known density of graphite, 2.27 g/cm³.

2.3. Results and discussion

2.3.1. Nitrogen-containing graphite

The deposits formed on the substrates and quartz reactor wall are black, and have a smooth, mirror-like, metallic appearance. When the deposits from the wall are removed and ground with a mortar and pestle, a finely divided black graphitic-looking powder results.

2.3.1.1. Compositions

The compositions of the CₓN materials were determined by elemental analysis and the data are given in Table 2.1. The analyses also show small amounts of H and Cl present. These may be due to trapped HCI within the microcrystalline lattice or possibly to unreacted sites in the material or at the crystallite edges. It should be noted that the uncertainty on the hydrogen content is high due to its low atomic weight. Figure 2.2 shows that the percentage of nitrogen in the samples depends strongly on the reaction temperature. This dependence of atomic percent nitrogen versus reaction temperature is nearly linear. The limiting composition of C₅N occurs at 680 °C and drops to C₁₃.₅N at 986 °C.
Table 2.1. The Composition of the CₓN materials (in ratio to nitrogen)

<table>
<thead>
<tr>
<th>RXN TEMP (°C)</th>
<th>CARBON</th>
<th>NITROGEN</th>
<th>HYDROGEN</th>
<th>CHLORINE</th>
</tr>
</thead>
<tbody>
<tr>
<td>680</td>
<td>4.92</td>
<td>1.0</td>
<td>0.98</td>
<td>0.17</td>
</tr>
<tr>
<td>731</td>
<td>5.62</td>
<td>1.0</td>
<td>0.65</td>
<td>0.23</td>
</tr>
<tr>
<td>773</td>
<td>6.68</td>
<td>1.0</td>
<td>0.31</td>
<td>0.19</td>
</tr>
<tr>
<td>832</td>
<td>7.12</td>
<td>1.0</td>
<td>0.33</td>
<td>0.14</td>
</tr>
<tr>
<td>868</td>
<td>9.72</td>
<td>1.0</td>
<td>0.49</td>
<td>0.15</td>
</tr>
<tr>
<td>946</td>
<td>14.4</td>
<td>1.0</td>
<td>1.30</td>
<td>0.09</td>
</tr>
<tr>
<td>986</td>
<td>13.46</td>
<td>1.0</td>
<td>0.78</td>
<td>0.02</td>
</tr>
</tbody>
</table>

2.3.1.2. Gas phase IR study of the self decomposition of CₓHₓN and the interaction of CₓHₓN and Cl₂

To understand how the carbon-nitrogen system loses nitrogen with increasing reaction temperature, gas phase IR spectroscopy was used to examine the gaseous byproducts at the hot-zone exit.

The IR spectra of the self-decomposition of pyridine are shown in Figure 2.3. No detectable decomposition of pyridine was observed at 680 °C. It is noted that the composition of the CₓN material is close to a stoichiometric C₅N at this temperature. No significant decomposition could be seen until the reaction temperature was raised to 832 °C, when a significant amount of HCN was observed. When the reaction temperature was raised to 986 °C, most of the pyridine was decomposed into small fragments such as HCN and there was also a deposit on the reactor wall resembling carbon black.

The IR spectrum taken of the chlorination reaction at 680 °C does not show the presence of pyridine (see Figure 2.4). The P and R branches of the gaseous product HCl are very pronounced in the spectrum. Evidently all pyridine was consumed, at that temperature, in the reaction. The P and R
branches of the cyanogen molecule, \((\text{CN})_2\), can be just detected\(^6\) at 680 °C, though it is not yet very significant. Evidently, already at this point \((\text{CN})_2\) elimination is contributing to reaction efficiency if not to nitrogen deficiency in this solid product. At reaction temperatures higher than 680 °C, linear molecules, such as diatomic HCl, triatomic HCN and CICN\(^6\), and tetra-atomic \((\text{CN})_2\) are all present in the spectra (see Figure 2.4). Above 680 °C the reaction should therefore be generalized as follows:

\[
\text{C}_5\text{H}_5\text{N}(g) + \text{Cl}_2(g) \rightarrow \text{C}_x\text{N}(s) + \text{HCl}(g) + \text{X-CN}(g) \\
X = \text{H, Cl, NC}
\]

With increasing \(\text{Cl}_2\) concentration in the gas mixture, the HCN signal was depressed, and finally nearly disappeared, whereas the CICN signal became more and more pronounced (see Figure 2.5). In addition, part of the cyanogen was converted to CICN and HCl. This phenomenon can be accounted for by reactions 5 - 8 in the gas phase. \((\text{CN})_2\) is also produced in reaction 6 and reaction 7.

\[
\text{HCN} + \text{Cl}_2 \rightarrow \text{CICN} + \text{HCl} \\
\text{CICN} + \text{HCN} \rightarrow (\text{CN})_2 + \text{HCl} \\
2\text{HCN} + \text{Cl}_2 \rightarrow (\text{CN})_2 + 2\text{HCl} \\
(\text{CN})_2 + \text{Cl}_2 \rightarrow 2 \text{CICN}
\]
2.3.1.3. X-ray powder diffraction

The carbon containing products synthesized at lower temperature appear to be without much long range order since the X-ray diffraction patterns usually consisted of very broad halos. The patterns became more graphite-like (although of very small particle size) with the increasing reaction temperature, perhaps as a consequence of the loss of nitrogen from the matrix. X-ray powder diffraction patterns usually contained only a few broad lines. Comparison of the X-ray powder diffraction with the graphite pattern indicates that the strongest observed lines could be indexed as (001) and (100) with a hexagonal symmetry. The interlayer spacings ($d_c$) and the $a$ parameters are given in Table 2.2. There are changes in apparent interlayer spacing (from 3.52 to 3.43 Å) as the reaction temperature increases or the amount of nitrogen substitution decreases. Because of the sharpening of the lines in the higher temperature products their parameters are more precise. The differences as a function of temperature could be significant. The values of the interlayer spacings are close to the graphite interlayer spacing of 3.35 Å. The hexagonal $a$ parameter of C$_x$N samples does not change significantly over the temperature range studied. The average $a$ parameter of 2.40 Å is slightly smaller than the 2.46 Å $a$ parameter of graphite. Since nitrogen has a smaller atomic radius than carbon, substitution of this smaller atom in the sheets could account for the slight contraction seen here. On the other hand, if the extra electron from nitrogen goes into the conduction band which is the antibonding $\pi^*$ system, a small expansion of the $a$ parameter would be expected. However, it is possible that some or all nitrogen atoms are in pyramidal positions, $\begin{array}{c} C \end{array}$N, projecting out of the sheet rather than in a
planar, trigonal configuration in the matrix, with the lone pair of nitrogen electrons then not available to π system. This would also result in a contraction in the \( a \) parameter, but would add to the effective thickness of the sheets. These expectations are in accord with the observed parameters. It should be noted that as the reflection lines are very broad due to the microcrystalline nature of the \( C_xN \) materials, there is a high uncertainty on the \( a \) parameters.

The absence of (hkl) reflections indicates a lack of ordering in stacking sequence along the c-axis, i.e. these \( C_xN \) samples are turbostratic, while the stacking in graphite is ordered in an ABAB... type stacking sequence.

Table 2.2. Interlayer spacing (\( l_c \)) and \( a \) parameter and density of the \( C_xN \) materials

<table>
<thead>
<tr>
<th>RXN TEMP ('C)</th>
<th>( l_c ) (Å)</th>
<th>( a ) (Å)</th>
<th>density (g/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>680</td>
<td>- - -</td>
<td>- - -</td>
<td>2.1</td>
</tr>
<tr>
<td>731</td>
<td>- - -</td>
<td>- - -</td>
<td>2</td>
</tr>
<tr>
<td>773</td>
<td>- - -</td>
<td>- - -</td>
<td>2.01</td>
</tr>
<tr>
<td>832</td>
<td>3.52</td>
<td>2.40</td>
<td>2</td>
</tr>
<tr>
<td>868</td>
<td>3.52</td>
<td>2.41</td>
<td>1.97</td>
</tr>
<tr>
<td>946</td>
<td>3.46</td>
<td>2.39</td>
<td>1.95</td>
</tr>
<tr>
<td>986</td>
<td>3.43</td>
<td>2.41</td>
<td>1.93</td>
</tr>
</tbody>
</table>

2.3.1.4. Density

The densities of the \( C_xN \) materials are in the range of 1.93 - 2.10 g/cm\(^3\) (see Table 2.2). For comparison, the density of single crystal graphite is 2.27 g/cm\(^3\), and the densities of pyrolytic graphite are usually in the range of 1.6 to 1.9 g/cm\(^3\).
The densities of the CₓN materials decrease slightly with increasing reaction temperature. There are two major competing factors influencing the density. On one hand, CₓN has less nitrogen with increasing reaction temperature and this by itself would lower the density, on the other hand, the interlayer spacing decreases with the increasing reaction temperature and this alone would cause the material to be more dense.

2.3.1.5. Sheet resistivity

The sheet resistivity of CₓN thin films, which is the specific resistivity divided by the thickness of the thin film, has been measured by a four-point probe method. The sheet resistivity is plotted versus nitrogen content in CₓN and also versus the reaction temperature (see Figure 2.6 (a) (b)). Though there is a scattering of data due to some variation in thickness in each sample, the trend can still be easily seen: the sheet resistivity decreases with the increasing reaction temperature or the improved crystallinity, and decreases as the nitrogen content decreases. The thickness of the thin films was estimated to be approximately 1 micron.

In graphite, the free charge carrier concentration is only ~10⁻⁴ per carbon atom. It is the extremely high mobility of the free charge carriers which gives graphite a relatively high conductivity. In the CₓN material, as pointed out before, the nitrogen atom might be in a pyramidal position, projecting out of the sheet. Therefore nitrogen atoms and as well as the boundaries of small microcrystallites could be the scattering centers which decrease the mobility of free charge carriers. With less nitrogen and improved crystallinity, it is expected that the mobility of free charge carriers goes up, leading to higher conductivity or lower sheet resistivity.
2.3.1.6. X-ray Photoelectron Spectroscopy (XPS) and Electron Energy Loss Spectrometry (EELS)

The surface composition of the CₓN thin films was studied by X-ray Photoelectron Spectroscopy (XPS) on a Perkin-Elmer PHI-5300 ESCA system equipped with an Apollo Domain 3500 workstation for data acquisition and analysis. The thin films were transferred from the DRILAB to the ESCA system with a special sample transfer chamber in order to prevent the exposure of the thin film to air. The XPS spectra were analyzed by curve-fitting with mixed Gaussian-Lorentzian functions. The binding energies of C-1s and N-1s photoelectrons are listed in Table 2.3 and the XPS spectra of the CₓN samples synthesized at 680 °C and 868 °C are shown in Figure 2.7 (a) (b).

The principal C-1s peaks at 284.6 - 285 eV are similar to the C-1s peak, 284.5 eV, of graphite. Secondary peaks are fitted at 285.6 - 285.8 eV to account for the broadening and the asymmetry of the principal C-1s peak. The C-1s peak positions of the principal peak and the secondary peak are shifted slightly to the higher binding energy compared to the C-1s peak in graphite. This is probably due to the presence of the more electronegative nitrogen in the material. The peaks at 288.2 - 288.7 eV usually account for approximately 15.4% of carbon in the CₓN 986 °C to 22.1% in the CₓN 686, and it is possible that these peaks are associated with the carbon atoms directly bonded to the nitrogen atoms.

The primary asymmetric N-1s peaks centered at around 401 eV compare well with the N-1s peak in hexagonal boron nitride. They can be assigned to nitrogen in the sp² hybridization. Secondary peaks are fitted at about 402 eV to account for the broadening and the asymmetry of the primary N-1s peaks.
Interestingly, there is another smaller but definite peak centered at 398.3 - 398.4 eV, accounting for about 21.9 to 24.5% of the nitrogen signal in all the samples. Compared to the N-1s peak positions in different environments (Table 2.4), it may be assigned to pyridine-like nitrogen, \( \text{CN}= \), i.e. nitrogen coordinated to only two carbons (e.g. at a sheet or particle edge). This can account partly for the microcrystalline nature of the \( \text{C}_x\text{N} \) material; crystal growth will be promptly terminated at the site of pyridine-like nitrogen since the coordination around the pyridine-like nitrogen is already saturated. It should also be noted that the overall features of the N-1s region are very similar among the \( \text{C}_x\text{N} \) materials prepared at different temperatures.

XPS also shows that nearly all the chlorine present in the \( \text{C}_x\text{N} \) samples synthesized at 680 °C and 868 °C is covalently bonded (Cl-2p\( _{1/2} \) peak at 201 eV). In the sample synthesized at 986 °C, most of the chlorine is present in the covalent form but some occurs as an anion Cl\( ^- \) (Cl-2p\( _{1/2} \) peak at 199 eV). Any covalently bonded chlorine must also terminate sheet extension at that point.

**Table 2.3.** C-1s and N-1s peaks from XPS data for the C/N thin films

<table>
<thead>
<tr>
<th>Rxn Temperature</th>
<th>C-1s 680 °C</th>
<th>C-1s 868 °C</th>
<th>C-1s 986 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.E. (eV)</td>
<td>284.8</td>
<td>284.9</td>
<td>284.6</td>
</tr>
<tr>
<td>Area (%)</td>
<td>37.0</td>
<td>41.0</td>
<td>52.6</td>
</tr>
<tr>
<td>B.E. (eV)</td>
<td>285.7</td>
<td>285.8</td>
<td>285.6</td>
</tr>
<tr>
<td>Area (%)</td>
<td>40.9</td>
<td>38.8</td>
<td>32.0</td>
</tr>
<tr>
<td>B.E. (eV)</td>
<td>288.2</td>
<td>288.6</td>
<td>288.7</td>
</tr>
<tr>
<td>Compounds</td>
<td>B.E. (eV)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------------</td>
<td>-----------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_5H_5N</td>
<td>398.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_6H_5)NH_2</td>
<td>399.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_6H_5)CN</td>
<td>399</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_4H_12)NH_2</td>
<td>398.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_6H_5)N=N(C_6H_5)</td>
<td>399.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Me_4N^+Cl^-</td>
<td>402.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EtNH_3^+Cl^-</td>
<td>401</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Me_3NO</td>
<td>402.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.4. N-1s peaks in different environments\(^7\)
The EELS experiment was performed on a JEOL 200CX analytical electron microscope operating at an accelerating voltage of 120 kV and fitted with a Gatan 607 magnetic sector energy loss spectrometer. Specimens for electron microscopy were prepared by floating powder samples onto holey carbon grids. EELS data were collected on the $C_XN$ sample synthesized at 680 °C which has a composition close to $C_5N$ as determined by the elemental analysis. The spectra of carbon and nitrogen K-edges are shown in Figure 2.8. The K-edges of both carbon and nitrogen show prominent graphite-like features corresponding to the antibonding $\pi^*$ and $\sigma^*$ states in the conduction band. The $\pi^*$ and $\sigma^*$ positions of carbon are 286.7 eV and 295 eV, respectively. And the $\pi^*$ and $\sigma^*$ positions of nitrogen are 401.4 eV and 407.5 eV, respectively. This provides strong evidence that carbon and nitrogen atoms, at least the majority of them, are in sp$^2$ hybridization and have planar-trigonal coordination in a graphite-like network. The $\pi^*$ position of nitrogen agrees with the assignment of the XPS peaks at around 400.0 - 402.2 eV to sp$^2$ hybridized nitrogen atoms. The EELS data of this $C_XN$ sample are also tabulated with the other related materials in Chapter 3 Table 3.5. From the EELS data, the composition was estimated to be $C_{6.0\pm0.7}N$, in rough agreement with the elemental analysis.

2.3.2. Phosphorus-containing graphite

In Marinkovic's work$^9,^{10}$, a high-temperature pyrolysis of methane plus reduction of $PCl_3$ was used (reaction 9). Thermodynamics evaluation indicates that the reaction temperature has to be above 1200 °C to reduce $PCl_3$ to
elemental P by hydrogen. It was found that the maximum content of phosphorus was only \( \sim 2 \text{ at.\%} \), and some of that phosphorus was present as second phase particles of red phosphorus rather than substitution of carbon atoms.

\[
\text{CH}_4 + \text{PCl}_3 (\text{H}_2) \rightarrow \text{PC}_x (\text{P}) + \text{H}_2 + \text{HCl} \quad (9)
\]

In our experiment, PC_x has been synthesized via interaction of PCl_3 and benzene with the elimination of the thermodynamically stable molecule HCl (reaction 10). In the range of reaction temperature from 730 to 950 °C, the phosphorus content ranges from approximately 10.6 atomic percent to about 4.6 atomic percent. Figure 2.9 shows that the phosphorus content depends strongly on the reaction temperature (Marinkovic's result is included for comparison). Red and white phosphorus are observed outside the hot reaction zone. This phosphorus-containing graphite was not very crystalline although the crystallinity improved with increasing temperature. All experiments showed that phosphorus tends to separate as an elemental second phase. No doubt as a consequence of its large atomic size phosphorus substitution for carbon does not appear to be extensive.

\[
\text{C}_6\text{H}_6 + 2\text{PCl}_3 \rightarrow 6\text{CP}_x + 6\text{HCl} + y\text{P}_4 \quad (10)
\]

2.4. Conclusions

The nitrogen-containing graphites, C_xN, have been prepared using a low-temperature synthetic route with pyridine and chlorine as precursors. The nitrogen content in these C_xN materials can approach the theoretical value of C_5N at 682 °C but falls to C_{14}N at 980 °C. The loss of nitrogen at high
temperatures is attributable to the formation of stable small molecules such as HCN, (CN)\textsubscript{2}.

Unfortunately, these C\textsubscript{x}N materials are very poor in crystallinity, which limits the utility of many conventional techniques and makes it difficult to draw unambiguous conclusions. This poor crystallinity could be due to some of the nitrogen atoms being in pyridine-like form which would limit the graphite network development. Some other N atoms could be in pyramidal coordination which would also disrupt the sheet-like structure. However, the EELS shows that the majority of the N atoms appear to in a π-bonded graphite network.

EELS and X-ray diffraction convincingly demonstrate the overall graphite nature of these C\textsubscript{x}N materials. Both carbon and nitrogen regions in the EELS spectrum display prominent K-edge features corresponding to π* and σ* states in the conduction band. These K-edge features indicate that carbon and nitrogen are sp\textsuperscript{2} hybridized and they occupy planar-trigonal sites in a graphite-like network. X-ray powder diffraction data also supported the graphitic nature of these C\textsubscript{x}N materials. Unfortunately, a very useful technique, high energy electron transmission electron microscopy, was not readily available to this study. The high energy electron diffraction is more sensitive to the short range ordering due to its very short wavelength. High resolution imaging in combination with EELS will be very useful in characterizing the microcrystallites.
2.5. References


Hirai, T., J. Japanese Metalurgy Soc., 1972, 8, 577


Nakamoto, K. Infrared Spectra of Inorganic and Coordination Compounds; Wiley: New York, 1963; Part II.


Marinkovic, S., Suznjevic, C., Tukovic, A., Dezarov, and Cerovic, D., Carbon, 1974, 12, 57.
Figure 2.1. Schematic drawing of the CVD apparatus
Figure 2.2. The composition of the CₓN materials
Figure 2.3. IR study of the self-decomposition of pyridine
Figure 2.4. IR study of the reaction of pyridine and chlorine
Figure 2.5. IR study of the effect of the chlorine concentration
Figure 2.6 (a) The sheet resistivity vs. nitrogen content

Figure 2.6 (b) The sheet resistivity vs. reaction temperature
Figure 2.7 (a) XPS spectra of CₓN thin film deposited at 680°C
Figure 2.7 (b) XPS spectra of C<sub>x</sub>N thin film deposited at 868°C.
Figure 2.8. EELS spectra of the CₓN material deposited at 680 °C: core-loss regions (K-edge) of carbon and nitrogen.
Figure 2.9. The composition of the CₓP materials
Chapter 3

Synthesis and Characterization of Graphite-Like Boron-Carbon Materials

3.1. Introduction

Although planar trigonal coordination of boron occurs in systems such as hexagonal boron nitride (h-BN), borazine and a number of other heterocyclic compounds, an extensive graphite-like network with boron and carbon on the planar trigonal-coordinated sites is not found in nature. Some researchers have reported attempts to dope boron into the carbon matrix of graphite. For example, Lowell\(^1\) reported that the substitution of boron for carbon in graphite is only 2.35 atom % at 2350 °C. Other attempts to dope boron into graphite were extensively reviewed by Marinkovic\(^2\).

In 1986, this laboratory\(^3\) reported the synthesis, by chemical vapor deposition (CVD), of a novel graphite-like boron-carbon (B/C) material that had an approximate stoichiometry of BC\(_3\) via the interaction of benzene and BCI\(_3\) at \(\sim 800 \, ^\circ\)C. The equation below represents the reaction to produce ideal BC\(_3\):

\[
C_6H_6 (g) + BCl_3 (g) \rightarrow 6HCl (g) + 2BC_3 (s) \quad (1)
\]

A structural model proposed for this graphite-like BC\(_3\) material is shown in Figure 3.1. This low-temperature synthetic route was designed to take advantage of the elimination of thermodynamically stable HCl molecules and the favorable entropy term of the reaction.

Since then, theoretical calculations had been carried out by Cohen and his co-workers\(^4,5,6\) and Lee and Kertez\(^7\) on the electronic structure of this novel
material. Cohen and his co-workers showed that graphitic BC$_3$ may have a unique electronic structure different from that of graphite.

With carefully selected or designed precursors, the moderate-temperature synthetic route provides an opportunity to synthesize a range of graphite-like materials possessing unique physical and chemical properties. These materials could have potential applications in batteries, microelectronics, photoenergy conversion, and oxidation-resistant protective coatings. These novel materials also present new challenges in materials characterization. A better understanding on the structures and properties of these materials can only be obtained with a variety of characterization techniques. A detailed discussion on some of those available physical characterization techniques for carbon-related materials is provided in a review paper by Tsai and Bogy.$^8$

The novel aspects of graphite-like B/C, C/N, and B/C/N materials have been briefly discussed in an earlier preliminary report.$^9$ This chapter provides a full report on the preparation and characterization of the graphite-like boron-carbon materials. The synthesis of boron-carbon materials at temperatures between 800 °C and 1000 °C is described. Volatile compounds and products of the CVD process have been identified by gas phase IR spectroscopy. The solid products of boron-carbon materials have been characterized by X-ray powder diffraction, Rutherford Backscattering Spectroscopy (RBS), Transmission Electron Microscopy (TEM) and Electron Energy Loss Spectrometry (EELS), X-ray Photoelectron Spectroscopy (XPS), density and conductivity measurements. The intercalation chemistry of the boron-carbon materials and the reaction of the boron-carbon materials with chlorine will also be discussed.

3.2. Experimental
The preparations of the B/C materials were carried out in a conventional horizontal chemical vapor deposition (CVD) apparatus which consisted of a fused silica tube heated resistively to temperatures between 800 °C and 1000 °C. In all the reactions, BCl₃ (99.9% or 99.995%, Matheson Gas Products) and benzene (Spectrophotometric grade, Fisher Scientific Co.) were used as precursors. The benzene was dried statically over 4 Å molecular sieves and degassed before it was used. Ultra-pure helium (99.999%, Matheson Gas Products) was used as the carrier gas with its flow rates controlled by two electronic mass flow meters. The typical partial vapor pressures used were 4 torr (at -23 °C), 25 torr (at 0 °C), or 90 torr (at 25 °C) for benzene, and approximately 5 torr (at -78 °C) for BCl₃. BCl₃ and benzene were kept separate until each of them had been introduced into the reaction zone by the carrier gas. The delivery rates of the precursors were controlled by both the flow rates of the carrier gas and the partial vapor pressures of the precursors. The flow rate of helium into BCl₃ was 22.0 - 30.0 cm³ min⁻¹. The molar quantity of BCl₃ introduced was at least 2.5 times that of C₆H₆ to keep BCl₃ in excess during the reaction. The system pressure was approximately 800 torr, slightly higher than the atmospheric pressure. The gaseous by-products were collected in a cold trap. The B/C material was allowed to deposit on the inner wall of the fused silica tube for 6 to 72 hours. Thin films of the material were also deposited on to flat, rectangular sections of fused silica, isotropic carbon, highly-oriented pyrolytic graphite (HOPG), or highly-oriented pyrolytic boron nitride (HOPBN) placed in the center of the fused silica tube.

To determine what gaseous species were present in the reactions between BCl₃ and benzene, an evacuated 8-cm short path gas cell fitted with AgCl windows was connected to the exit end of the reaction tube in order to
collect a gaseous sample. During reactions, 50 - 100 torr of the gaseous species present were collected into the gas cell. A Nicolet FTIR spectrometer was used to analyze the gas sample at a resolution of 2 cm⁻¹. A separate study was conducted to observe the thermal stability of benzene. Benzene (at 25 °C) was delivered by helium at the flow rate of 10 cm³ min⁻¹ into the fused silica tube maintained at temperatures between 25 °C and 950 °C and gaseous samples in the tube were collected in the gas cell and were examined by IR spectroscopy.

After each reaction, the B/C material was scraped off the wall of the fused silica tube as flakes or powder with a stainless steel spatula. Since iron was sometimes introduced into the collected powder through hard scraping with the steel spatula, the powder was washed with concentrated HCl and then rinsed with distilled water. A yellowish gelatinous organic substance resulting from incomplete reaction of the precursors was usually found at both ends of the fused silica tube and this substance sometimes would contaminate the B/C flakes or powder as they were removed from the fused silica tube. The contaminant was removed by washing the flakes or powder with acetone and methanol. The substrates coated with the boron-carbon thin films were retrieved either in a glove bag filled with dry nitrogen or in the dry box. The thin films were stored in closed containers in the dry box to minimize surface contamination.

The TEM and EELS experiments on a sample of B/C material deposited at 830 °C was performed on a JEOL 200CX analytical electron microscope operating at an accelerating voltage of 120 kV and fitted with a Gatan 607 magnetic sector energy loss spectrometer. Specimens for electron microscopy were prepared by floating powder sample onto holey carbon grids.

The bulk composition of some B/C thin films was determined by Rutherford Backscattering Spectrometry (RBS). The RBS measurements were
carried out with a 2.0 MeV \( ^4\text{He}^+ \) beam generated by a 2.5 MeV Van de Graaff electrostatic accelerator. The backscattered particles were collected by a silicon surface barrier detector positioned at 165° with respect to the beam.

The surface composition of the B/C thin films was studied by X-ray Photoelectron Spectroscopy (XPS) on a Perkin-Elmer PHI-5300 ESCA system equipped with an Apollo Domain 3500 workstation for data acquisition and analysis. The thin films were transferred from the dry box to the ESCA system with a special sample transfer chamber in order to prevent the exposure of the thin film to air. The XPS spectra were analyzed by curve-fitting with mixed Gaussian-Lorentzian functions.

The apparent density of the B/C flakes was determined by a flotation technique developed by Cullis et. al.\(^ {13} \) for porous and void-containing pyrolytic carbons. The density of the matching CHCl\(_3\) and CHBr\(_3\) solution was measured by gravimetry.

The in-plane conductivity of some as-deposited thin films on silica substrates was measured by the four-point probe method\(^ {14} \). A razor blade was used to remove a small strip of the thin film along each edge of the substrate to create an isolated rectangular area for measurement. A Tencor Alpha-Step 100 profilometer was used to determine the thickness of the thin film.

Powder samples or thin films of B/C materials were allowed to react with 400 torr of gaseous chlorine (99.96%, Matheson Gas Products) in a fused silica tube at temperatures between 280 °C - 300 °C. The duration of the reactions was 12 to 48 hours. After cooling the reaction tube to room temperature, 50 to 200 torr of the gaseous species was collected in the IR gas cell fitted with AgCl windows. After evacuation of the reaction tube, it was opened in air to retrieve
the solid samples. The powder samples were studied by X-ray powder
diffraction and the thin films were studied by XPS.

Attempts to intercalate the B/C materials with potassium were performed
using the two-bulb method described by Hérold\textsuperscript{15}. The end of the tube
containing the B/C material was placed at the center of the tube furnace and was
heated at 260 °C for 72 hours. The temperature of the potassium was estimated
to be 20 - 30 °C less than that of the B/C material. After each reaction, the
resulting material was studied by X-ray powder diffraction.

3.3. Results and discussion

3.3.1. Materials preparation

Due to the high reactivity of the hot gaseous reaction by-product HCl, the
number of materials suitable for substrates and reactor construction is limited.
Common substrates such as silicon and sapphire were attacked by HCl at the
reaction temperatures. Therefore, materials such as fused silica, highly oriented
pyrolytic boron nitride (HOPBN), and isotropic carbon were used as substrates.
The as-deposited thin films on smooth substrates all have a metallic black,
mirror-like appearance. The typical thickness of the thin films was under 4 μm
as measured by the profilometer. (Attempts to determine the mass and the
thickness of the thin films by gravimetry were unsuccessful.) Typical growth
rates of the thin films were about 0.1 - 0.2 μm/hour. The growth rate increased
with increasing reaction temperature. For reactions carried out at above 900 °C,
thin films tend to crack or exfoliate. Heating a small amount of boron-carbon
material in vacuum at 1200 °C resulted in partial decomposition of the material.
Therefore, these B/C materials were not annealed after they were deposited in
the reaction system.

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It was also noticed that a section of the inner wall of the fused silica tube at the hot reaction zone was etched during reactions carried out at above 950 °C. The fused silica was probably reduced by the deposited boron-carbon film. Since Jong\(^\text{16}\) has reported that carbon and silica (SiO\(_2\)) react to produce SiC and CO at 900 °C when the partial pressure of CO is below 10\(^{-5}\) atm, and since Jeffes and Alcock\(^\text{17}\) have reported that SiC can react with HCl efficiently between 550 °C and 950 °C, silicon could be transported as chlorosilanes and contaminate the boron-carbon materials. It is possible that these reactions occurred inside the fused silica tube to produce gaseous species containing oxygen or silicon which could be trapped in the deposited film. The sources of the impurities found in these boron-carbon films will be discussed further later.

3.3.2. Study of the CVD process by gas phase IR spectroscopy

The IR spectra collected from reactions between BCl\(_3\) and benzene between 800 °C and 1000 °C had similar features. Prominent absorptions peaks from HCl and unreacted benzene and BCl\(_3\) were observed in all the spectra. A typical IR spectrum of the major absorption peaks is shown in Figure 3.2, and the major peaks observed in the spectrum are listed in Table 3.1. No other gaseous species were detected. Although hydrogen from pyrolysis of benzene would not have been detected, other hydrocarbons would have been observed.

Table 3.1. IR spectrum of the gaseous species from the interaction of BCl\(_3\) and benzene at 910 °C

<table>
<thead>
<tr>
<th>Wavenumbers (cm(^{-1}))</th>
<th>Intensity</th>
<th>Peak Assignment(^\text{18, 19})</th>
<th>Literature Value (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>3100</td>
<td>w</td>
<td>C(<em>6)H(<em>6), \nu</em>{12}^{CH}(E</em>{1u})</td>
<td>3099</td>
</tr>
<tr>
<td>3044</td>
<td>w</td>
<td>C(<em>6)H(<em>6), \nu</em>{13} + \nu</em>{16}(E_{1u})</td>
<td>3045</td>
</tr>
</tbody>
</table>
When only benzene was passed with helium into the reaction tube maintained between 25 °C and 750 °C, only benzene was observed in the gaseous sample by IR spectroscopy (Figure 3.3). However, a trace amount of CH$_4$ (v$_3$ = 3019 cm$^{-1}$ and v$_4$ = 1306 cm$^{-1}$) appeared in the IR spectrum of the gas sample collected at 800 °C. The intensities of these absorptions increased as the temperature of the reaction tube was raised. It was also observed that a black coating of pyrolytic carbon film began to form on the inner wall of the fused silica tube at 800 °C. These observations indicate that benzene had partially pyrolyzed to form smaller hydrocarbon species and pyrolytic carbon film at 800 °C and above. Therefore, when benzene and BCl$_3$ are introduced into the fused silica tube at 800 °C and above, the reaction between BCl$_3$ and benzene must compete with the pyrolysis of benzene to form pyrolytic carbon film as well as with the interaction between BCl$_3$ and the hydrocarbon species from the decomposition of benzene in the hot zone. Consequently, the carbon-to-boron ratio should increase beyond 3:1 as the temperature of the reaction zone increases beyond 800 °C.

3.3.3. Rutherford Backscattering Spectrometry

In determining the compositions of the solid BC$_x$ deposits, the suitability of those more common techniques for composition analysis is greatly affected by these factors: the light elements that compose the materials, the small quantities of the products, the formation of glassy boron oxide during the conventional
combustion analysis, and the lack of appropriate standards for thin film characterization techniques.

Rutherford Backscattering Spectrometry (RBS) has been successfully applied to determine the compositions of these B/C materials. RBS is a non-destructive, relatively simple and accurate mass-sensitive characterization technique with depth profiling capability. The thin films studied by RBS were deposited either on fused silica or on isotropic carbon. In order to avoid any signal interference from the substrate, the thickness of these thin films examined was at least 1 μm. A typical RBS spectrum of thin film of the boron-carbon material is shown in Figure 3.4 and the elemental composition of the films analyzed are tabulated in Table 3.2. The accuracy of the measurement is estimated to be within 10%. As expected, the carbon-to-boron ratio of the graphite-like materials increased as the deposition temperature was raised. The ratio increased from 3.1:1 at 800 °C to 5.6:1 at 1000 °C.

**Table 3.2.** 2.0 MeV $^4\text{He}^+$ RBS analysis of the boron-carbon thin films

<table>
<thead>
<tr>
<th>Deposition Temperature (°C)</th>
<th>Bulk Composition (uncertainty: ± 10%)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>B$1.00C3.08O0.19Cl0.02$</td>
<td>Si accumulated on surface of film.</td>
</tr>
<tr>
<td>830</td>
<td>B$1.00C3.57O0.29Cl0.03$</td>
<td>Si accumulated on surface of film.</td>
</tr>
<tr>
<td>830</td>
<td>B$1.00C3.30O0.02Cl0.02$</td>
<td>Si accumulated on surface of film. Slight non-uniformity of O content in the film.</td>
</tr>
<tr>
<td>900</td>
<td>B$1.00C3.00O0.09Cl0.004$</td>
<td>Si accumulated on surface of film.</td>
</tr>
<tr>
<td>910</td>
<td>B$1.00C4.10O0.05Cl0.005$</td>
<td>Si accumulated on surface of film.</td>
</tr>
<tr>
<td>1000</td>
<td>B$1.0C5.6O0.1$</td>
<td></td>
</tr>
</tbody>
</table>
The RBS spectra clearly indicate the presence of impurities in these thin films. There is silicon contamination of a few atomic layers on both the thin films deposited on the fused silica substrate and the isotropic carbon substrate. This surface contamination by silicon seems to decrease with increasing reaction temperatures. The level of chlorine impurity in the bulk is generally low. The oxygen impurity is also present in the bulk with a certain degree of surface enrichment. It should be mentioned that Auger Electron Spectroscopy (AES) showed that the oxygen concentration diminished shortly after the depth-profiling was initiated. This is probably due to the fast desorption of very electronegative elements such as oxygen during sputtering\textsuperscript{20}.

3.3.4. X-ray powder diffraction measurement

Broad lines appeared on X-ray powder diffraction photographs of the B/C materials. The most intense line with \(d\) values between 3.34 Å - 3.39 Å were observed for each boron-carbon sample. This line corresponds to the interlayer spacing (\(I_C\)) of the B/C material. The \(I_C\)'s are listed in Table 3.3. For comparison, the ideal interlayer spacing in graphite is 3.35 Å. Since this line was more well-defined for samples deposited above 900 °C, the B/C materials must be more crystalline when deposited at higher temperature. For these samples, a line with \(d\) values between 2.11 Å - 2.15 Å was also clearly observed, corresponding to the (100) reflection of turbostratic graphite (2.13 Å). Higher order (00\(l\)) and (\(hk0\)) reflections were sometimes observed. However, no general (\(hkl\)) type reflections were observed in any of the X-ray photographs. These results indicate that these boron-carbon materials have a layered graphitic structure in which the long range order of sheet-to-sheet registry does not exist. The \(a\) parameter of the materials listed in Table 3.3 was calculated assuming a

42
pseudo-hexagonal unit cell. No significant trends in the variation of the lattice parameters with respect to the deposition temperature were found.

Table 3.3. Interlayer spacing (l_c) and calculated a parameter from X-ray powder diffraction patterns of samples of B/C

<table>
<thead>
<tr>
<th>Deposition Temperature (°C)</th>
<th>l_c (Å)</th>
<th>a (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>3.34 ± 0.02</td>
<td>-------</td>
</tr>
<tr>
<td>830</td>
<td>3.37 ± 0.02</td>
<td>-------</td>
</tr>
<tr>
<td>830</td>
<td>3.39 ± 0.02</td>
<td>-------</td>
</tr>
<tr>
<td>830</td>
<td>3.39 ± 0.02</td>
<td>-------</td>
</tr>
<tr>
<td>870</td>
<td>3.36 ± 0.02</td>
<td>-------</td>
</tr>
<tr>
<td>900</td>
<td>3.37 ± 0.02</td>
<td>2.47 ± 0.02</td>
</tr>
<tr>
<td>900</td>
<td>3.37 ± 0.02</td>
<td>2.49 ± 0.02</td>
</tr>
<tr>
<td>910</td>
<td>3.34 ± 0.02</td>
<td>-------</td>
</tr>
<tr>
<td>950</td>
<td>3.38 ± 0.02</td>
<td>2.47 ± 0.02</td>
</tr>
<tr>
<td>950</td>
<td>3.35 ± 0.02</td>
<td>2.46 ± 0.02</td>
</tr>
<tr>
<td>950</td>
<td>3.37 ± 0.02</td>
<td>2.45 ± 0.02</td>
</tr>
<tr>
<td>970</td>
<td>3.36 ± 0.02</td>
<td>2.48 ± 0.02</td>
</tr>
<tr>
<td>990</td>
<td>3.36 ± 0.04</td>
<td>2.48 ± 0.02</td>
</tr>
<tr>
<td>1000</td>
<td>3.38 ± 0.02</td>
<td>2.47 ± 0.02</td>
</tr>
<tr>
<td>1000</td>
<td>3.38 ± 0.02</td>
<td>2.48 ± 0.02</td>
</tr>
<tr>
<td>1000</td>
<td>3.38 ± 0.02</td>
<td>2.48 ± 0.02</td>
</tr>
</tbody>
</table>

3.3.5. Transmission Electron Microscopy (TEM) and Electron Energy Loss Spectrometry (EELS)

While X-ray microanalysis is usually ineffective with low atomic number elements such as boron and carbon, Electron Energy Loss Spectrometry (EELS) is capable of not only distinguishing the low atomic number elements but also providing bonding and structural information.
Electron diffraction patterns of sample of B/C materials showed hexagonal symmetry. Rings of reflections could be indexed as \((hk0)\) reflections. Streak-like \((00l)\) reflections could be obtained by large angle tilt. The diffraction data is presented in Table 3.4. The indicated lattice parameters are \(a = 2.4 \text{ Å}\) and \(c = 3.4 \text{ Å}\). No general \((hkl)\) type reflections were observed. Moreover, superlattice effects could not be observed because the atomic scattering factors for boron and carbon are close for both electron and X-ray diffraction.

**Table 3.4.** Electron Diffraction patterns of a sample of B/C

<table>
<thead>
<tr>
<th>(d(\text{Å}))</th>
<th>(hk0) (rings)</th>
<th>(00l) (streaks)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.09</td>
<td>100</td>
<td>3.32</td>
</tr>
<tr>
<td>1.18</td>
<td>110</td>
<td>1.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.84</td>
</tr>
</tbody>
</table>

\(a = 2.4 \text{ Å}, \quad c = 3.4 \text{ Å}\).

EELS data was collected on the sample of B/C material deposited at 830 \(^\circ\text{C}\). Crystalline Graphite and hexagonal boron nitride were also examined for comparison and the results are shown in Table 3.5. The EELS spectrum of the boron-carbon material, shown in Figure 3.5, exhibits graphite-like features both in the low-loss region and the core-loss edges (K-edges) which indirectly reflect the density of unoccupied states. The K-edges of both carbon and boron show prominent features corresponding to antibonding \(\pi^*\) and \(\sigma^*\) states in the conduction band. This indicates that both boron and carbon have trigonal-planar coordination and occupy the sites in a graphite-like network.
Table 3.5. EELS data of graphite\textsuperscript{9}, h-BN\textsuperscript{9}, diamond\textsuperscript{8}, the B/C material deposited at 830 °C, and the C\textsubscript{x}N material (Chapter 2) deposited at 680 °C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\pi^*) edges (K-edge) (eV)</th>
<th>(\sigma^*) edges (K-edge) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>Graphite</td>
<td>-----</td>
<td>284.0</td>
</tr>
<tr>
<td>h-BN</td>
<td>191.0</td>
<td>-----</td>
</tr>
<tr>
<td>Diamond</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>B/C (830 °C)</td>
<td>190.2</td>
<td>280.0</td>
</tr>
<tr>
<td>C/N (680 °C)</td>
<td>-----</td>
<td>286.7</td>
</tr>
</tbody>
</table>

From the EELS data, the composition of this B/C sample deposited at 830 °C is BC\textsubscript{2.8}. The estimated uncertainty of the measured composition was 5%.

3.3.6. X-ray Photoelectron Spectroscopy (XPS)

XPS data reveal the presence of boron, carbon, oxygen, and very small amounts of silicon and chlorine on the surface of the thin films. The presence of impurities made peak assignments difficult. The binding energies of B-1s and C-1s photoelectrons are listed in Table 3.6 and representative spectra are shown in Figure 3.6.

Table 3.6. B-1s and C-1s peaks from XPS data for the B/C thin films.

<table>
<thead>
<tr>
<th>B-1s</th>
<th>800</th>
<th>830</th>
<th>900</th>
<th>910</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.E. (eV)</td>
<td>191.4</td>
<td>191.1</td>
<td>190.7</td>
<td>191.4</td>
<td>190.6</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>1.4</td>
<td>1.4</td>
<td>2.4</td>
<td>1.5</td>
<td>2.4</td>
</tr>
<tr>
<td>Area (%)</td>
<td>61.2</td>
<td>79.4</td>
<td>28.3</td>
<td>45.0</td>
<td>32.4</td>
</tr>
<tr>
<td>B.E. (eV)</td>
<td>189.2</td>
<td>189.0</td>
<td>188.7</td>
<td>188.6</td>
<td>188.7</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>2.1</td>
<td>1.8</td>
<td>2.1</td>
<td>3.0</td>
<td>1.6</td>
</tr>
<tr>
<td>Area (%)</td>
<td>15.6</td>
<td>10.4</td>
<td>25.8</td>
<td>32.3</td>
<td>26.7</td>
</tr>
</tbody>
</table>
The principal B-1s peaks at 190.4 - 191.4 eV appear to be similar to the B-1s peak of hexagonal boron nitride (190.3 eV)\textsuperscript{21}. These peaks could be assigned to the boron atoms in the B/C materials with the local environment of ideal BC\textsubscript{3}. The peaks at 186.7 - 187.0 eV and at 188.7 - 189.2 eV probably belong to boron bound to one or to two other boron atoms. Is so the data clearly show that such B-B bonding becomes markedly more important at higher temperatures. The small peaks at 192.7 - 193.4 eV are either due to B-O bonds

<table>
<thead>
<tr>
<th></th>
<th>800</th>
<th>830</th>
<th>900</th>
<th>910</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.E. (eV)</td>
<td>187.0</td>
<td>186.9</td>
<td>186.8</td>
<td>186.7</td>
<td>186.9</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>1.8</td>
<td>1.6</td>
<td>1.9</td>
<td>1.4</td>
<td>1.8</td>
</tr>
<tr>
<td>Area (%)</td>
<td>11.4</td>
<td>3.4</td>
<td>27.9</td>
<td>17.1</td>
<td>22.7</td>
</tr>
<tr>
<td>B.E. (eV)</td>
<td>193.3</td>
<td>193.1</td>
<td>193.5</td>
<td>193.0</td>
<td>192.7</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>2.7</td>
<td>1.8</td>
<td>3.2</td>
<td>1.4</td>
<td>2.0</td>
</tr>
<tr>
<td>Area (%)</td>
<td>11.8</td>
<td>6.8</td>
<td>18.0</td>
<td>5.6</td>
<td>18.2</td>
</tr>
</tbody>
</table>

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>B.E. (eV)</td>
<td>284.1</td>
<td>283.9</td>
<td>283.8</td>
<td>283.8</td>
<td>283.9</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>1.7</td>
<td>1.4</td>
</tr>
<tr>
<td>Area (%)</td>
<td>82.2</td>
<td>90.2</td>
<td>47.4</td>
<td>57.5</td>
<td>53.4</td>
</tr>
<tr>
<td>B.E. (eV)</td>
<td>285.6</td>
<td>285.6</td>
<td>285.1</td>
<td>284.5</td>
<td>285.2</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>1.8</td>
<td>1.3</td>
<td>3.0</td>
<td>3.5</td>
<td>2.1</td>
</tr>
<tr>
<td>Area (%)</td>
<td>8.2</td>
<td>2.0</td>
<td>28.8</td>
<td>24.2</td>
<td>22.4</td>
</tr>
<tr>
<td>B.E. (eV)</td>
<td>282.6</td>
<td>282.4</td>
<td>282.6</td>
<td>282.3</td>
<td>282.7</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>1.1</td>
<td>1.2</td>
<td>1.5</td>
<td>1.1</td>
<td>1.5</td>
</tr>
<tr>
<td>Area (%)</td>
<td>5.9</td>
<td>3.8</td>
<td>12.4</td>
<td>6.9</td>
<td>12.2</td>
</tr>
<tr>
<td>B.E. (eV)</td>
<td>290.3</td>
<td>290.2</td>
<td>290.5</td>
<td>289.8</td>
<td>290.2</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>1.8</td>
<td>1.5</td>
<td>3.1</td>
<td>4.7</td>
<td>2.7</td>
</tr>
<tr>
<td>Area (%)</td>
<td>3.7</td>
<td>4.0</td>
<td>6.3</td>
<td>11.4</td>
<td>4.8</td>
</tr>
<tr>
<td>B.E. (eV)</td>
<td>----</td>
<td>----</td>
<td>288.3</td>
<td>----</td>
<td>287.5</td>
</tr>
<tr>
<td>FWHM (eV)</td>
<td>----</td>
<td>----</td>
<td>2.2</td>
<td>----</td>
<td>2.4</td>
</tr>
<tr>
<td>Area (%)</td>
<td>----</td>
<td>----</td>
<td>5.7</td>
<td>----</td>
<td>7.1</td>
</tr>
</tbody>
</table>
formed by boron atoms with oxygen impurity on the surface or to B-Cl bonds from incomplete reaction of BCl₃ with benzene.

The principal C-1s peaks at 283.8 - 284.1 eV appear similar to the C-1s peak of graphite (284.5 eV)²¹. These peaks could be assigned to the carbon atoms in the B/C materials with the local environment of ideal BC₃. Secondary peaks are fitted at 284.5 - 285.6 eV to account for the broadening and the asymmetry of the principal C-1s peak²². The peaks at 282.3 - 282.7 eV probably belong to the carbon atoms in the B/C films with boron-rich local environments. The small C-1s peaks at 287.5 - 290.3 eV are probably associated with the presence of oxygen impurities on the surface of the films.

Cl-2p₁/₂ peaks at approximately 199 eV and 201 eV correspond to chlorine of anionic and covalently-bonded characters respectively²¹. The presence of these two types of chlorine may be due to the incompleteness of reaction and the incorporation of reaction byproduct HCl during film growth. The source of oxygen and silicon impurities is most likely to be due to reaction of the B/C materials with the fused silica tube as previously alluded to. Surface oxidation by molecular oxygen probably also contributed to the presence of oxygen on the surface of the thin films.

3.3.7. Density measurement

Table 3.7 lists the apparent densities of the B/C materials. The apparent densities range from 2.08 g cm⁻³ to 2.24 g cm⁻³. No relationship between the apparent densities and deposition temperature was evident. The B/C flakes are slightly denser than the pyrolytic carbon (~2.00 g cm⁻³) examined by Cullis¹³, but the B/C flakes are less dense than crystalline graphite (2.26 g cm⁻³).

Table 3.7. Apparent Densities of the boron-carbon flakes
<table>
<thead>
<tr>
<th>Deposition Temperature (°C)</th>
<th>Apparent Density (g cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>870</td>
<td>2.17 ± 0.02</td>
</tr>
<tr>
<td>910</td>
<td>2.244 ± 0.006</td>
</tr>
<tr>
<td>950</td>
<td>2.122 ± 0.002</td>
</tr>
<tr>
<td>970</td>
<td>2.081 ± 0.006</td>
</tr>
<tr>
<td>990</td>
<td>2.170 ± 0.006</td>
</tr>
<tr>
<td>1000</td>
<td>2.13 ± 0.01</td>
</tr>
</tbody>
</table>

3.3.8. Conductivity measurement

Since it was difficult to obtain thickness measurements on the thin films deposited at temperatures below 900 °C because these thin films are usually too thin to create a step-like edge for profilometry, and since many of the thin films deposited at temperatures above 900 °C have visible cracks, satisfactory measurements were obtained only for a few thin films. The results of the in-plane conductivity measurements are listed in Table 3.8. The specific in-plane conductivity values of the B/C films are two to three times higher than the reported values for carbon films obtained by the interaction of aromatic hydrocarbons and chlorine in about the same temperature range\(^{23}\). The in-plane conductivity was expected to increase with the crystallinity of the materials which should improve with increasing reaction temperature. However, the B/C film deposited at 1000 °C was much lower in conductivity than the thin films made between 900 °C and 950 °C. This may indicate a change in the conduction mechanism as the carbon-to-boron ratio increases, resulting in a different structure or atomic arrangement.

Table 3.8. Room Temperature conductivity of boron-carbon films
<table>
<thead>
<tr>
<th>Deposition Temperature (°C)</th>
<th>Thickness (µm)</th>
<th>Conductivity (S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>0.66 ± 0.03</td>
<td>5x10²</td>
</tr>
<tr>
<td>900</td>
<td>3.9 ± 0.1</td>
<td>8x10²</td>
</tr>
<tr>
<td>900</td>
<td>1.47 ± 0.09</td>
<td>1x10³</td>
</tr>
<tr>
<td>910</td>
<td>2.05 ± 0.07</td>
<td>8x10²</td>
</tr>
<tr>
<td>950</td>
<td>1.5 ± 0.3</td>
<td>9x10²</td>
</tr>
<tr>
<td>1000</td>
<td>0.634 ± 0.002</td>
<td>6x10²</td>
</tr>
</tbody>
</table>

3.3.9. Reaction of B/C materials with chlorine

XPS data of the thin films after reaction with chlorine showed significant increase of chlorine and decrease of boron on the film surfaces. The IR spectra of the gaseous species collected from the reaction of several samples of B/C materials with chlorine were similar. A representative spectrum is shown in Figure 3.7, and the IR absorption peaks of this spectrum are listed in Table 3.9. The evolution of BCl₃ and small amounts of CCl₄ in each reaction indicates that chlorine removed boron and carbon from the B/C material. X-ray powder diffraction revealed that the layered structure of the B/C materials was gradually destroyed during the reaction with chlorine. The B/C material deposited at higher temperatures seemed to retain some degree of crystallinity after 24 hours of reaction with chlorine even though a significant amount of BCl₃ was detected in the gas phase by IR spectroscopy. Therefore, boron was removed by chlorine from the graphite-like matrix of the B/C materials. Since HCl, CO₂, and COCl₂ were also evolved in the reaction, either chlorine had reacted with the impurities present on the surface of the microcrystalline B/C material to form these gases, or these gases were liberated from the material upon the destruction of the graphite-like matrix.
Table 3.9. IR Spectrum of gaseous species collected from the chlorination at 280°C of B/C (deposited at 1000°C).

<table>
<thead>
<tr>
<th>Wavenumbers (cm⁻¹)</th>
<th>Intensity</th>
<th>Peak Assignment</th>
<th>Literature Value (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2886</td>
<td>w</td>
<td>HCl, v</td>
<td>2886</td>
</tr>
<tr>
<td>2348</td>
<td>m</td>
<td>CO₂, v₃</td>
<td>2349</td>
</tr>
<tr>
<td>1827</td>
<td>w</td>
<td>COCl₂, v₁(A₁)</td>
<td>1827</td>
</tr>
<tr>
<td>994</td>
<td>m</td>
<td>¹⁰BCl₃, v₃</td>
<td>995</td>
</tr>
<tr>
<td>956</td>
<td>s</td>
<td>¹¹BCl₃, v₃</td>
<td>956</td>
</tr>
<tr>
<td>850</td>
<td>mw</td>
<td>COCl₂, v₄(B₂)</td>
<td>849</td>
</tr>
<tr>
<td>792</td>
<td>mw</td>
<td>CCl₄, v₃</td>
<td>790</td>
</tr>
<tr>
<td>667</td>
<td>m</td>
<td>CO₂, v₂</td>
<td>667</td>
</tr>
</tbody>
</table>

In separate control experiments, spectroscopic grade (SP1) graphite or graphitic carbon obtained by the pyrolysis of benzene at 1000 °C was separately heated to 280 °C with 400 torr of chlorine. Even though HCl, CO₂, COCl₂, and traces of CCl₄ were observed in the IR spectra of the gaseous samples collected from both experiments, the X-ray powder diffraction photographs of both materials after treatment with chlorine were identical to the photographs of the materials before treatment. Therefore, the structural integrity of both materials was not affected. Ross and Lemay also reported that at 600 °C chlorine reacts with the surface of powdered graphite to yield minute amounts of chloro-aromatic carbon species detected by gas chromatography. Therefore, it is very likely that chlorine reacts with active carbon atoms on the surface of all the graphite-like materials, but chlorine could not remove carbon atoms from the bulk of such materials. The small amount of CCl₄ evolved from the reaction of chlorine with the B/C materials was probably from the reaction of chlorine with such active carbon atoms.
3.3.10. Intercalation chemistry

The B/C materials deposited at temperatures above 900 °C were intercalated by potassium using the two-bulb technique. Intercalation of the samples yielded first stage intercalation compounds with a B/C interlayer spacing ($l_C$) of 5.3 - 5.4 Å. Unlike the brassy-golden first stage potassium intercalated graphite ($l_C = 5.41$ Å), the potassium intercalated B/C materials appeared dull black.

The intercalation chemistry of the B/C material with the approximate composition of BC$_3$ had been described in the earlier reports. The bronze sodium-intercalated compound is first-stage with a B/C interlayer spacing ($l_C$) of ~4.3 Å. Among the alkali metals, sodium is the least effective in intercalating crystalline graphite, although it intercalates hard carbons readily. The deep blue (SO$_3$F)$_2$ intercalated compound is also a first stage compound with an interlayer spacing ($l_C$) of ~8.1 Å.

3.4. Conclusions

The graphite-like nature of these B/C materials was demonstrated most convincingly with EELS. Both the boron and carbon regions of the EELS spectrum of the B/C material deposited at 830 °C displayed prominent K-edge features corresponding to antibonding $\pi^*$ and $\sigma^*$ states in the conduction band. These K-edge features indicated that both boron and carbon have trigonal-planar coordination and occupy the sites in a graphite-like network. X-ray and electron diffraction data confirmed the graphite-like structure of these B/C materials. The interlayer spacing of these B/C materials (3.34 - 3.39 Å) is similar to that of graphite (3.35 Å). These B/C materials exhibit no long-range sheet-to-
sheet registry since only broad (00l) and (hk0) reflections are observed. Because benzene pyrolyzes to form smaller hydrocarbon species and carbon at temperatures above 800 °C, the carbon-to-boron ratio of the deposited B/C materials increased from 3.1:1 at 800 °C to 5.6:1 at 1000 °C. Reaction of these B/C materials with chlorine at 280 - 300 °C resulted in the removal of boron from the graphite-like matrix and consequently the destruction of the graphite-like structure. The intercalation chemistry of the B/C materials was also similar to that of other pyrolytic graphite-like carbons.

Both XPS and RBS reveal impurities such as oxygen, silicon, and chlorine in the B/C materials. Reduction of the fused silica tube with the deposited B/C material contributed to the presence of O and Si. Alternate methods should be explored to prepare these B/C materials without introducing significant amounts of impurities. For example, the B/C materials can be deposited on substrates such as highly oriented BN placed on an inductively-heated carbon raster. The conductivity of these pristine B/C materials can then be determined more accurately and the conduction mechanism in these materials will then possibly become clear. Furthermore, the two-dimensional atomic arrangement of these B/C materials can be studied with Scanning Tunneling Microscopy (STM) if thin films with pristine surfaces can be prepared.
3.5. References


Figure 3.1. Proposed structure of BC₃.
Figure 3.2. IR spectrum of gaseous species collected from the reaction of BCl₃ and benzene at 910 °C.
Figure 3.3 (a) IR spectra of benzene after passing through the fused silica tube at 25 °C.
Figure 3.3 (b) IR spectra of benzene after passing through the fused silica tube at 900 °C. Absorptions due to CH₄ are indicated by arrows.
Figure 3.4. RBS spectrum of B/C thin film deposited on fused silica at 800 °C. The accompanying simulation assumed that the thin film was contaminated with 5 Å of SiO₂ on the surface. The bulk composition is BC₃.₀₈O₀.₁₉Cl₀.₀₂.
Figure 3.5. EELS spectrum of the B/C material deposited at 830 °C: core-loss region (K-edge) of boron and carbon. The $\sigma^*$ and $\pi^*$ features are evident for both boron and carbon.
Figure 3.6 (a) XPS spectrum of B/C thin film deposited at 800 °C: B-1s region.
Figure 3.6 (b) XPS spectrum of B/C thin film deposited at 800 °C: C-1s region.
Figure 3.7. IR spectrum of gaseous sample collected after the B/C material deposited at 1000 °C was heated in chlorine for 24 hours at 300 °C.
Chapter 4

Synthesis of Lithium-graphite Intercalation Compounds and Attempted Synthesis of a Mixed Conductor $C_x^+Li_2N^-$

4.1. Introduction

Lithium nitride, Li$_3$N, has generated much interest as a promising solid ionic conductor$^1$. The Li$_3$N sinters and single crystals have high Li-ion conductivity of the order $10^{-3} \Omega^{-1} \text{cm}^{-1}$ at ambient temperature$^2$. Li$_3$N is hexagonal with $a = 3.69$ Å, $c = 3.86$ Å and space group $P6/mmm$.$^3$, $^4$ The structure is lamellar as Li$^+$ and Li$_2$N$^-$ layers stack upon each other with Li$^+$ cation in the Li$^+$ layer sitting right above the nominal N$^{3-}$ anion in the Li$_2$N$^-$ layer. The Li-ion conductivity is in the Li$_2$N$^-$ layer as Li ions diffuse among the vacancies on the Li sites in the Li$_2$N$^-$ layer. The goal of this work was to attempt to synthesize a novel lamellar material, $C_x^+Li_2N^-$, in which the graphitic carbon layer and the Li$_2$N$^-$ layer are interlaced. It is anticipated that such a material would have high electronic conductivity in the $C_x^+$ carbon layer and high ionic conductivity in the Li$_2$N$^-$ layer, and would therefore be a very good mixed conductor. Mixed ion conductors have potential applications in batteries, fuel cell electrodes, electrochromic displays and so on$^5$. For example, tungsten bronze, a mixed conductor, has been used as an ionically and electronically reversible electrode and has been extensively studied for use in electrochromic devices. As Li-graphite intercalation compounds may be suitable precursors for synthesizing $C_x^+Li_2N^-$, the synthesis of Li-graphite intercalation compounds was therefore studied in order to find a simple synthetic method.
The study on the intercalation of graphite by lithium was first carried out by Hérold in 1955\textsuperscript{6}. Since then, several synthetic methods have been developed for preparing Li-graphite intercalation compounds (GIC) of the first, second and higher stages\textsuperscript{7,8,9}. The stoichiometry and structure of the first stage Li GIC have been established\textsuperscript{7} as C\textsubscript{6}Li, and space group P\textsubscript{6}/mmm with \(a = 4.305\ \text{Å}\) and \(c = 3.706\ \text{Å}\). Li GIC's of the second and higher stages are known to exhibit wide variations in stoichiometry. The second stage Li GIC usually has a varying composition\textsuperscript{9} between C\textsubscript{12}Li and C\textsubscript{18}Li.

Due to the low vapor pressure of Li at elevated temperature, high reactivity of Li vapor and the rapid formation of lithium acetylide at higher reaction temperature, the synthesis of Li GIC's is more difficult and demanding than those of potassium, rubidium and cesium graphite intercalation compounds. Quartz or glass cannot be used as reaction vessels since Li vapor attacks them at elevated temperature. Metals such as stainless steel have to be used instead. Hérold has reported\textsuperscript{7} a vapor phase synthetic method, in which the reaction was carried out at slightly above 400 °C in a vacuum-sealed metal tube. The reaction yields the first stage Li GIC containing as much as 10\% Li\textsubscript{2}C\textsubscript{2}. In the liquid phase synthesis, which was first investigated by Hérold\textsuperscript{8} and further developed by Fischer\textsuperscript{9}, small pieces of highly oriented pyrolytic graphite (HOPG) were immersed in molten lithium or lithium-sodium solution inside a dry box dedicated to that purpose. Excess lithium on the intercalated HOPG was removed by scrapping with a knife or centrifuging the sample while the lithium was still molten.

It is apparent that the dependence of the liquid phase technique on specialized equipment renders the synthesis of Li GIC's unavailable to most laboratories. In our study of the synthesis of Li GIC's, a simplified procedure for
the liquid phase synthesis was developed. The effect of the reaction temperature on the intercalation will also be discussed. The use of Li GIC's as the precursors for synthesizing \( C_x^+\text{Li}_2\text{N}^- \) has been explored. Some other synthetic routes to make \( C_x^+\text{Li}_2\text{N}^- \) have also been investigated.

**4.2. Experimental**

**4.2.1. Synthesis of Lithium-graphite intercalation compounds**

Seven in. long and 0.5 in. o.d. stainless steel tubes with both ends capped by Swagelok tube fittings were used as reaction vessels. Degassed SP-1 graphite powder (spectroscopic grade, Union Carbide) and lithium powder (99.9%, Aldrich) in approximately 1:5 or 1:6 molar ratio were mixed well and then loaded into the reaction tube inside the DRILAB. The X-ray powder diffraction patterns of the lithium powder showed the presence of lithium only. Lithium was in large excess to ensure maximum contact of molten lithium with graphite powder during the reaction. The loaded tube was closed tightly in the DRILAB and then brought out. The reactions were run at temperatures from 225 °C to 500 °C in a Mellen muffle furnace with a Eurotherm 808 temperature controller for 2-6 days. The temperature effect on the intercalation was examined at 25 °C interval. The reaction tube was placed in a slanted position and tapped a few times during the reaction. In the end, the reactor was cooled slowly at a cooling rate lower than 0.25 °C/min until the temperature was well below the melting point of lithium (180.5 °C). The slow cooling rate allowed for a satisfactory phase separation between the reaction product and unreacted lithium. The greenish golden powdered product was separated from the solidified massive lithium inside the DRILAB. A metal mesh was sometimes used to sift out the intercalation products. Occasionally, a small amount of lithium metal was found
to be present by X-ray powder diffraction in the separated reaction product. By fine-tuning the cooling rate in the vicinity of the melting point of lithium, one should be able to improve the phase separation and the purity.

4.2.1.1. Synthesis of lithium acetylide

In a control experiment, the mixture of graphite powder and lithium powder was heated at 700 °C to synthesize lithium acetylide, Li2C2, using the same apparatus. The bulk of the product looked grayish white. X-ray powder photography showed it to be Li2C2.

4.2.2. Preparation of Li3N

Lithium nitride, Li3N, was prepared in a direct interaction of the elements by a modification of the literature method10. The reactor used was much simpler than that in the literature. It was made of a ½" stainless steel tube, the end of which was fitted with a Swagelok cap and the other end capped with a Whitey valve through a reducing union and a section of ¼" o.d. tubing. A nickel mesh was placed on the bottom of the reactor. Freshly cleaned lithium strips were loaded into the reactor inside the DRILAB. The reactor was evacuated to a vacuum of 10⁻³ torr, flushed with dry nitrogen twice and then pressurized with N₂ to a total pressure of ~10 atm. It was placed in a clamshell furnace with the bottom of the reactor (where the Li charge was located) approximately at the center of the furnace. The top of the ½" tubing, the ¼" section, and the Whitey valve extended outside the furnace. The furnace was controlled with a Eurotherm 808 temperature controller. The reaction was heated at a rate of 12°C/min in order to initiate the reaction. The heating was ramped to about 300°C and was usually repeated again to make sure the reaction had been
initiated and had completed. The reactor was then cooled down to room temperature and the remaining N₂ evacuated. The product was retrieved and manipulated inside the DRILAB. The brick red and sometimes dark red solid chunks were very hard and brittle. X-ray powder photography showed the pattern of Li₃N with only traces of impurity. The Li₃N chunks were powdered in a deep glass mortar.

4.2.3. Nitriding of Li-graphite intercalation compounds

In the first run, a mixture of the 1st stage C₆Li and 2nd stage C₁₂Li was used in the nitriding. The reactor and condition were identical to those in the synthesis of Li₃N. The reactor was pressurized with 10 atm N₂ and the heating was ramped twice at the rate of 12°C/min up to about 300°C. After the reactor was cooled down and excessive N₂ removed, it was opened the DRILAB. X-ray powder photography showed that the product after nitriding was mainly 2nd stage C₁₂Li with some faint lines which appeared to belong to Li₃N.

In the second run, very pure 1st stage C₆Li was used in the nitriding and the reaction conditions were the same. X-ray powder photograph of the product showed the presence of the 2nd stage C₁₂Li and Li₃N, and the pattern of the 1st stage C₆Li was absent.

4.2.4. Annealing of Li₃N/graphite or Li/graphite under N₂ atmosphere

Li₃N Powder and graphite powder were mixed in 1:1 molar ratio and pressed into pellets using a Wilmad evacuatable 13 mm die. The pellet was loaded into the reactor for nitriding. About 4 atm. N₂ was added to the reactor. The reaction was run at 700 °C for three days. The Whitey valve was cooled with a stream of air blowing directly at the valve. After the reactor was cooled down
and excess N₂ removed, it was opened inside the DRILAB. Large clear colorless crystals were seen on the wall of the top part of the ½" tubing where it was cooled during the reaction. There were red and white powders on the bottom of the reactor. The clear colorless crystals were ground into powder inside the DRILAB for X-ray powder diffraction. The X-ray powder pattern was identified to be that of tetragonal Li₂NCN.¹¹,¹² X-ray powder photographs showed the red and white powders on the bottom of the reactor to be a mixture of Li₃N and Li₂NCN. In other experiments, the ratio of Li₃N to graphite used in making pellets was varied and reactions were heated from 2 to 4 days, but lithium cyanimide, Li₂NCN, was always a major product. When the reaction was heated at a lower temperature, 350 °C, for three days, the Li₃N/graphite pellet was intact and X-ray powder photography showed that there had been no reaction.

In a separate experiment, a mixture of Li and graphite powders was pressed into a pellet. The pellet was loaded into the reactor inside the DRILAB. The reactor was then pressurized with ~4 atm. N₂. After heating at 700 °C for three days, it was cooled to room temperature. The pressure inside the reactor was found to be zero, indicating that all the N₂ had been consumed. After the reactor was opened inside the DRILAB, clear crystals of Li₂NCN were seen on the wall of the cooled top part of the ½" tubing.

4.2.5. Interaction of Li₃N and graphite

This reaction was designed to investigate the interaction of Li₃N and graphite in a lithium melt. Inside the DRILAB, Li₃N powder, graphite powder and Li strips were loaded into a reactor identical to that used in the synthesis of Li-graphite GIC compounds. The reactor was heated in the Mellen muffle furnace at 350 °C for 2 - 4 days. After cooling down to room temperature, the reactor was
brought into the DRILAB. X-ray powder photography showed the product to be mainly Li-graphite intercalation compounds with some other lines, none of which was attributable to Li$_3$N. In a similar reaction, Li$_3$N chunks were used instead of the Li$_3$N powder. Only Li-graphite intercalation compounds were present in the product as shown by X-ray powder diffraction. A Na melt was also used for the reaction between Li$_3$N powder and graphite powder instead of the Li melt. The reaction conditions were otherwise the same. After the reaction, X-ray powder photography showed the solid was still a mixture of Li$_3$N and graphite, indicating that there was no interaction between the two in the Na melt.

4.2.6. Interaction of Li$_3$N and LiN$_3$

This reaction was to explore the possibility of synthesizing Li$_2$N$_2$. Lithium azide, LiN$_3$, was synthesized through a metathesis reaction between Li$_2$SO$_4$ and NaN$_3$. X-ray powder photography showed the recrystallized product to be very pure LiN$_3$ with a trace amount of NaN$_3$. Inside the DRILAB, Li$_3$N and LiN$_3$ in 1:1 molar ratio were loaded into a reactor identical to that used in the synthesis of Li-graphite GIC compounds. The reactor was heated in the muffle furnace first at a rate of 1 °C/min to 100 °C and left at 100 °C for one day. The temperature was then ramped to 300 °C at a rate of 1 °C/min and the reaction was left at 300 °C for another day. After cooling down to room temperature, the reactor was brought into the DRILAB. The solid in the reactor was brick red and X-ray powder photography showed it to be only Li$_3$N. In a second run, the reaction temperature was lowered to 100 °C and the reaction heated for two days. After the reaction, there appeared to be no change in the solids in the reactor. X-ray powder photography showed that the solids were still a mixture of Li$_3$N and LiN$_3$. 

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4.3. Results and Discussion

4.3.1. Synthesis of Lithium-graphite intercalation compounds and effect of temperature on the intercalation

When preparations of the lithium-graphite intercalation compounds contained the first and second stages. The X-ray powder diffraction photographs showed the first stage parameters to be those of $C_6Li$ ($a = 4.32$ Å and $c = 3.71$ Å) and the second stage to be of $C_{12}Li$ ($a = 4.29$ Å and $c = 7.04$ Å) as previously reported. According to Herold, the reflection (100) at 6.40 Å of the ordered $C_{18}Li$ type can be seen in addition to the reflection (110) at 3.70 Å (the reflection (100) of the $C_{12}Li$ type is also at 3.70 Å). In our study, the line at 6.40 Å was not observed.

The optimum reaction temperature for preparing the first stage $C_6Li$ is about 315 °C, at which the final product contains only a trace amount of the second stage $C_{12}Li$. Fischer has also reported observing extra lines attributable to the second stage in the X-ray diffraction on the first stage Li-HOPG sample synthesized with the liquid phase method. And in another report by Fischer, the optical reflectivity measurement suggests that a small fraction of stage 2 material might be present in the core of the first stage Li-HOPG sample. Therefore, it appears difficult to produce $C_6Li$ entirely free of contamination by the second stage material.

When the reaction temperature was below 275 °C, only the second stage $C_{12}Li$ and unreacted graphite were present in the reaction product. In the temperature range of 275 °C - 315 °C, the first stage $C_6Li$ started to appear and unreacted graphite was now no longer present. The amount of $C_6Li$ increased as the temperature approached 315 °C. At 315 °C, the yield of $C_6Li$ reached...
maximum, and the product contained a negligible amount of the second stage material. Above 315 °C, we again observed a mixture of the first and second stage lithium graphite compounds, the amount of the first stage diminishing with increasing temperature. Above 400 °C, the second stage C₁₂Li formed the majority of the product, and the first stage was no longer present. Instead, Lithium acetylide, Li₂C₂, the major impurity at higher reaction temperatures was detected. The disappearance of the first stage lithium graphite with increasing temperature under saturation conditions implies that the negative ΔG of the liquid phase reaction (eq. 1), which produces the first stage C₆Li, becomes positive above 315 °C at ordinary pressures.

\[
6C(s) + Li(l) \rightarrow C₆Li(s) \quad (1)
\]

At 315 °C, since \(\Delta G^° = 0\), \(\Delta H^° < 0\) and \(\Delta S^° < 0\), evidently at higher temperatures \(-T\Delta S^°\) overwhelms \(\Delta H^°\). But at higher temperatures, the more favorable thermodynamic reaction product lithium acetylide begins to be formed, as the activation energy barrier for the cission of the graphite network is surmounted. A similar temperature effect was previously observed in the other alkali metal (K, Rb, Cs) graphite systems\(^{16,17}\). However, the surface energy term might need to be taken into account in describing the thermodynamics of the system, since Li has large surface tension and does not wet graphite very well.

4.3.1.1. The crystal structure of lithium acetylide

In 1962, a brief study on the structure of lithium acetylide by Secrist and Wisný\(^{18,19}\) identified lithium acetylide as monoclinic. Juza et al\(^{20}\) employed a different reaction setup and different conditions in the temperature range of 800 -
900 °C. The unit cell was found to be orthorhombic, space group Immm. Juza noticed some mistakes in the calculation of Secrist and Wisnyi, but found the discrepancy hard to explain. In our study, lithium acetylide synthesized at 700 °C using the same reaction conditions as in the work of Secrist and Wisnyi, is identical with the orthorhombic phase reported by Juza et al rather than the monoclinic phase reported by Secrist and Wisnyi (see Table 4.1). In the synthesis of lithium graphite compounds at temperatures above 400 °C, the impurity lithium acetylide present is also found to be the orthorhombic phase.

Table 4.1. X-ray Powder Diffraction Data for Li₂C₂³ (CuKα Ni Filter)

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aOrthorhombic unit cell with \( a = 3.665 \, \text{Å} \), \( b = 5.440 \, \text{Å} \), \( c = 4.833 \, \text{Å} \), space group \( \text{Immm} \).

4.3.2. Attempted synthesis of \( \text{C}_x^+\text{Li}_2\text{N}^- \)

It was reasoned that nitriding the Li intercalant layers in the Li-graphite intercalation compounds might produce \( \text{Li}_2\text{N}^- \) layers which would be then already in between the graphite layers. The 1st stage \( \text{C}_6\text{Li} \) was reacted with 10 atm \( \text{N}_2 \) at a rate of 12 °C/min to 300 °C. Unfortunately, only \( \text{Li}_3\text{N} \) and the 2nd stage \( \text{C}_{12}\text{Li} \) were produced:

\[
6\text{C}_6\text{Li} + \frac{1}{2}\text{N}_2 \rightarrow \text{Li}_3\text{N} + 3\text{C}_{12}\text{Li}
\]

(2)

A similar nitriding of a mixture of the 1st stage \( \text{C}_6\text{Li} \) and 2nd stage \( \text{C}_{12}\text{Li} \) also only yielded \( \text{Li}_3\text{N} \) and \( \text{C}_{12}\text{Li} \). No new phase was obtained from the nitriding of Li GIC's. It is possible that \( \text{Li}_3\text{N} \) is thermodynamically more stable at 300 °C \( (\Delta G_f \text{ Li}_3\text{N} = -20 \text{ kcal/mol}) \), than a compound like \( \text{C}_x^+\text{Li}_2\text{N}^- \) because of a very favorable lattice energy for \( \text{Li}_3\text{N} \). The nitriding of \( \text{C}_6\text{Li} \) to yield \( \text{Li}_3\text{N} \) and \( \text{C}_{12}\text{Li} \) shows that the latters are thermodynamically preferred. Here we see the first
stage C₆Li compound acting as an effective lithiating reagent. It may still be possible to use C₆Li or higher stage Li GIC's as precursors in a reaction with NH₃ or NR₃ to synthesize a lamellar material similar to Cₓ⁺Li₂N⁻.

The synthesis of Cₓ⁺Li₂N⁻ was also attempted in a way roughly analogous to the syntheses of ternary lithium-metal-nitride system such as²² LiSrN, in which lithium nitride was reacted with the corresponding metal at very high temperature. The pressed pellet of Li₃N/graphite was annealed at 700 °C under a nitrogen atmosphere. Interestingly, the reaction generated lithium cyanimide, Li₂NCN.

\[
2\text{Li}_3\text{N} + \text{C} + 2\text{N}_2 \rightarrow 3\text{Li}_2\text{NCN}
\]  (3)

Large clear crystals of Li₂NCN were formed on the cooler region of the reactor. When the reaction temperature was lowered to 350 °C, no interaction between Li₃N and graphite was observed over 3 days.

In the work by Pulham and et al, Li₂NCN was synthesized via the interaction of Li₂C₂ and Li₃N in molten Li at 600 °C (reaction 3). The NCN²⁻ anion ("N=C=N") is isoelectronic with CO₂. Apparently it is a very stable anion as it is the only known heteroatom anion stable in a lithium melt.

\[
\text{Li}_2\text{C}_2 + 4\text{Li}_3\text{N} \rightarrow \text{Li}_2\text{NCN} + 10\text{Li}
\]  (4)

Annealing a pellet of Li/graphite under a nitrogen atmosphere at 700 °C also produced Li₂NCN:

\[
2\text{Li} + \text{C} + \text{N}_2 \rightarrow \text{Li}_2\text{NCN}
\]  (5)

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Reaction 4 has a very high ratio of dinitrogen fixation per mole Li, $1/2\text{N}_2 / \text{Li}$. For comparison, Li itself fixes dinitrogen in a ratio of $1/6\text{N}_2 / \text{Li}$. The cyanamide reaction, therefore provides a very efficient way to fix dinitrogen. Reaction 4 is also much simpler and straightforward in making Li$_2$NCN than the other known methods.

As Li$_3$N has reasonably good solubility$^{23}$, in molten Li, a Li melt was used as a solvent for the reaction between Li$_3$N and graphite at 350 °C. Such reactions over 2 - 4 days only yielded Li-graphite intercalation compounds. Molten Na was also used as a solvent as it has the advantage of not forming intercalation compounds with graphite under this condition. But no interaction between Li$_3$N and graphite was found in a Na melt. It seems that alloying of lithium with sodium is energetically more favorable than the formation of graphite lithium intercalation compounds.

The possibility of synthesizing a new compound Li$_2$N$_2$, in which there would be a divalent dinitrogenyl anion, has been explored by interacting Li$_3$N with LiN$_3$ in hope that the reaction would proceed as follows:

$$\text{Li}_3\text{N} + \text{LiN}_3 \rightarrow \text{Li}_2\text{N}_2 \quad (6)$$

Heating a mixture of Li$_3$N with LiN$_3$ slowly to 300 °C only produced Li$_3$N, as LiN$_3$ is not stable at moderately high temperature and decomposed into Li$_3$N and N$_2$. When the reaction temperature was reduced to 100 °C, LiN$_3$ was found to be stable but there was no interaction between Li$_3$N and LiN$_3$.

4.4. Conclusions
A simplified liquid phase synthesis of lithium-graphite intercalation compounds has been developed. The temperature effect on Li-intercalation reactions has been investigated. The projected synthesis of $C_x^+Li_2N^-$ failed. It had been undertaken in order to produce a mixed conductor which would have high electronic conductivity as well as high ionic conductivity. The utility of lithium-graphite intercalation compounds as precursors in the synthesis of $C_x^+Li_2N^-$ has been explored. Annealing $Li_3N$ with graphite, or $Li$ with graphite, under $N_2$ atmosphere at high temperature produced, in a surprisingly efficient reaction, lithium cyanimide, $Li_2NCN$. This may have potential application as it provides a very efficient way to fix dinitrogen. It is still possible that materials similar to $C_x^+Li_2N^-$ can be synthesized, e.g., via the interaction of ammonia, $NH_3$, with lithium-graphite intercalation compounds.
4.5. References


7 Guérard, D., Hérold, A. Carbon, 1975, 13, 337.


Chapter 5

Vapor-phase Ammoniation of Stage 1 C₈K Graphite Intercalation Compound

5.1. Introduction

Since the first alkali metal-ammonia-graphite ternary intercalation compounds were synthesized by Rüdorff and Schultze in 1954, the chemistry and physics of metal-ammonia-graphite ternary systems have been extensively explored. The opportunity afforded by these systems to study the two-dimensional K-NH₃ liquid in between hexagonal carbon layers has especially attracted much research interest in recent years. This research, in turn, has generated a wealth of information about the first stage GIC C₂₄K(NH₃)ₓ systems with x up to 4.3, and the interaction of the second stage C₂₄K with gaseous ammonia. Although Sodo et al. noticed a rapid uptake of NH₃ by their K-graphite complexes in 1969, it is surprising that no study on the interaction of C₈K with gaseous NH₃ was undertaken until Akuzawa et al. carried out the experiments on the absorption of NH₃ by the first stage alkali metal-graphite intercalation compounds. This lack of study on the interaction of the first stage C₈K with gaseous NH₃ is probably due to the general perception that this interaction is energetically unfavorable. This perception is quite reasonable since the arrangement of potassium in C₈K is rather crowded, and the reaction between graphite and liquid K-NH₃ solution or between C₈K and liquid ammonia only yields the first stage intercalation compounds with compositions close to C₁₂K(NH₃)₂.
In the absorption study by Akuzawa et al., a significant uptake of gaseous ammonia by first stage alkali metal-graphite intercalation compounds, CaM (M= K, Rb, Cs), was observed. For the K-graphite, the uptake of ammonia is somewhere between 1.0 and 1.33 in molar ratio of NH3/K. But they reported that the X-ray diffraction patterns of their CaM(NH3)x materials were so complicated that they were unable to determine the interlayer spacing.

In our attempts to synthesize a novel lamellar material in which alkali metal nitride anions, M2N−, and graphite carbon layers are interlaced, we examined the interaction of CaK with gaseous NH3 at ambient temperature. A new first stage ternary K-NH3-graphite intercalation compound was discovered. Some structural information on CaK(NH3)x was obtained. The interaction of K-graphites with gaseous NH3 was investigated by In Situ X-ray powder diffraction, and In Situ contactless basal plane electrical conductivity measurements.

5.2. Experimental Section

5.2.1. Preparation of CaK.

The brassy golden CaK samples were prepared by the two-bulb technique described by Hérold. SP-1 graphite (Union Carbide, spectroscopic powder) was degassed before use. The surface of potassium chunks was cleaned prior to use and potassium was distilled once during the reaction. X-ray powder diffraction confirmed the brassy golden product to be CaK as all the reflections can be indexed for CaK. CaK was usually retrieved from its two-bulb reaction tube in the DRILAB immediately prior to the ammoniation experiments.

Highly oriented pyrolytic graphite (HOPG) (Union Carbide) of roughly 5x5x1 mm in dimensions was used to synthesize the bulk samples of CaK for an electrical conductivity study. The reaction was run for over four days to ensure its
completeness. The product was cleaved and the exposed interior looked uniformly golden. This indicated that the intercalation was complete.

5.2.2. Vapor-phase Ammoniation of C₈K.

Pyrex tubing (¼” o.d.) was used for the reaction vessel. One end of the tubing was drawn out into a capillary of about 0.5 mm o.d. for In Situ X-ray diffraction studies. The tube was slightly bent approximately one inch from the capillary portion to provide a constriction. This constriction not only helped to prevent the C₈K powder sample from falling into the capillary during the ammoniation, but also made it easier to control the loading of the ammoniation product into the capillary for the X-ray diffraction after the reaction.

C₈K was loaded inside the DRILAB into the reaction vessel described above. Care was taken to prevent the powder sample from falling into the capillary at this point. The reaction tube was then fitted with a Whitey valve. Anhydrous NH₃ (Matheson, 99.99%) used for the ammoniation was examined by gas phase FTIR spectroscopy, and the presence of water was not detected. In some cases, ammonia was further purified by treating it with sodium metal in a "freeze-pump-thaw" procedure before use. The ammoniation using treated NH₃ showed no difference in the final results from that using untreated NH₃.

All the vapor phase ammoniation reactions were carried out at 22 °C. The ammonia pressure used in the reaction was varied from 50 to 650 torr at an interval of 100 torr. When ammonia pressures were above 200 torr, the color change of C₈K was almost instantaneous upon the introduction of ammonia. The brassy golden color quickly darkened and turned dark blue. After the reaction was run for at least 24 hours, a small portion of the powder sample was tapped
into the capillary at the end of the tube. The capillary was then sealed off with a microflame for the X-ray powder diffraction study.

The X-ray powder diffraction photographs of dark blue C₈K(NH₃)ₓ products synthesized with ammonia pressure in the range of 250 - 650 torr closely resembled one another. These X-ray powder diffraction photographs also showed that neither graphite, elemental potassium, nor any known phases of potassium amides, KNH₂, were present. The X-ray powder data are given in Table 5.1. In the X-ray diffraction photographs of C₈K(NH₃)ₓ obtained from ammoniation at pressures below 200 torr, reflections of unreacted C₈K were found to be present.

Table 5.1. X-ray Powder Diffraction Data for C₈K(NH₃)ₓ prepared at NH₃ pressure of 250 torr (CuKα Ni Filter)

<table>
<thead>
<tr>
<th>( \frac{1}{d^2} \times 10^4 )</th>
<th>( l/i )</th>
<th>obsd</th>
<th>calcd</th>
<th>hkl</th>
</tr>
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<tr>
<td>w.sh</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>s</td>
<td>238</td>
<td>239</td>
<td>001</td>
<td></td>
</tr>
<tr>
<td>vw.sh</td>
<td>464</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>w</td>
<td>574</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>vw</td>
<td>806</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>vs</td>
<td>959</td>
<td>955</td>
<td>002</td>
<td></td>
</tr>
<tr>
<td>ms.sh</td>
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<td></td>
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<tr>
<td>ms.sh</td>
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</tr>
<tr>
<td>vw</td>
<td>1314</td>
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<td></td>
<td></td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>1781</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m</td>
<td>2177</td>
<td>2179</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>vw</td>
<td>2299</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m</td>
<td>2413</td>
<td>2418</td>
<td>101</td>
<td></td>
</tr>
</tbody>
</table>
ash = sharp. The X-ray diffraction data is partially indexed for the carbon sub-lattice, hexagonal cell with \( a_0 = 2.47 \, \text{Å}, \quad c_0 = 6.47 \, \text{Å} \).

### 5.2.3. Electrical Conductivity Measurement.

The In Situ measurements of basal plane electrical conductivities were made by the contactless radio frequency inductive technique described by Zeller et al.\(^4\). The technique utilizes eddy currents generated by an rf electromagnetic field. The induced eddy current was sensed in a secondary circuit and the conductivity was derived from the semi-empirical equation:

\[
\Delta V = K(area)^2\sigma
\]

where \( \Delta V \) represents the voltage output change (sample in field - sample out of field); \( K \), a proportionality constant calibrated by a Cu standard of similar dimensions; \( area \), the ab-plane surface area; \( t \), the sample thickness; and \( \sigma \), the specific conductivity. This technique is most suitable for the In Situ electrical conductivity measurement of very anisotropic materials such as graphite intercalation compounds.
The reaction vessel was made of a quartz tube (3/8" o.d.) joined to a piece of flat quartz tube. The flat quartz tube where the sample was located fit well into the 1.0 cm air gap of the ferromagnetic core magnet. The K-intercalated HOPG piece (C₈K) of roughly 5x5x0.7 mm in dimensions was loaded into the flat tube inside the DRILAB. The ammonia was introduced over the brassy golden C₈K at 750 torr and 450 torr in two separate runs. The edges of the C₈K sample turned blue immediately upon the introduction of ammonia, and the blue color quickly diffused towards the center. The final product looked completely metallic blue. At the same time, exfoliation also took place. The conductivity of the sample was monitored In Situ as a function of the reaction time. The final conductivity was measured after the reaction was run for at least 5 days. For comparison, measurements on HOPG and K-intercalated HOPG piece (C₈K) were also made.

5.3. Results and Discussion

5.3.1. Structure

The In Situ X-ray powder diffraction photographs indicate that the dark blue C₈K(NH₃)x products synthesized with ammonia pressure in the range of 250 - 650 torr are the same phase. Although the diffraction pattern is seemingly simple, it can only be partially indexed for the carbon sub-lattice (see Table 5.1). C₈K(NH₃)x is a first stage graphite intercalation compound, with the interlayer spacing or gallery height, \( d_h \) (which is also the identity period, \( l_d \), in this case) equal to 6.47 Å. The presence of \( (hkl) \) reflections indicates that the carbon sub-lattice is tridimensional. The arrangement of carbon layers and the intercalant layers is of the expected sequence AIAIA... The \( a \) parameter of the carbon sub-lattice is 2.47 Å, slightly larger than that of graphite (2.46 Å), but somewhat
smaller than that of C$_8$K (2.485 Å). The honeycomb carbon layers are slightly expanded compared to those in graphite, and therefore this GIC is of donor-guest type.

This smaller expansion of the a parameter compared to that in C$_8$K indicates that the electron population in the antibonding $\pi^*$ band (conduction band) of the carbon layer in C$_8$K(NH$_3$)$_x$ is lower than that in the case of C$_8$K. This decrease of the electron population in the $\pi^*$ band is probably because the intercalated ammonia molecules have solvated some of those electrons as in the well-known potassium-liquid ammonia system.

None of the reflections associated with the octal potassium array in the parent compound$^4$ C$_8$K are observed in the ammoniate, indicating that the potassium has changed with the ammoniation. There are some very weak reflections which appear to be related to the (hk0) reflections of the carbon sub-lattice. It is possible that these lines are associated with the K-NH$_3$ periodic arrays. These need not be commensurate with the carbon framework, each however being periodic. In such a case, no unique crystallographic unit cell could be assigned. In that case the crystal system would be biperiodic$^4$. Many such biperiodic graphite intercalation compounds have already been discovered$^4$. To find the structural arrangement for the intercalants, a more detailed study using single crystals is required.

The powder X-ray diffraction studies showed that C$_8$K(NH$_3$)$_x$ obtained from ammoniation at pressures bellow 200 torr still contained unreacted C$_8$K. The absorption isotherms for C$_8$K-NH$_3$ reported by Akuzawa et al.$^{12}$ show that the absorption does not reach saturation at lower NH$_3$ pressures (see Figure 5.1). X-ray diffraction results from this study confirm the trend exhibited in the absorption isotherms. At very low ammonia pressure, the reaction was not
complete and some of the C₈K remained, even over a prolonged reaction time. Meanwhile, complex intermediate phases started to appear with increasing ammonia pressures. When the ammonia pressure was above 250 torr, the same reaction product was always obtained.

The interlayer spacings or the gallery heights, \( d_j \), of K-NH₃-graphite GIC compounds have a slight variation with respect to the amount of K and NH₃ in the intercalated layer (Table 5.2). Rüdorff reported an interlayer spacing of 6.56 Å for the first stage \( \text{C}_{12.5} \text{K(NH}_3\text{)}_{2.1}\). Using similar preparation methods, Solin and his coworkers found \( d_j = 6.516 \) Å for the GIC prepared from \( \text{C}_8 \text{K + NH}_3\text{(l)} \), and \( d_j = 6.586 \) Å from HOPG + K-NH₃(l). They also reported that the first stage \( \text{C}_{24} \text{K(NH}_3\text{)}_{4.3} \) has \( d_j = 6.633 \) Å. From our study, the GIC obtained from \( \text{C}_8 \text{K + NH}_3\text{(g)} \) has an interlayer spacing of 6.47 Å. This is the smallest among the known K-NH₃-graphite intercalation compounds. It also appears that the interlayer spacing, \( d_j \), is related to the ratio of NH₃/K intercalated. A higher ratio of NH₃/K in the intercalant layer results in larger interlayer spacing. This is probably because the K-NH₃ layer with higher NH₃/K ratio has more of the characteristics of a two-dimensional liquid in which the orientation and motion of NH₃ molecules is more at random, resulting in a "thicker" intercalant layer.

Table 5.2. Interlayer Spacing, \( d_j \), for different K-NH₃-Graphites

<table>
<thead>
<tr>
<th>K-NH₃-Graphite</th>
<th>( d_j ) (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_{12.5} \text{K(NH}<em>3\text{)}</em>{2.1} ) from ( \text{C}_8 \text{K + NH}_3\text{(l)} )</td>
<td>6.56</td>
<td>Rüdorff et al²,³</td>
</tr>
<tr>
<td>( \text{C}_{24} \text{K(NH}<em>3\text{)}</em>{4.3} ) from HOPG + K-NH₃(l)</td>
<td>6.516</td>
<td>Solin et al⁷</td>
</tr>
<tr>
<td>( \text{C}_8 \text{K(NH}<em>3\text{)}</em>{1.1} )</td>
<td>6.47</td>
<td>This work</td>
</tr>
</tbody>
</table>
5.3.2. Composition

The results of the absorption study by Akuzawa et al\textsuperscript{12} indicate that the amount of NH\textsubscript{3} absorbed by C\textsubscript{8}K at ambient temperature under the ammonia pressure of 400 torr is somewhere between 1.0 and 1.33 in molar ratio of NH\textsubscript{3}/K.

From the X-ray diffraction data in this work, the volume available for all intercalant species in the gallery of 3.12 Å high (subtracting 3.35 Å from 6.47 Å) and cross-section corresponding to 8 carbon atoms is approximately 66.5 Å\textsuperscript{3}. The effective volume of the K\textsuperscript{+} cation is \textasciitilde 19 Å\textsuperscript{3}. This leaves approximately 47.5 Å\textsuperscript{3} for x NH\textsubscript{3} molecules. The effective molecular volume of NH\textsubscript{3} is between \textasciitilde 46 Å\textsuperscript{3} (estimated from the density of ammonia liquid at 293 K) and \textasciitilde 34 Å\textsuperscript{3} (from the density of solid ammonia at 88 K). It is reasonable to use the effective molecular volume of NH\textsubscript{3} derived from the similar first stage GIC C\textsubscript{24}K(NH\textsubscript{3})\textsubscript{4.3} which is \textasciitilde 44 Å\textsuperscript{3}. Using Setton’s model\textsuperscript{15}, x is thus estimated to be approximately 1.1, which falls into the range of 1.0 - 1.33 from the absorption study by Akuzawa et al\textsuperscript{12}. Therefore, this new first stage K-NH\textsubscript{3}-graphite ternary intercalation compound probably has approximately the composition of C\textsubscript{8}K(NH\textsubscript{3})\textsubscript{1.1}.

5.3.3. The electrical conductivity

In the electrical conductivity measurement, the \(\sigma_{ab}\) of HOPG used in the synthesis of C\textsubscript{8}K was found to be approximately 1.6\texttimes 10\textsuperscript{4} \(\Omega^{-1}\text{cm}^{-1}\); and the \(\sigma_{ab}\) of C\textsubscript{8}K was approximately 8.8\texttimes 10\textsuperscript{4} \(\Omega^{-1}\text{cm}^{-1}\), which agrees well with the values reported by Murray and Ubbelohde\textsuperscript{16}. The basal plane conductivity of C\textsubscript{8}K(NH\textsubscript{3})\textsubscript{1.1} after vapor-phase ammoniation was measured to be approximately 5.5\texttimes 10\textsuperscript{4} \(\Omega^{-1}\text{cm}^{-1}\). Although the \(\sigma_{ab}\) of C\textsubscript{8}K(NH\textsubscript{3})\textsubscript{1.1} is more than 3 times that of graphite, there is a decrease in conductivity compared to C\textsubscript{8}K. Disregarding the possible contribution from the K-NH\textsubscript{3} layer and correcting for
the expansion of the cross section compared to CaK, the $\sigma_{ab}^{corr}$ is then $6.7 \times 10^4 \Omega^{-1} \text{cm}^{-1}$, still lower than that of CaK.

This decrease in conductivity compared to CaK appears to correlate with the smaller expansion of the $a$ parameter in $\text{CaK(NH}_3\text{)}_{1.1}$. The smaller expansion of the $a$ parameter is attributed to the decrease of electron population in the $\pi^*$ band of the carbon layer as a consequence of ammonia molecules solvating some of those electrons. The decrease of free charge carrier concentration in the $\pi^*$ band of the carbon layer would certainly reduce the conductivity in the carbon layer. The K-NH$_3$ in between the carbon layers is expected to behave like a two-dimensional liquid metal and therefore should contribute to the overall apparent conductivity. It appears that the conductivity in the K-NH$_3$ layer is not very high if the K-NH$_3$ layer is indeed conductive. This consequently results in an overall decrease of conductivity in $\text{CaK(NH}_3\text{)}_{1.1}$ compared to CaK.

It will be very interesting to compare the conductivity of $\text{CaK(NH}_3\text{)}_{1.1}$ with those of the other K-NH$_3$-graphite intercalation compounds, especially that of $\text{C}_{24}\text{K(NH}_3\text{)}_{4.3}$. The NH$_3$/K layer in $\text{C}_{24}\text{K(NH}_3\text{)}_{4.3}$ is expected to resemble the K-liq. NH$_3$ system more closely as the ratio of NH$_3$/K is higher. Therefore, the K-NH$_3$ layer in $\text{C}_{24}\text{K(NH}_3\text{)}_{4.3}$ is probably more metallic compared to those in the other ternary intercalation compounds. Unfortunately, it appears that the conductivities of these ternary K-NH$_3$-graphite intercalation compounds have not yet been studied.

5.4. Conclusions

A new first stage K-NH$_3$-graphite ternary intercalation compound, $\text{C}_{8}\text{K(NH}_3\text{)}_{1.1}$, was prepared by reacting $\text{C}_{8}\text{K}$ with gaseous ammonia at ambient
temperature. The material has been characterized using X-ray powder diffraction and conductivity measurement. The interaction between NH$_3$ and K in the intercalant layer appears to decrease the concentration of electrons in the conduction band, resulting in a smaller expansion of the $a$ parameter and a decrease in electronic conductivity, compared to CaK. This is attributed to the intercalated NH$_3$ solvating electrons from the conduction band. CaK(NH$_3$)$_{1.1}$ has the smallest gallery height among first stage K-NH$_3$-graphite ternary intercalation compounds. Its structure appears to be biperiodic. A more detailed study using single crystal and neutron diffraction will be needed to obtain the structural information of the K-NH$_3$ intercalant layers. The approximate composition has been derived from the structural information. Since this material is not vacuum-stable, an *In Situ* measurement of weight uptake of CaK in NH$_3$ using a microbalance, in combination with *In Situ* X-ray diffraction study, will be essential to determine the composition more accurately.
5.5. References

3 Rüdorff, W. *Chimia* 1965, 19, 489.
Chapter 6

Stability and Conductivity of Boron Nitride Fluorosulfate (BN)₃SO₃F

6.1. Introduction

The hexagonal boron nitride, h-BN, is isoelectronic with graphite and its structure is very similar to that of graphite (graphite: \(a = 2.464\ \text{Å}, \ c = 6.708\ \text{Å};\) h-BN: \(a = 2.504\ \text{Å}, \ c = 6.660\ \text{Å}\)) except for the difference in the stacking of the layers. In h-BN, the B and N atoms in the neighboring sheets are always on top of each other, giving rise to a stronger interaction between the sheets.

The structure of a single graphite layer and the Brillouin zone are shown in Figure 6.1; the band structure and density of states for the \(\pi\) bands are shown in Figure 6.2.¹ The two crystal orbital combinations at the point \(P\) are entirely nonbonding, each located on a different non-equivalent set of atoms which are differentiated by the nature of the stacking in three-dimensional graphite (see Figure 6.3). These two orbital combinations are at the same energy level in an isolated sheet, and the energy gap between the upper \(\pi\) band (conduction band) and the lower band (the valence band) in graphite is zero for such a sheet. The three-dimensional structure results in an overlap of 0.04 eV due to a small bonding interaction between the carbon atoms of one layer that are eclipsed above and below by like carbon atoms of the layers above and below. Graphite is a semi-metal with a charge concentration of approximately \(10^{-4}\) per atom at room temperature. Under oxidative or reductive intercalation, holes can be introduced in the lower \(\pi\) band or electrons in the upper one. This increase in charge carrier concentration usually leads to a higher electrical conductivity than that of pure graphite².
The $\pi$ band structure of h-BN resembles that of graphite, but in BN the lower band now has more nitrogen character and the upper one more from boron. Moreover, at the point $P$, which in graphite is the nonbonding point, one of the combinations involves all nitrogen $p_z$ orbitals, and the other combination all from boron. The two crystal orbital combinations at the point $P$ are no longer at the same energy level due to the difference in the energies of the distinctive sets of contributing atomic orbitals. h-BN is therefore a very good insulator with a large band gap of 4 eV. The electrons in the valence band are more tightly bound and the conduction band is at a higher energy level than in graphite. It is therefore much more difficult to form intercalation compounds of BN. There has been much controversy about the existence of intercalation compounds of BN. Many of those claims are as yet unsubstantiated. So far, the only established intercalation compound of BN is boron nitride fluorosulfate, $(BN)_3SO_3F$, first prepared in this laboratory. As the oxidative intercalation of BN creates holes in the valence band, $(BN)_3SO_3F$ is expected to become a conductor with greatly enhanced electrical conductivity. The conductivity studies by Biagioni and Mayorga in these laboratories showed that $(BN)_3SO_3F$ is indeed conductive although the work by Hoolei failed to confirm this. Therefore, this study was to provide a reliable set of data to support the hole conductor supposition for $(BN)_3SO_3F$. The stability of $(BN)_3SO_3F$ under various conditions has also been reinvestigated. Special attention was given to the attempt to bridge the gap between the chemistry and physics of solids as the comparison between graphite, hexagonal boron nitride and their intercalation compounds provides a good opportunity for relating solid state physics concepts to the chemistry of solids.
6.2. Experimental

6.2.1. Reagents

BN powder (Ventron, Beverly, Mass.) was used in the synthesis of powder samples of \((\text{BN})_3\text{SO}_3\text{F}\). Highly oriented boron nitride\(^{15}\) (Union Carbide), HOBN, was used to prepare \((\text{BN})_3\text{SO}_3\text{F}\) for the conductivity measurement. The BN powder and HOBN were degassed under a dynamic vacuum of \(10^{-8}\) torr, heated occasionally with a gas flame. XeF\(_2\) was prepared photochemically according to the literature method\(^{16}\). HS\(_2\text{O}_3\text{F}\) (Allied Chemical Co., Morristown, N.J.) was distilled and stored in a Pyrex vessel with a break-seal, prior to use.

Peroxydisulfuryl difluoride, S\(_2\text{O}_6\text{F}_2\), was prepared via the interaction of XeF\(_2\) and HS\(_2\text{O}_3\text{F}\) (reaction 1) and the subsequent decomposition of Xe(S\(_2\text{O}_3\text{F}\))\(_2\) (reaction 2) according to the literature method\(^{17}\). S\(_2\text{O}_6\text{F}_2\) was stored over KF to ensure S\(_2\text{O}_6\text{F}_2\) was free of HF in a Pyrex glass vessel with a greaseless J. Young glass-Teflon valve.

\[
\text{XeF}_2 + 2\text{HSO}_3\text{F} \rightarrow \text{Xe(SO}_3\text{F)}_2
\]

\[
\text{Xe(SO}_3\text{F)}_2 \rightarrow \text{S}_2\text{O}_6\text{F}_2 + \text{Xe}
\]

6.2.2. Preparation of \((\text{BN})_3\text{SO}_3\text{F}\)

Reactors were usually constructed by joining \(\frac{1}{4}\)" FEP tubing or Pyrex tubing to a Teflon valve. The samples of \((\text{BN})_3\text{SO}_3\text{F}\) were prepared by condensing S\(_2\text{O}_6\text{F}_2\) over BN such that the BN sample was completely immersed in the liquid S\(_2\text{O}_6\text{F}_2\). For powder samples, the reaction was usually complete in half an hour and a deep blue product was obtained. Excess S\(_2\text{O}_6\text{F}_2\) was removed in a dynamic vacuum and the product was further evacuated for
approximately 10 minutes. The typical compositions of the powder BN fluorosulfate obtained were \((\text{BN})_{3.1}\text{SO}_3\text{F}\) to \((\text{BN})_{3.3}\text{SO}_3\text{F}\), close to those reported by Mayorga\textsuperscript{12}.

For the HOBN sample, the intercalation was done in a large glass reactor joined to a greaseless J. Young glass-Teflon valve. The center of the HOBN sample was not yet completely blue after 2 days. The entire sample was deep blue after 3 days, and there was some exfoliation of the sample. The reaction was run for 5 days in total to ensure complete intercalation. The weight of HOBN sample used was 0.0640 g (2.58 mmole). The weight of the product after the intercalation was 0.187 g, indicating a composition of \((\text{BN})_{2.1}\text{SO}_3\text{F}\). The higher content of \text{SO}_3\text{F} is probably due to some absorption of \text{S}_2\text{O}_6\text{F}_2 in between the layers of the intercalation compound.

6.2.3. Stability of \((\text{BN})_3\text{SO}_3\text{F}\)

6.2.3.1. Stability of \((\text{BN})_3\text{SO}_3\text{F}\) in sealed tube

A powder sample of \((\text{BN})_3\text{SO}_3\text{F}\) was prepared in a \(\frac{3}{4}\)" Pyrex tubing. After the reaction was complete and excess \text{S}_2\text{O}_6\text{F}_2 removed, the Pyrex tubing was sealed off with a gas-oxygen flame under vacuum. The sealed Pyrex tubing containing the product was stored in the DRILAB. There appeared to be no visible color change over several months.

6.2.3.2. Stability of \((\text{BN})_3\text{SO}_3\text{F}\) in liq. AHF

\((\text{BN})_3\text{SO}_3\text{F}\) (33 mg) was loaded into a one-arm \(\frac{3}{4}\)" FEP reactor inside the DRILAB. \text{S}_2\text{O}_6\text{F}_2 (~0.1 ml) was vacuum transferred on to the \((\text{BN})_3\text{SO}_3\text{F}\) and the amount of liquid \text{S}_2\text{O}_6\text{F}_2 was sufficient to cover the \((\text{BN})_3\text{SO}_3\text{F}\) solid. Then, AHF (~1.5 ml), dried over \text{K}_2\text{NiF}_6, was condensed into the reactor. As this
mixture was warmed up to room temperature, the deep blue \((\text{BN})_3\text{SO}_3\text{F}\) quickly started to lose its color. In approximately two hours, all the blue solid had disappeared and the product was white. The liquid phase was slightly yellow tinged. The IR spectrum of the vapor over the liquid only showed the presence of \(\text{S}_2\text{O}_6\text{F}_2\) and HF.

6.2.3.3. Stability of \((\text{BN})_3\text{SO}_3\text{F}\) towards HF vapor and moisture

HF vapor (~100 torr) was introduced into the \(\frac{1}{4}\)" FEP reactor containing freshly made \((\text{BN})_3\text{SO}_3\text{F}\). There was no obvious change in the appearance or color of \((\text{BN})_3\text{SO}_3\text{F}\) over ~24 hrs except that a trace amount of powder which was stuck on the wall turned pale blue. The reactor was evacuated and brought into the DRILAB, and a tiny strand of quartz wool was inserted into the reactor. HF vapor (~100 torr) was added again so that a trace amount of \(\text{H}_2\text{O}\) could be generated via the interaction of \(\text{SiO}_2\) and HF. There was some discoloration on the top of the \((\text{BN})_3\text{SO}_3\text{F}\) solid but the bulk of the solid remained deep blue. Small droplets of liquid were observed on the wall. The bulk of the solid was still blue, although not as deep blue, after 2 weeks.

6.2.4. Conductivity measurement

The intercalated HOBN sample was used for a four-point probe conductivity measurement. The intercalated HOBN was sandwiched between two Teflon sheets and an opening was cut in the top Teflon sheet for the probes. A steady current was applied across the outer two leads with a PAR model M273 potentiostat/galvanostat (Princeton Applied Research) and the potential drop across the inner two leads was measured with a voltmeter. A series of data points of voltage vs. current was obtained to check the linearity. Because of the
nature of its layered structure, (BN)$_3$SO$_3$F is expected to be conductive in the BN sheets \((ab\) plane) and the conductivity along the \(c\) axis is probably very poor. The four sharp osmium probes were pressed through the entire thickness of the sample to ensure a good contact with the sample. And the specific conductivity at a given temperature was calculated by equation 1 for a two dimensional metal. The extrapolated slope of voltage vs. current data points was used for \((V/I)\) in the calculation.

\[
\rho = \frac{V}{i \cdot \pi \cdot \ln 2 \cdot t} \tag{1}
\]

The dimensions of the sample are as follows: length = 10.40 mm, width = 5.53 mm, and thickness = 0.785 mm. The measurement of the specific conductivity at room temperature was done inside the DRILAB with electrical leads connecting the four-point probe device to the potentiostat and voltmeter outside the DRILAB. A special apparatus was constructed for the temperature-dependent conductivity measurement (see Figure 6.4). The Pyrex apparatus had a top and bottom part, connected by an O-ring joint. The Four electrical leads and a thermocouple wire were sealed in the top part. The Four electrical leads are connected with the four-point probe device on the bottom of the apparatus, and the thermocouple tip was placed just underneath the sample. The bottom part of the apparatus was wrapped with heating tape and then inserted snugly into a Pyrex beaker. The Pyrex beaker was then immersed in liquid nitrogen and the temperature was regulated by a Eurotherm 808 temperature controller connected with the thermocouple and the heating tape.

6.3. Results and discussion
6.3.1. Composition and stability of (BN)\textsubscript{3}SO\textsubscript{3}F

The composition for the powder samples proved to be close to (BN)\textsubscript{3}SO\textsubscript{3}F. This implies that the SO\textsubscript{3}F species must be closely packed between the BN sheets\textsuperscript{11}. Dry (BN)\textsubscript{3}SO\textsubscript{3}F appears to be quite stable, as it was stored in an evacuated ampoule for months without any apparent decomposition. When AHF was added to the deep blue (BN)\textsubscript{3}SO\textsubscript{3}F, it decomposed quickly and the blue solid became white and S\textsubscript{2}O\textsubscript{6}F\textsubscript{2} was detected in the gas phase product. A small amount of S\textsubscript{2}O\textsubscript{6}F\textsubscript{2} was added to (BN)\textsubscript{3}SO\textsubscript{3}F prior to the addition of AHF to ensure that there was always enough S\textsubscript{2}O\textsubscript{6}F\textsubscript{2} present and the decomposition was not a consequence of S\textsubscript{2}O\textsubscript{6}F\textsubscript{2} diffusing into the AHF solution from the (BN)\textsubscript{3}SO\textsubscript{3}F. When (BN)\textsubscript{3}SO\textsubscript{3}F was exposed to HF vapor and later a small amount of moisture, quite unexpectedly the deep blue (BN)\textsubscript{3}SO\textsubscript{3}F did not decompose quickly. Over two weeks, the deep blue color faded considerably but the bulk of the solid remained still blue.

The rapid interaction of the (BN)\textsubscript{3}SO\textsubscript{3}F\textsuperscript{−} salt with HF must be a consequence of addition of H-F to the BN framework as a consequence of initial F\textsuperscript{−} attack at the positive B sites. It is claimed\textsuperscript{18} that BN alone will interact with HF to eventually form NH\textsubscript{4}+BF\textsubscript{4}−. This if true must involve multiple HF addition to the B-N network with F bonding to B and H to N as envisioned here.

6.3.2. Conductivity of (BN)\textsubscript{3}SO\textsubscript{3}F

In previous studies, a four-probe technique was employed, in which four platinum wires were used for electrical contact, and the samples were prepared by pressing powdered polycrystalline material into pellets. Because the platinum wires and the pellet surface are not ideally flat, a uniform intimate contact cannot be assured between the four platinum wires and the pellet. The boundary effect
due to the polycrystalline nature of the pellet sample also renders the conductivity measurements, on pressed powder unreliable.

A four-point probe measurement and an intercalated highly oriented boron nitride sample were used in this conductivity study. The specific conductivity of (BN)$_3$SO$_3$F was determined to be $\sim$1.5 Scm$^{-1}$. This value is rather low compared to the graphite intercalation compounds, or even to the highly crystalline pure HOPG which has a conductivity of $\sim$2.0x10$^4$ Scm$^{-1}$. The attempt to use a contactless radio frequency inductive technique described by Zeller et al$^9$ (see Chapter 5) failed because this technique is not sensitive to low conductivities. The temperature dependence of the conductivity of (BN)$_3$SO$_3$F down to $\sim$100 K clearly shows that the conductivity increases with decreasing temperature, indicating a metallic behavior (see Figure 6.5).

For comparison, the conductivity of fluorosulfate-intercalated highly oriented graphite with a composition of C$_8$,$\,_{\text{3}}$SO$_3$F is approximately 1.1x10$^5$ Scm$^{-1}$, representing a 5-fold increase over that of HOPG. The charge carrier concentration in C$_8$,$\,_{\text{3}}$SO$_3$F should be comparable to that in (BN)$_3$SO$_3$F if there is complete electron transfer to form SO$_3$F$^-$ as the sole guest species. Therefore, the low conductivity of (BN)$_3$SO$_3$F is unlikely to arise simply from difference in charge carrier concentration.

The specific conductivity, $\sigma$, is not only related to the concentration of free charge carriers, $n$, but also to the mobility, $\mu$, of the charge carriers:

$$\sigma = n\varepsilon_{\mu_e} + p\varepsilon_{\mu_p}$$  \hspace{1cm} (2)

For graphite itself, the free charge carriers are produced as a result of a slight overlap of the conduction band and the valence band. The concentration of the
free charge carriers is nevertheless small, which characterizes graphite as a semi-metal. The high conductivity of graphite is a result of the very high mobility of the free charge carriers in graphite.

The mobility of the charge carrier is related to the effective mass, \( m^* \), of the carrier and the average time between scattering events for the carrier, \( \tau \):

\[
\mu = \frac{e \nu \tau}{m^*}
\]  

(3)

In general, the charge carrier has a small effective mass in wide bands and a large effective mass in narrow bands. For example, in a monoatomic chain with an interatomic spacing of \( a \), and an interaction between neighboring atoms of \( \beta \) (\( \beta \) negative for bonding), the band width is \( 4|\beta| \) and the mobility of an electron near the bottom of the band is:

\[
m^* = -\frac{\hbar^2}{2|\beta| a^2}
\]  

(4)

More generally, the effective mass for charge carriers at any point in a band depends on the curvature of \( E(k) \). Overall, a narrow band is flatter and results in large effective mass, whereas a wide band is more curved and thus results in small effective mass (see Figure 6.6).

\[
m^* = \left| \frac{\hbar^2}{2 \left( \frac{d^2E}{dk^2} \right)} \right|
\]  

(5)
Figure 6.6. Effective mass and the curvature of $E(k)$

Charge carriers with small effective mass behave as "light", mobile particles, whereas "heavy" carriers with large effective mass have lower mobilities. In a chemical sense, the band width is proportional to the degree of interaction between neighboring atoms. Thus, strongly overlapping orbitals give wide bands, the electron is more delocalized and can move about more freely. At the other extreme, electrons are localized at more electronegative atom sites. Such atoms have contracted atomic orbitals that do not overlap very well with the orbitals of the neighboring atoms.

For a heteropolar, heteronuclear system, AB, the band width depends on the degree of interaction or the overlap between A and B orbitals, and inversely on the energy difference between the atomic orbitals. If the energy difference is large, the mixing of A and B orbitals will be small and the bands narrow. Graphite is a homonuclear system. Therefore, good mixing of the $p_z$ orbitals is expected to give a wide $\pi$ band, and the charge carriers will have high mobility. For hexagonal boron nitride, there is a large energy difference between the valence atomic orbitals as evidenced by their large difference in the first ionization potentials\(^{20}\), I.P.(B) = 8.298 eV and I.P.(N) = 14.534 eV. Therefore, BN has some
ionic character and the $\pi$ bands are expected to be much narrower, and the charge carriers are "heavier" and less mobile compared to the graphite system. In chemical phraseology, the charge carriers, holes in this case, are not as delocalized over the BN sheet as in graphite, instead, they are more likely to be confined on the boron sites for most of time and therefore do not move about as freely as in the graphite system. It is highly probable that the low observed conductivity of (BN)$_3$SO$_3$F is a consequence of this low mobility of hole charge carriers in the (BN)$_3$SO$_3$F salt.

6.4. Conclusion

Boron nitride fluorosulfate (BN)$_3$SO$_3$F has been found to be quite stable in a dry environment. (BN)$_3$SO$_3$F quickly decomposed in the presence of liquid HF. When it was exposed to HF vapor or moisture, it appeared to decompose rather slowly.

Boron nitride fluorosulfate (BN)$_3$SO$_3$F has been clearly shown to be conductive, with the specific conductivity being approximately 1.5 S cm$^{-1}$. The much lower conductivity of (BN)$_3$SO$_3$F, compared to that of the corresponding graphite fluorosulfate, is probably a result of the low mobility of hole charge carriers in the heteronuclear BN sheets in (BN)$_3$SO$_3$F. This low mobility is due to the high effective mass of charge carrier holes in a narrow valence band, the narrow band width being a consequence of the large energy difference between the atomic orbitals of boron and nitride. Chemically, this means the holes are not as delocalized as in the carbon sheets, and are more likely to be confined on the electropositive boron sites. It will be interesting to determine the mobility of holes in (BN)$_3$SO$_3$F experimentally from the Hall effect.
6.5. Reference

Figure 6.1. The structure of a single graphite layer and the Brillouin zone.

Figure 6.2. The band structure and density of states for the $\pi$ bands of graphite.

Figure 6.3. Two nonbonding crystal orbital combinations at the point $P$. 
Figure 6.5. Temperature dependence of the conductivity of (BN)$_3$SO$_3$F
Chapter 7

Lewis Acid-Assisted Oxidation of Xenon by Fluorine at Low Temperatures

7.1. Introduction

It has been generally accepted that the oxidation of Xe by F₂ requires some type of activation such as thermal activation, photochemical activation, or electric discharge. Stein has shown¹, however, that molecular F₂ has enhanced oxidizing power in the presence of liquid SbF₅, a strong Lewis acid, and is able to react with Xe spontaneously in the dark to form a solution of XeF⁺Sb₂F₁₁⁻ at room temperature. However, O₂, F₂, and SbF₅ did not interact under the same reaction condition in spite of O₂ and Xe having indistinguishable ionization potentials². This enhanced oxidizing power of F₂ in the presence of Lewis acid was also shown by Hagiwara³ when he found that molecular F₂ was unable to oxidize very pure AgF in AHF to AgF₂. When Hagiwara used a catalytic amount of BF₃ in AHF, a solution of AgF was quickly oxidized by F₂ and AgF₂ was produced.

In this study, the oxidizing power of F₂/Lewis acid systems has been systematically investigated. A reaction mechanism of the Lewis acid-assisted oxidation of Xe by F₂ is proposed. The thermodynamic aspects of the reaction will also be discussed.

7.2. Experimental

7.2.1. Reagents
Xenon and krypton (Airco, Riverton, NJ) were used as received. House 
O\textsubscript{2} was passed through a metal coil cooled down to -78°C to remove any 
moisture. NF\textsubscript{3} was prepared by direct fluorination of N\textsubscript{2}F\textsubscript{4} (Airco, Riverton, NJ) 
at room temperature. BrF\textsubscript{5} was prepared by direct fluorination of Br\textsubscript{2} first at 
room temperature and then heated to 300°C with 10 atm F\textsubscript{2}. IF\textsubscript{5} was treated 
with F\textsubscript{2} at low temperature before use.

7.2.2. Reaction in the gas phase

7.2.2.1. Interaction of Xe, F\textsubscript{2} and AsF\textsubscript{5} in the dark

The reactor was made by joining a heavy-walled Pyrex tube to a 
greaseless J. Young glass valve with Teflon O-rings. The volume of the reactor 
was ~25 ml. The reactor was flame dried under a dynamic vacuum of 10\textsuperscript{-7} torr. 
A thick clear plastic sleeve was put onto the reactor as a shield for protection 
against shattering or explosion. Xe, AsF\textsubscript{5}, and F\textsubscript{2} (each 3.5 mmole) were 
condensed into the Pyrex reactor. It was warmed to room temperature, when the 
total pressure in the reactor was ~10 atm. The reactor was kept in the dark. 
After ~20 hrs the glass reactor still remained clear and there was no solid deposit 
on the glass wall.

7.2.2.2. Interaction of Xe, F\textsubscript{2} and AsF\textsubscript{5} with light

A 1 liter Pyrex bulb with a glass-to-copper seal was fitted with a Whitey 
valve. It was flame dried under a dynamic vacuum of 10\textsuperscript{-7} torr. Xe, AsF\textsubscript{5}, and F\textsubscript{2} 
were condensed into the reactor and the vapor pressures of Xe, AsF\textsubscript{5}, and F\textsubscript{2} 
were 50.4 torr, 51.7 torr, and 101.8 torr, respectively, in the reaction vessel. The 
reaction vessel was then exposed to sunlight for ~12 hrs. in total. The glass wall 
of the reactor was coated with very finely divided white powder. The white
powder was scraped out with a Teflon-coated stirring bar inside the DRILAB. The weight of the recovered product was 0.4053 g. X-ray powder photography and Raman spectroscopy showed the product to be XeFAsF$_6$ only. The Raman spectrum of XeFAsF$_6$ is shown in Figure 7.1$^4$. The theoretical yield, based on the limiting reagent Xe, is 0.9364 g. Therefore, the yield of this photochemical reaction is greater than 43% since it was difficult to recover all the product through scraping.

7.2.2.3. Interaction of O$_2$, F$_2$ and AsF$_5$ in the dark

The reaction was carried out in a Monel can fitted with a Whitey valve. The volume was approximately 140 ml. 5.79 mmole AsF$_5$, 5.79 mmole O$_2$, and 3.98 F$_2$ were condensed into the Monel can. The total pressure inside the Monel can was ~2.7 atm. After 2 days, the can was opened to the vacuum line with a calibrated volume. The total pressure inside the can after 2 days of reaction was estimated to be ~2.6 atm from tensimetry. There was essentially no pressure drop in the reaction vessel.

7.2.3. With WF$_6$ as a solvent

7.2.3.1. Interaction of O$_2$, F$_2$ and AsF$_5$ in the dark

A Pyrex reactor was made by joining a Pyrex tube to a greaseless J. Young glass valve with Teflon O-rings. The end section of the glass reactor was bent up by ~30° so that the solvent would be spread out to give a large surface area. 2 ml WF$_6$ and AsF$_5$ (0.64 mmole), O$_2$ (0.82 mmole) and F$_2$ (0.43 mmole) were condensed into the reactor. The reaction vessel was always kept in the dark and shaken mechanically. After 2 days of reaction, there was no solid
produced in the solution. Unreacted volatiles were evacuated through a soda lime tower. There was no reaction in this case.

7.2.3.2. Interaction of Xe, F₂ and AsF₅ in the dark

The reaction setup was the same as in section 7.2.3.1. WF₆ (2 ml) and AsF₅ (0.64 mmole), Xe (0.71 mmole) and F₂ (0.75 mmole) were condensed into the reactor. The reaction vessel was always kept in the dark and shaken mechanically for 2 days. Large white crystals were formed in the solvent on the glass wall. Unreacted F₂ was evacuated through a soda lime tower at -196 °C, and the other volatiles were removed at -15 °C. The crystals were then dried at this temperature with a vacuum of 10⁻³ torr. At this point, the crystals appeared to have a tinge of green. The crystals were characterized by Raman spectroscopy to be XeFAsF₅. The weight of the product was 0.1177 g. The reaction yield is ~54% based on the limiting reagent AsF₅.

7.2.3.3. Interaction of Xe, F₂ in the dark

The Pyrex reactor was essentially the same as described in the section above. 2 ml WF₆ and Xe (0.69 mmole) and F₂ (0.71 mmole) were condensed into the reactor. The reaction vessel was always kept in the dark and shaken mechanically. After 2 days of reaction, there was no solid product present in the solution. Unreacted F₂ was evacuated through a soda lime tower at -196 °C. Xe and WF₆ were removed at -25 °C. There was a minuscule amount of white solid present when all the volatiles had been removed. The amount of the white solid was so little that attempts to characterize it were unsuccessful. In the following experiment, a 3 mm o.d. thin Pyrex tubing was fused to the reactor at ~2 in. away from the end and pointed upwards so that the solvent would not get in
during the reaction. Following the same reaction conditions, a minuscule amount of white solid was again obtained. The solid was tapped into the thin tubing and a Raman spectrum was successfully acquired. The Raman spectrum showed that the white solid was definitely not XeF₂ but some mixed tungsten oxyfluorides (see Figure 7.2).

7.2.4. With HF as a solvent

7.2.4.1. Interaction of Xe, F₂ and AsF₅ in the dark

The reactor was made of a ½" FEP tubing joined to a Teflon valve. The volume of the reactor was approximately 35 ml. The end section of the FEP tubing was bent up by −30° so that the solvent would be spread out to give a large surface area. 2 ml AHF and 0.58 mmole Xe, 0.71 mmole AsF₅, 0.90 mmole F₂ were condensed into the FEP reactor. The reaction was run in the dark for 24 hrs. The solvent and excess reactants were then removed at -20°C, leaving behind a white solid with a greenish tinge. Raman spectroscopy and X-ray powder photography showed it was only XeFAsF₅. The weight of the product was 0.1144 g, giving a reaction yield of ~ 60%.

7.2.4.2. Interaction of Xe, F₂ in the dark

The volume of the FEP reactor was approximately 42 ml. A mixture of F₂ (1.65 mmole) and Xe (1.26 mmole) and 2 ml AHF were condensed into the reactor. The reaction was kept in the dark and vigorously stirred for 12 hrs. HF and the other unreacted volatiles were evacuated at -30°C. A white solid was formed when all the HF had been removed. The white solid was characterized by Raman spectroscopy to be XeF₂ (identified by its strong Raman band at 495 cm⁻¹.
1, see Figure 7.3). The weight of the white solid was 0.134 g. Therefore, the reaction yield was ~63% in 12 hrs.

7.2.4.3. Interaction of Xe, F₂ and BF₃ in the dark

The volume of the FEP reactor was approximately 38 ml. F₂ (0.51 mmole), Xe (0.51 mmole), BF₃ (1.02 mmole) and 2 ml AHF were condensed into the reactor. The reaction was kept in the dark and agitated by tapping the reactor for over 24 hrs. The solution remained colorless. HF, BF₃, and the other unreacted volatiles were removed slowly at -25°C. As the amount of liquid was getting very low, an orange-colored solid started to form. When all the liquid had been removed, the reactor was cooled down to around -35°C and evacuated for another 1½ hrs. During the evacuation, the color of the solid became paler and paler, and eventually became white. Raman spectroscopy showed that the white solid was only XeF₂ (identified by its strong Raman band at 495 cm⁻¹). The recovered product weighed 0.029 g. Therefore, the reaction yield was greater than 33%.

7.2.4.4. Interaction of O₂, F₂ and AsF₅ in acid rich HF

A ½" T-shaped FEP reactor with a Teflon-coated magnetic stirring bar in the main tube was used. About 1 ml AsF₅ and 2 ml HF were condensed into the main tube. The molar concentration of AsF₅ in this AsF₅/HF mixture was ~0.1. A mixture of O₂ and F₂ in 10:7 ratio was admitted into the reactor and the reactor was pressurized with ~2.5 atm of this gas mixture. The volume of the reactor was approximately 30 ml. Therefore, there were ~1.8 mmole O₂ and ~1.3 mmole F₂ inside the reactor. The reaction was kept in the dark at around -78°C. The AsF₅/HF solution was stirred very vigorously with the stirring bar. After 2½ days
of reaction, the total pressure inside the reactor was checked with the pressure
gauge, but there did not seem to be any substantial pressure drop. And there
was no solid present in the solution (the solubility of $\text{O}_2\text{AsF}_6$ would be very low
in the acid-rich HF at this temperature). The volatiles were removed and there
was no reaction product from this reaction.

7.2.5. With liquid $\text{AsF}_5$ as a solvent

7.2.5.1. Interaction of $\text{Xe}$, $\text{F}_2$ and $\text{AsF}_5$ in the dark

The same type heavy-walled reactor used in Section 7.2.2.1 was used in
this reaction. The volume of the reactor was ~25 ml. A Teflon-coated magnetic
stirring bar was loaded into the reactor. The reactor was then flame-dried under
a dynamic vacuum of $10^{-7}$ torr. A thick clear plastic tube was put onto the reactor
as a shield for protection against shattering or explosion. 1.4 mmole $\text{AsF}_5$, 1.42
mmole $\text{Xe}$, and 2.13 mmole $\text{F}_2$ were condensed into the Pyrex reactor. The
liquid $\text{AsF}_5$ was approximately 1 ml in the reactor. The reaction temperature was
maintained at -60°C with an acetone bath cooled down by dry ice. Vigorous
stirring was achieved with the Teflon-coated magnetic stirring bar. After 12 hrs of
reaction, there was a large amount of white-greenish solid in the liquid $\text{AsF}_5$.
Liquid $\text{AsF}_5$ and other unreacted volatiles were removed. And the solid was
further evacuated at -30°C. The weight of the product was 0.377 g. Raman
spectroscopy and X-ray powder photography showed this solid was $\text{XeFAsF}_6$.
The yield of this reaction was 78%.

In a separate experiment, $\text{AsF}_5$ (2.6 mmole), $\text{Xe}$ (2.6 mmole), and $\text{F}_2$ (3.0
mmole) were condensed into the reactor. The volume of the liquid $\text{AsF}_5$ was
about 0.35 ml. The reaction was agitated by sloshing the liquid $\text{AsF}_5$ around.
The progress of the reaction was checked every five to ten minutes for one hour.
Within 2 or 3 minutes, the liquid AsF₅ was opalescent and a white granular precipitate started to form. In 10 to 15 minutes, the amount of the solid was about one-third of the original volume of the liquid. Between 20 and 30 minutes, the amount of the solid was about one-half of the original volume of the liquid. In 45 minutes, the amount of the solid was about two-thirds of the original volume of the liquid. In 60 minutes, the amount of the solid was close to four-fifths of the original volume of the liquid.

**7.2.5.2. Interaction of O₂, F₂ and AsF₅ in the dark**

The same type heavy-walled reactor used in Section 7.2.2.1 was used in this reaction. The volume of the reactor was ~13 ml. About 0.35 ml AsF₅, 2.69 mmole O₂ (~5 atm partial pressure in the reactor), and 1.46 F₂ (~2.7 atm partial pressure) were condensed into the reactor. The reaction temperature was maintained at -60°C to -80°C with a dry ice-acetone bath. The liquid AsF₅ was sloshed around by mechanically shaking the reactor. The reaction was run for one week. There appeared to be a minuscule amount of the solid in the solution, but its amount did not seem to be increasing with the reaction time. The unreacted reagents were removed at the end of the reaction. On the glass wall, there was only a trace amount of white solid which was too little to be characterized.

**7.2.5.3. Interaction of NF₃, F₂ and AsF₅ in the dark**

The same type heavy-walled reactor used in Section 7.2.2.1 was used in this reaction. The volume of the reactor was ~24 ml. About 0.35 ml liq. AsF₅, 2.85 mmole O₂ and 2.85 mmole F₂ were condensed into the reactor. The reaction temperature was maintained between -60°C and -80°C with a dry ice-
acetone bath. The liquid AsF$_5$ was sloshed around by mechanically shaking the reactor. The reaction was run for 48 hrs. There was no solid present in the liq. AsF$_5$. The unreacted reagents were removed at the end of the reaction. There was no reaction product from this reaction.

7.2.5.4. Interaction of Xe, GeF$_4$, and F$_2$ in the dark

The same type heavy-walled reactor used in Section 7.2.2.1 was used in this reaction. The volume of the reactor was ~24 ml. About 4.39 mmole GeF$_4$, 2.02 mmole Xe and 2.14 mmole F$_2$ were condensed into the reactor. The reaction was run at 0°C since GeF$_4$ would solidify at lower temperature. At 0°C, there still was some solid GeF$_4$ in the solution. The liquid GeF$_4$ was sloshed around by mechanically shaking the reactor. The reaction was run for over 12 hrs. There did not appear to be a solid product forming in the liq. GeF$_4$. The reactor was cooled down to -80°C to measure the total pressure. It was then cooled down to -196°C and F$_2$ was evacuated at this temperature. The total pressure was measured again at -80°C. The difference in pressure reading should be the F$_2$ pressure in the reaction system; it indicated no F$_2$ uptake. The unreacted reagents were removed at the end of the reaction. There was no reaction product from this reaction.

7.2.5.5. Interaction of Kr, AsF$_5$, and F$_2$ in the dark

The same type heavy-walled reactor used in Section 7.2.2.1 was used in this reaction. The volume of the reactor was ~25 ml. About 1 ml liq. AsF$_5$, 2.38 mmole Kr and 2.79 mmole F$_2$ were condensed into the reactor. The reaction temperature was maintained between -60°C and -80°C with a dry ice-acetone bath. The liquid AsF$_5$ was sloshed around by mechanically shaking the reactor.
The reaction was run for 2 days. There was no solid product forming in liq. AsF₅. The unreacted reagents were removed at the end of the reaction at -65°C. No reaction product was obtained from this reaction.

### 7.2.5.6. Interaction of O₂, F₂ and AsF₅ in liq. BrF₅ in the dark

The volume of the ½" FEP reactor was approximately 44 ml. About 1 ml BrF₅, 0.89 mmole AsF₅, 0.89 mmole O₂ and 0.81 mmole F₂ were condensed into the reactor. Liq. BrF₅ was used as a solvent and the reaction was agitated by mechanically shaking the reactor. The reaction was run at room temperature for 2 days. When all the volatiles were removed at the end, there was only a trace amount of the white coating on the reactor wall. This was probably from the impurity BrF₃ present in BrF₅, which would react with AsF₅ to yield BrF₂AsF₆.

### 7.2.5.7. Interaction of BrF₅, AsF₅, and F₂ in the dark

The volume of the ½" FEP reactor was approximately 48 ml. About 1 ml AsF₅, 0.89 mmole BrF₅ and 2 mmole F₂ were condensed into the reactor. The reaction was run at ~-60°C. A large amount of pinkish solid formed in the liq. AsF₅ at this temperature. This pinkish solid was probably an adduct of BrF₅ and AsF₅. The reaction was agitated vigorously to stir up the solid so that it would have a better chance to react with F₂. The reaction was run for ~12 hrs and there did not appear to be any changes to the pinkish solid. The volatiles were removed at the end. The pinkish solid dissociated in the dynamic vacuum and completely volatilized. When the reactor had been thoroughly evacuated, a trace amount of the white coating was observed on the reactor wall where the liq. AsF₅ had been. This was probably from the impurity BrF₃ present in BrF₅, which would react with AsF₅ to yield BrF₂AsF₆.
7.2.5.8. Interaction of IF₅, AsF₅, and F₂ in the dark

The volume of the ½" FEP reactor was approximately 45 ml. IF₅ was pretreated with F₂ in a separate reactor at ~-20°C until the IF₅ was colorless. About 1 ml IF₅ (1.44 mmole), 1.52 mmole AsF₅, and 1.87 mmole F₂ were condensed into the FEP reactor. The reaction was agitated with a Teflon-coated magnetic stirring bar for 12 hrs at room temperature. There was no solid forming in the liq. IF₅. At the end of the reaction, the volatiles were removed at room temperature. A white solid precipitated as the last of the liquid IF₅ was removed. X-ray powder photography showed it was IF₆AsF₆. The weight of the product was 0.074 g, giving a reaction yield of ~12%.

To determine the mechanism for the formation of IF₆AsF₆ obtained in the above reaction, the interaction between IF₅ and F₂ was investigated. 1 ml IF₅ (1.44 mmole) and 1.87 mmole F₂ were reacted under the same reaction condition. After 12 hrs, F₂ was removed at -196°C. The reactor was then warmed up to room temperature and the vapor pressure above the liquid was slightly higher than that of IF₅. The volatiles were collected in an IR cell fitted with AgCl windows. The characteristic bands of IF₇ at 748, 676, 426 and 365 cm⁻¹ were very prominent in the IR spectrum. The IR cell was flushed again with the vapor pressure head. Another sample of volatiles was collected. But this time the IR spectrum did not show the presence of IF₇. In a separate reaction, 1 ml IF₅ (1.44 mmole) and 1.87 mmole F₂ were first reacted under the same reaction condition for 12 hrs. F₂ was then removed at -196°C. 1.52 mmole AsF₅ was admitted into the reactor and the reaction was stirred for another few hours. At the end when all the volatiles had been removed, there was a small amount of the white solid. The yield was ~13%.
7.3. Results and discussion

7.3.1. Reactions

The high fluoride ion affinity of Lewis acids (A) such as AsF₅, BF₃, PF₅, or HF enhances the oxidizing power of fluorine, as exemplified by the much more negative enthalpy changes for \( \{ e^- + 1/2F_2(g) + A(g) \rightarrow AF^-(g) \} \) in Table 7.1. For instance, the enthalpy change \( \Delta H^o (e^- + 1/2F_2(g) + AsF_5(g) \rightarrow AsF_6^-(g)) = -171 \) kcal/mole, whereas \( \Delta H^o (e^- + 1/2F_2(g) \rightarrow F^-(g)) \) is only -60 kcal/mole.

Table 7.1. Standard Enthalpy \( \Delta H^o \) (kcal/mol) for the fluoride affinity of Lewis acids and for \( F_2/Lewis \) acid oxidization half-reaction.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta H^o ) (kcal/mol)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF(g) + F^-(g) \rightarrow HF_2^-(g)</td>
<td>-37±2</td>
<td>Ref. 6</td>
</tr>
<tr>
<td>BF₃(g) + F^-(g) \rightarrow BF₄^-(g)</td>
<td>-92±6</td>
<td>Ref. 7</td>
</tr>
<tr>
<td>PF₅(g) + F^-(g) \rightarrow PF₆^-(g)</td>
<td>-101±8</td>
<td>Ref. 7</td>
</tr>
<tr>
<td>AsF₅(g) + F^-(g) \rightarrow AsF₆^-(g)</td>
<td>-111±4</td>
<td>Ref. 7</td>
</tr>
<tr>
<td>F(g) + e^- \rightarrow F^-(g)</td>
<td>-79</td>
<td></td>
</tr>
<tr>
<td>HF(g) + F(g) + e^- \rightarrow HF_2^-(g)</td>
<td>-116±2</td>
<td></td>
</tr>
<tr>
<td>BF₃(g) + F(g) + e^- \rightarrow BF₄^-(g)</td>
<td>-171±6</td>
<td></td>
</tr>
<tr>
<td>PF₅(g) + F(g) + e^- \rightarrow PF₆^-(g)</td>
<td>-180±8</td>
<td></td>
</tr>
<tr>
<td>AsF₅(g) + F(g) + e^- \rightarrow AsF₆^-(g)</td>
<td>-190±4</td>
<td></td>
</tr>
<tr>
<td>( 1/2F_2(g) + e^- \rightarrow F^-(g)</td>
<td>-60</td>
<td></td>
</tr>
<tr>
<td>HF(g) + ( 1/2F_2(g) + e^- \rightarrow HF_2^-(g)</td>
<td>-97±2</td>
<td></td>
</tr>
<tr>
<td>BF₃(g) + ( 1/2F_2(g) + e^- \rightarrow BF₄^-(g)</td>
<td>-152±6</td>
<td></td>
</tr>
<tr>
<td>PF₅(g) + ( 1/2F_2(g) + e^- \rightarrow PF₆^-(g)</td>
<td>-161±8</td>
<td></td>
</tr>
<tr>
<td>AsF₅(g) + ( 1/2F_2(g) + e^- \rightarrow AsF₆^-(g)</td>
<td>-171±4</td>
<td></td>
</tr>
</tbody>
</table>
Gaseous mixtures of Xe, AsF₅, and F₂ did not interact in the dark, even to a total pressure of 10 atmospheres, over one day. With sunlight radiation, Xe, AsF₅ and F₂ in the gas phase with a total pressure of only 200 torr quickly reacted, XeFAsF₆ being the only product:

\[
\begin{align*}
Xe(g) + AsF_5(g) + F_2(g) & \quad (P_{\text{total}} = 10 \text{ atm}) \rightarrow \text{No Reaction} \quad (1) \\
Xe(g) + AsF_5(g) + F_2(g) \xrightarrow{hv} XeFAsF_6(s) & \quad (2)
\end{align*}
\]

In contrast, with the presence of a condensed phase such as liquid AHF, WF₆ and AsF₅, the oxidation of Xe by F₂ in combination with a Lewis acid took place in the dark to form XeFAsF₆ at room temperature or below without any thermal or photochemical activation. In the absence of Lewis acids such as AsF₅ or HF, Xe and F₂ did not interact with liq. WF₆ as the solvent.

\[
\begin{align*}
Xe + AsF_5 + F_2 \xrightarrow{\text{liq. WF}_6} XeFAsF_6 & \quad (3) \\
Xe + F_2 \xrightarrow{\text{liq. WF}_6} \text{no reaction} & \quad (4)
\end{align*}
\]

When liquid AsF₅ was used both as a Lewis acid and as a solvent at ~-65°C, reaction 5 was very rapid even in the absence of light. Within a few minutes the liquid AsF₅ became opalescent and a white solid started to precipitate. The yield of XeFAsF₆ in 12 hrs with vigorous stirring is as high as 78%. At low temperatures, F₂ must be primarily in the molecular form and the concentration of fluorine radicals must be very low.
\[ \text{Xe} + \text{AsF}_5 + \text{F}_2 \xrightarrow{\text{liq. AsFs}} \text{XeFAsF}_6 \] (5)

When irradiated with sunlight, the gaseous mixture of O$_2$/F$_2$/AsF$_5$ rapidly generates\(^8\) the dioxygenyl salt O$_2$AsF$_6$. Xe and O$_2$ have indistinguishable ionization potentials (IP = 12.13 eV)\(^2\), yet O$_2^+$AsF$_6^-$ was not formed when O$_2$ was substituted for Xe in similar reactions. A mixture of O$_2$, F$_2$ and liquid AsF$_5$ agitated at -65° for one week yielded no solid product. Nor did a mixture of AsF$_5$, F$_2$ and O$_2$ over liquid WF$_6$ at 20° give the salt O$_2^+$AsF$_6^-$. The oxidation of O$_2$ was also attempted in acid-rich HF at -78°C with vigorous stirring but no reaction was observed. Under the similar acid rich condition, Ag$^{2+}$ has been found to be capable of oxidizing O$_2$ to O$_2$AsF$_6$ (see Chapter 8 and reference \(^9\)).

\[ \text{O}_2 + \text{AsF}_5 + \text{F}_2 \rightarrow \text{no reaction} \] (6)

The reaction of Xe and F$_2$ in AHF in the dark at ~20°C was initially designed as a control experiment. It was found that this reaction produced XeF$_2$. The yield of XeF$_2$ is as high as 63% in 12 hrs. It should be noted that there was no interaction between Xe and F$_2$ with liquid WF$_6$ as solvent. XeF$_2$ was also obtained from the interaction of Xe, F$_2$ and BF$_3$ in AHF (reaction 8).

\[ \text{Xe} + \text{F}_2 \xrightarrow{\text{AHF}} \text{XeF}_2 \] (7)

\[ \text{Xe} + \text{BF}_3 + \text{F}_2 \xrightarrow{\text{AHF}} \text{XeF}_2 + \text{BF}_3 \] (8)

No interaction was observed for Kr (1st IP = 13.99 eV), NF$_3$ (1st IP = 13.20 eV), and BrF$_5$ (1st IP = 13.20 eV). In the case of BrF$_5$, it formed a solid
adduct with AsF$_5$ at low temperature but no BrF$_6^+$/AsF$_6^-$ was produced. A small quantity of IF$_6$AsF$_6$ was obtained from the interaction of IF$_5$, F$_2$, and AsF$_5$. It was shown by IR spectroscopy that IF$_5$ and F$_2$ reacted slowly at room temperature to form a small quantity of IF$_7$. Upon the addition of AsF$_5$, IF$_6$AsF$_6$ was formed from the interaction of IF$_7$ and AsF$_5$. The yield of IF$_6$AsF$_6$ obtained this way is essentially the same as that from IF$_5$, F$_2$, and AsF$_5$ for the same reaction duration. Therefore, the formation of IF$_6$AsF$_6$ is not through a Lewis acid-assisted fluorination.

7.3.2. Energetics

The enthalpy change of the reaction of Xe, F$_2$ and liq. AsF$_5$ (reaction 5) can be evaluated in a Born-Harber cycle given in Figure 7.4. The lattice energy and the entropy of a solid can be estimated from the molecular volume of the solid$^{10}$. The molecular volume of XeFAsF$_6$ is 156.2 Å$^3$ from the crystallographic data$^{11}$. The lattice energy is calculated to be -130 kcal/mole although it could be higher due to the strong interaction between the cation and anion in the solid XeFAsF$_6$. 
Figure 7.4. Acid assisted fluorination - Energetics (values in kcal/mol)

Since liquid AsF$_5$ is used in the reaction, the enthalpy change should be corrected for the latent heat of vaporization, $\Delta H_V$, of AsF$_5$. $\Delta H_V$ can be evaluated by Trouton's law. The boiling point of AsF$_5$ is -53.2°C. Therefore, $\Delta H_V$ of AsF$_5$ is approximately 4.5 kcal/mole. We have

$$\Delta H = -44.5 \text{ kcal/mole}$$

The entropy change of reaction can be estimated from the following:

$$\text{Xe}(g) + \text{AsF}_5(\text{liq}) + F_2(g) \rightarrow \text{XeFAsF}_6(s)$$

\[ S^o = 41 \quad 56 \quad 48 \quad 69 \]

$$\Delta S^o = -76 \text{ e.u.}$$

$$T\Delta S = -16 \text{ kcal mole}^{-1} \text{ at } 208 \text{ K (-65°C)}$$
We have the free energy change $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$:

$$\Delta G^\circ = -28.5 \text{ kcal mole}^{-1}$$

Therefore, the reaction of Xe, F$_2$ and liq. AsF$_5$ is highly favored thermodynamically.

By analogy to the above analysis for the Xe case, the energetics of O$_2$AsF$_6$ reaction can also be evaluated (Figure 7.5).

![Diagram](image)

**Figure 7.5.** Enthalpy change for the acid-assisted oxidation of O$_2$

Corrected with the $\Delta H_f$ of liquid AsF$_5$, the enthalpy change for the reaction of O$_2$/liq. AsF$_5$/F$_2$ at -65°C is:

$$\Delta H = -17.5 \text{ kcal/mole}$$

$$O_2(g) + AsF_5(\text{liq}) + 1/2F_2(g) \rightarrow O_2AsF_6(s)$$
\[ \Delta S^\circ = -63 \text{ e.u.} \]
\[ \Delta G^\circ = -4.5 \text{ kcal mole}^{-1} \]

Again, although the free energy change is smaller than that for the oxidation of Xe, the oxidation of O\textsubscript{2} is highly favorable thermodynamically. It should be noted, however, that this favorability is less sure than in the XeFAsF\textsubscript{6} case because of the uncertainties in some thermodynamic values used in the evaluation.

### 7.3.3. Mechanism

The ready fixation of xenon by fluorine in the presence of the liquid Lewis acids (A) AsF\textsubscript{5} or HF, suggests that a concerted interaction of the xenon donor (D) with F\textsubscript{2} and the acid (A) is occurring in these reactions (see Figure 7.6). This interaction probably involves the sigma HOMO of the donor, the sigma antibonding LUMO (\(\sigma^*\)) of the F\textsubscript{2}, the \(\pi^*\) HOMO of the F\textsubscript{2}, and the sigma LUMO of the acid. Donation of the Xe electron pair to the \(\sigma^*\) of the F\textsubscript{2} is more probable if the Lewis acid is already associated with the F\textsubscript{2} molecule (i.e. F\textsubscript{2}:\(\rightarrow\)A) via the F\textsubscript{2} HOMO (\(\pi^*\)) and the AsF\textsubscript{5} LUMO, the three reactants smoothly moving to products, as the (Xe-F\textsuperscript{+}) bond is made and the F-F bond is broken heterolytically:

\[ D: \text{ F:F A} \rightarrow (D:F)^+ (F:A)^- \] (9)
If $D$ is a strong base, e.g., $IF_5$ or $BrF_5$, DA forms a strong linkage or even a solid adduct, $F_2$ is excluded and no reaction occurs.

![Image of a chemical reaction diagram](image)

Figure 7.6. Heterolytic cleavage of $F_2$ in acid-assisted fluorination

The bonding of $Xe^+$ with $F$ atom, for which $\Delta H^\circ \{Xe(g)^+ + F(g) \rightarrow (Xe-F)^+\} \geq 47$ kcal/mole (2.03 eV), contrasts with that of $O_2^+$, for which $\Delta H^\circ \{O_2^+(g) + F(g) \rightarrow (O_2F)(g)^+\}$ is probably close to zero. This latter effect is a consequence of the F-O bond electrons having an antibonding effect on the O-O bonding in any $(O_2F)^+$ species. The ion pair energy for $(DF)^+$ with $(AF)^-$ should be nearly the same in the two cases. All other enthalpy and entropy changes are either the same or comparable. Thus the $(D-F)^+$ bond energy becomes crucial in determining that the xenon reaction proceeds, and the oxygen reaction does
not. Bond formation in the cation (D-F)⁺ drops the ionization potential of D by the amount of the net bond energy gain for \( \{D^+(g) + F(g) \rightarrow (D-F)^+(g)\} \). In general, the greater that bond energy change, the more likely it is that the oxidation by \( F_2 \), in combination with A, will proceed smoothly to the product (DF)⁺(AF)⁻.

The interaction of Xe and \( F_2 \) usually requires thermal activation at high temperature or irradiation with UV light. In this study, it was discovered that \( F_2 \) is capable of oxidizing Xe to XeF₂ in the dark with AHF as solvent. Although HF as a Lewis acid appears to be weak compared to the other acids (see Table I), the \( F(HF)_n^- \) ions, particularly \( HF_2^- \), are small and provide good coulomb energy of interaction with any cation.

Recently it was found by Lucier¹⁴ in these laboratories that IrF₆ rapidly oxidizes Xe to XeFIr₂F₁₁ in AHF while there is no interaction between them with the absence of AHF solvent.

(10.1) \( Xe(HF)_p \rightarrow Xe^+(HF)_q + e^- \)

(10.2) \( Xe^+(HF)_q \rightarrow XeF(HF)_r + H_2F^+ \)

(10.3) \( XeF(HF)_r \rightarrow XeF^+(HF)_s + e^- \)

The oxidation of Xe in AHF probably begins with the removal of an electron from the solvated Xe (eq. 10.1) for which the ionization potential is probably somewhat lower than 12.13 eV due to the "cage effect" of the donor solvent. Xe is very soluble in AHF due to its high polarizability. As Xe is "caged" by the solvent molecules, the interaction between Xe and the solvent molecules
probably lowers the ionization potential of Xe by making the nonbonding valence electrons of Xe more antibonding and therefore higher in energy and less bound. The expected high solvation energy of Xe\(^+\) in AHF would also contribute to this lowering of the apparent ionization energy. Xe\(^+\) is a strong Lewis acid and forms weakly bound XeF via interaction with F\(^-\) provided by auto-ionized HF (eq. 10.2). The solvated XeF must then be oxidized to (XeF)\(^+\) solvated in AHF (eq. 10.3). In the gas phase, the bond energy of XeF has been determined at 0.151 eV\(^{15}\). The ionization potential of XeF in the gas phase is thus estimated to be smaller than 9.95 eV from a thermal cycle given in Figure 7.7. In AHF, the apparent ionization potential of XeF is also expected to be lower than 9.95 eV due to the interactions with the solvent molecules. This rationale will be useful in understanding the apparent ease of oxidation of solvated Xe in AHF.

![Chemical Reaction Diagram]

\[
\begin{align*}
\text{XeF} & \overset{\text{IP}}{\rightarrow} (\text{XeF})^+ + e^- \\
0.151 & \quad \geq 2.03 \\
\text{Xe} + \text{F} & \overset{12.13}{\rightarrow} \text{Xe}^+ + \text{F} + e^- \\
\therefore \quad \text{IP}(\text{XeF}) & \leq 9.95 \text{ eV}
\end{align*}
\]

**Figure 7.7.** A thermal cycle for estimating IP(XeF)

Radioactive \(^{18}\text{F}\) (t\(_{1/2}\) = 109.7 min.) is a powerful tool in Fluorine chemistry, especially in the determination of labilities of fluorine bonds and the identification of reaction intermediates. A recent study of \(^{18}\text{F}\) exchange by Adams and

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Schrobilgen\textsuperscript{16} on the activation of F\textsubscript{2} by Lewis acids has ruled out the possibility of a radical mechanism and has provided strong evidence for the acid-activated mechanism we have proposed. In their study, no \textsuperscript{18}F exchange is observed in the systems of HF/F\textsubscript{2}, HF/AsF\textsubscript{5}/F\textsubscript{2} and AsF\textsubscript{5}/F\textsubscript{2} under similar reaction conditions. In the reaction system Xe/F\textsubscript{2}/liq. AsF\textsubscript{5}, \textsuperscript{18}F-labeled AsF\textsubscript{5} was used:

\[
\text{Xe} + \text{F}_2 + [^{18}\text{F}]-\text{AsF}_5(\ell) \rightarrow (\text{FXe})^+([^{18}\text{F}]-\text{AsF}_6^-) \tag{11}
\]

At the end of the reaction, the product XeFAsF\textsubscript{6} was found to contain some \textsuperscript{18}F activity but no transfer of \textsuperscript{18}F activity to F\textsubscript{2} was observed. If the reaction involved a radical mechanism and homolytic cleavage of F\textsubscript{2}, it would be expected to result in some \textsuperscript{18}F/\textsuperscript{19}F scrambling and consequently the transfer of \textsuperscript{18}F activity to F\textsubscript{2}.

From our proposed mechanism, it is expected that there should be no \textsuperscript{18}F activity contained in the (FXe)\textsuperscript{+} cation in the product (FXe)\textsuperscript{+}([\textsuperscript{18}F]-\text{AsF}_6^-) obtained in reaction 11. Therefore, it will be very interesting to carry out the following two experiments in the future \textsuperscript{18}F exchange study.

\[
2(\text{FXe})^+([^{18}\text{F}]-\text{AsF}_6^-) \xrightarrow{\text{evac.}} [^{18}\text{F}]-\text{(Xe}_2\text{F}_3)^+\text{AsF}_6^- + [^{18}\text{F}]-\text{AsF}_5 \tag{12}
\]

\[
(\text{FXe})^+([^{18}\text{F}]-\text{AsF}_6^-) + \text{NOF} \rightarrow \text{XeF}_2 + [^{18}\text{F}]-\text{NOAsF}_6 \tag{13}
\]

In reaction 12, XeFAsF\textsubscript{6} readily loses AsF\textsubscript{5} to give Xe\textsubscript{2}F\textsubscript{3}AsF\textsubscript{6} in a dynamic vacuum. Theoretically, the original \textsuperscript{18}F activity in XeFAsF\textsubscript{6} will be divided into a distribution of 7/12 in Xe\textsubscript{2}F\textsubscript{3}AsF\textsubscript{6} and 5/12 in AsF\textsubscript{5} if all the original \textsuperscript{18}F activity is only contained in AsF\textsubscript{6}\textsuperscript{-} and is randomized\textsuperscript{17}. In reaction 13, gaseous NOF, a
strong fluoride base, will interact with XeFAsF\(_6\) to make XeF\(_2\) and NOAsF\(_6\). All the original \(^{18}\)F activity in XeFAsF\(_6\) should be contained in NOAsF\(_6\) and no \(^{18}\)F activity should be found in XeF\(_2\). If the outcome of these two experiments is as anticipated, it will furnish support to our proposed mechanism.

7.4. Conclusions

The oxidizing power of F\(_2\)/Lewis acid systems has been systematically investigated. It has been shown that F\(_2\), in the presence of liquid AsF\(_5\) interacted with Xe rapidly in the dark at -65°C to make solid XeFAsF\(_6\), although similar F\(_2\)/Lewis acid systems were unable to oxidize O\(_2\), NF\(_3\), IF\(_5\), BrF\(_5\) or Kr. A mechanism has been proposed to explain the ability of the F\(_2\)/AsF\(_5\) system to oxidize Xe even at very low temperature and its inability to oxidize O\(_2\) under similar conditions despite the fact that they have indistinguishable ionization potentials. The thermodynamics of these oxidations have been evaluated. It is possible that F\(_2\), in the presence of liquid AsF\(_5\), may be able to interact with Cl\(_2\) to make Cl\(_2\)F\(^+\)AsF\(_6\)\(^{-18,19}\) at low temperatures in a manner similar to the Xe case. With donors such as BrF\(_3\), BrF\(_5\), IF\(_5\), the acids (A) appear to form strongly bound D:A adduct which prevents the heterolytic cleavage of the F\(_2\). For the F\(_2\) heterolytic cleavage to operate the donor D cannot be greatly superior to F\(_2\) as a donor, else the acid (A) is blocked and the F\(_2\) cleavage becomes impossible to achieve.
7.5. Reference


16 Richard Mark Adams, Master Thesis, McMaster University, Canada, 1992

17 A 50-50% distribution is possible.

Figure 7.1. Raman spectrum of XeFAsF₆

Figure 7.3. Raman spectrum of XeF₂
Figure 7.2. Raman spectrum of mixed tungsten oxyfluorides, region 1 and 2.
Chapter 8

The Oxidation Chemistry of \( \text{O}_2^+ \) and \( \text{Ag}^{2+} \) Cations

8.1. Introduction

In 1962, the first \( \text{O}_2^+ \) compound, \( \text{O}_2\text{PtF}_6 \), was described by Bartlett and Lohmann\(^1\). In one of the syntheses of \( \text{O}_2\text{PtF}_6 \), molecular \( \text{O}_2 \) was oxidized directly by \( \text{PtF}_6 \) at room temperature. This lead to another ground-breaking discovery as Bartlett reasoned that, if \( \text{O}_2 \) could be oxidized by \( \text{PtF}_6 \), so should Xe as they have indistinguishable ionization potentials\(^2\), and thus prepared the first compound of an inert gas element.

\( \text{O}_2^+ \) cation is a powerful one-electron oxidizer as indicated by the high electron affinity of gaseous \( \text{O}_2^+ \) ion, which is 12.13 eV. There is an advantage in its use to prepare other high oxidation state compounds since the byproduct is \( \text{O}_2 \), which is ordinarily lost from the reaction mixture as the gas. It was shown by Stein in 1973 that \( \text{O}_2\text{SbF}_6 \) in solid form can fix radon and also oxidize gaseous Xe to \( \text{XeF}_2\text{SbF}_6 \)\(^3\). Richardson, Tanzella and Bartlett\(^4\) also used \( \text{O}_2^+ \) to oxidize hexafluorobenzene and other perfluoroaromatics. In this study, the utility of \( \text{O}_2^+ \) compounds, especially \( \text{O}_2\text{AsF}_6 \), as a convenient one-electron oxidizer in the preparation of high oxidation state Ag compounds has been systematically studied. The use of \( \text{O}_2^+ \) salts in the syntheses of a new class of pseudo-trifluoride Ag compounds, \( (\text{AgF}_2)_3\text{MF}_6 \) (\( M = \text{As}, \text{Au}, \text{Pt} \)), will be discussed in detail in Chapter 10. In all this work the discovery that the \( \text{O}_2^+ \) salts dissolve in AHF to yield stable solutions has been of central importance.

It has been shown that solvated \( \text{Ag}^{2+} \) cation in AHF is a powerful oxidizer, capable of oxidizing Xe (Ref. \(^5\)), \( \text{C}_6\text{F}_6 \) and \( \text{C}_3\text{F}_6 \) (Ref. \(^6\)). Recently, the
remarkable oxidizing power of Ag$^{2+}$ was further demonstrated$^6$ by William Casteel in the oxidation of O$_2$ to O$_2$AsF$_6$ in AsF$_5$-rich HF below -60°C. In this work, a critical assessment of the thermodynamics of the oxidizing power of solvated Ag$^{2+}$ cation in AHF has been carried out. The oxidizing power of the Ag$^{2+}$ cation has been compared with that of solvated O$_2^+$ in AHF. The potential application of Ag$^{2+}$ as a clean, powerful oxidizing reagent in the synthesis of more exotic species has also been tentatively explored.

8.2. Experimental

8.2.1. Reagents

O$_2$AsF$_6$ was prepared according to literature method$^7$. KIrF$_6$ was prepared$^6$ by reducing IrF$_6$ with KBr. AgF$_2$ was prepared by fluorinating AgF in AHF. Purification of AgF was accomplished by recrystallization from AHF. The recrystallized AgF was further dried on the high vacuum line for a prolonged period under a dynamic vacuum of 10$^{-7}$ torr to ensure that there would be no silver bifluoride in the yellow AgF. The purified AgF was stored in the DRILAB in a capped FEP tube. The tube was covered with Aluminum foil during the purification and storage to minimize the exposure of AgF to the light.

8.2.2. The stability of O$_2$AsF$_6$

8.2.2.1. By itself

A 1000 ml Pyrex bulb fitted with a Whitey valve was used in the photo synthesis of O$_2$AsF$_6$ from O$_2$, AsF$_5$ and F$_2$. After scraping out most of the reaction product, there was still some white O$_2$AsF$_6$ on the glass wall. The closed reactor was left in the DRILAB for a few months, with the bottom of the reactor resting on the metal deck of the DRILAB. The white coating on the wall
gradually disappeared and recrystallized on the bottom of the reactor. The temperature inside the DRILAB is usually a few degrees higher than room temperature and the metal deck is probably cooler.

8.2.2.2. in HF

Inside the DRILAB, 0.1223 g (0.5536 mmole) $O_2AsF_6$ was loaded into an FEP reactor. About 1.5 ml AHF, which had been dried over $K_2NiF_6$, was condensed on to $O_2AsF_6$. All the $O_2AsF_6$ solids dissolved to give a colorless solution. After ~5 minutes of gentle agitation, HF was removed slowly to ensure that the white precipitate would not scatter into the vacuum line. The weight of the recovered $O_2AsF_6$ was 0.1169 g (0.5292 mmole), which represented a 96% recovery.

8.2.2.3. in BrF5

In the DRILAB, 0.0823 g $O_2AsF_6$ (0.373 mmole) was loaded into an FEP reactor. About 2 ml liq. BrF5 was condensed on to the solid. All the $O_2AsF_6$ dissolved to give a colorless solution. The vapor pressure over the solution was monitored with a Helicoid gauge. The pressure reading was ~354 torr and there was no noticeable increase with time. After the solution had been left overnight, BrF5 was evacuated and a white solid was left behind. X-ray powder photography showed it was pure $O_2AsF_6$. The weight of the recovered $O_2AsF_6$ was the same as the original weight.

8.2.3. The Oxidation chemistry of $O_2AsF_6$

8.2.3.1. reaction with $F^-$ in AHF
In the DRILAB, NaF (0.0258 g, 0.6144 mmole) and \( \text{O}_2\text{AsF}_6 \) (0.1391 g, 0.6296 mmole) were loaded into the main tube and the side arm of an FEP reactor, respectively. AHF (~1.5 ml) was condensed on to the \( \text{O}_2\text{AsF}_6 \) and NaF in approximately equal amounts. The \( \text{O}_2\text{AsF}_6 \) solution at \(-25^\circ\text{C}\) was poured slowly into the NaF solution. There was very vigorous gas evolution and a white solid started to precipitate from the solution. At the end of the reaction, the supernatant solution was decanted into the side arm and the HF was removed through the soda lime tower. The reaction product was white. X-ray powder photography showed that it was pure NaAsF\(_5\).

8.2.3.2. reaction with \( \text{IrF}_6^- \) in AHF

In the DRILAB, \( \text{O}_2\text{AsF}_6 \) (0.0788 g, 0.3567 mmole) and \( \text{KIrF}_6 \) (0.1216 g, 0.3521 mmole) were loaded into the side arm and the main tube of an FEP reactor, respectively. AHF (~1.5 ml in total) was condensed on to \( \text{O}_2\text{AsF}_6 \) and \( \text{KIrF}_6 \). \( \text{KIrF}_6 \) dissolved partially in the AHF. The \( \text{O}_2\text{AsF}_6 \) solution was poured into the \( \text{KIrF}_6 \) solution in small portions. The interface where the two solutions met turned yellow very quickly and there was vigorous gas evolution. Gradually, the pale purple \( \text{KIrF}_6 \) solid disappeared and a white solid crystallized from the solution. The whole solution became yellow. HF and the volatile yellow species (\( \text{IrF}_6 \)) were condensed into the side arm and kept at 0°C. SF\(_4\) was then introduced into the side arm. The yellow solution in the side arm became colorless in a short time and, on removal of HF and other volatiles, left behind a white solid. X-ray powder photography\(^8\) showed that the white solid in the side arm was \( \text{SF}_3\text{IrF}_6 \) and the white solid in the first tube was \( \text{KAsF}_6 \). The weight of \( \text{KAsF}_6 \), 0.0874 g, exceeded the calculated yield, 0.0803 g, probably because of the interaction of the Teflon container with the molecular \( \text{IrF}_6 \).
8.2.3.3. reaction with AgF in AHF

AHF was further dried over $\text{O}_2\text{AsF}_6$ in a separate FEP reactor after having been dried over $\text{K}_2\text{NiF}_6$. AgF (0.0632 g, 0.4981 mmole) and $\text{O}_2\text{AsF}_6$ (0.1101 g, 0.4984 mmole) were loaded into the main tube and the side arm of the reactor respectively. AHF (~2 ml in total) was condensed on to both the AgF and $\text{O}_2\text{AsF}_6$. The $\text{O}_2\text{AsF}_6$ solution was poured slowly in several batches into the AgF solution. Oxygen gas was evolved and initially some light brown-yellow solid was generated and its quantity increased as the $\text{O}_2\text{AsF}_6$ solution was added. Later, the interface where the $\text{O}_2\text{AsF}_6$ solution and the AgF solution met became blue. Gradually, as more $\text{O}_2\text{AsF}_6$ solution was added, the whole solution turned blue and a small amount of dark brown solid settled to the bottom of the reactor. When all gas evolution had ceased, the reactants having been fully mixed, the supernatant blue solution was decanted into the side arm. The brown solid was repeatedly washed until the HF solution was colorless. HF and volatiles were then removed under dynamic vacuum. The solid obtained from the blue solution was blue-green. X-ray powder photography showed it to be $\text{AgFAsF}_6$. Its weight was 0.1127 g. Compared to the calculated value of 0.1573 g, a reaction yield of ~72% was achieved. The weight of the dark brown solid was 0.0218 g. It was mainly AgF$_2$ as shown by X-ray powder photography. Assuming the Ag unaccounted for in $\text{AgFAsF}_6$ was all used to make AgF$_2$, the weight of AgF$_2$ was calculated to be 0.0218 g which was in excellent agreement with the measured value.

In a separate reaction, the AgF solution was poured into the $\text{O}_2\text{AsF}_6$ solution instead. AgF (0.0692 g, 0.5454 mmole) and $\text{O}_2\text{AsF}_6$ (0.1223 g, 0.5536 mmole) were used in this reaction. When the AgF solution was first poured into
the O$_2$AsF$_6$ solution, the colorless O$_2$AsF$_6$ solution turned blue immediately. As more AgF solution was added, the blue color became more intense, and some very dark brown solid now started to form in the solution. At this point, the dark brown solid was being generated very quickly at the interface where the AgF solution met the O$_2$AsF$_6$ solution. Gas evolution was taking place all the time during the reaction. At the end of the reaction, a bluish green solid was obtained in the side arm and was shown by X-ray powder photography to be AgFAsF$_6$. Its weight was 0.1300 g. Therefore, the reaction yield was $\sim$76%. The weight of the dark brown solid was 0.0184 g. It was mainly AgF$_2$, as shown by X-ray powder photography although weak lines attributable to (AgF$_2$)$_3$AsF$_6$ were present and showed that some of this material was formed in the reaction. If the Ag unaccounted for in AgFAsF$_6$ were all used to make AgF$_2$, the weight of AgF$_2$ would be 0.0195 g which was fairly close to the measured value.

8.2.3.4. reaction with AgAsF$_6$ in AHF

Inside the DRILAB, AgAsF$_6$ (0.1288 g, 0.4340 mmole) and O$_2$AsF$_6$ (0.1001 g, 0.4531 mmole) were loaded, respectively, into the main tube and the side arm of a T-shaped FEP reactor. AHF, treated by K$_2$NiF$_6$, was further dried over O$_2$AsF$_6$ in a separate FEP reactor before use. About 1.5 ml AHF in total was then condensed on to the AgAsF$_6$ and O$_2$AsF$_6$. Most of the AgAsF$_6$ did not dissolve in the HF solution. The O$_2$AsF$_6$ solution was poured slowly, in several batches, into the AgAsF$_6$ solution. As soon as the O$_2$AsF$_6$ solution was poured in, the AgAsF$_6$ solution turned blue with simultaneous vigorous evolution of oxygen. As more O$_2$AsF$_6$ solution was added, the blue color became more intense and the amount of the white solid AgAsF$_6$ diminished. When all of the O$_2$AsF$_6$ solution had been added, the solution was royal blue and no more solid
AgAsF$_6$ was discernible. After AHF and volatiles were removed, a blue-green solid was obtained. It was shown by X-ray powder photography to be AgFAsF$_6$. After correcting for the excess O$_2$AsF$_6$, the weight of the product was 0.1455 g, slightly higher than the theoretical yield 0.1370 g for AgFAsF$_6$. This indicated a quantitative conversion of AgAsF$_6$ to AgFAsF$_6$.

**8.2.3.5. reaction with AgF in basic AHF**

Inside the DRILAB, AgF (0.0729 g, 0.5746 mmole) and KF (0.1045 g, 1.799 mmole) were loaded into the main tube of a ½" FEP reactor together with a Teflon-coated magnetic stirring bar. 0.2653 g (1.201 mmole) O$_2$AsF$_6$ was loaded into the side arm of the reactor. About 2 ml AHF in total was condensed on to the KF + AgF mixture and the O$_2$AsF$_6$ solid separately. The dissolution of KF and AgF in AHF gave a milky suspension. The O$_2$AsF$_6$ solution was poured slowly into the KF + AgF solution, which was being vigorously stirred. At the interface where the O$_2$AsF$_6$ solution met the KF + AgF solution, the solution turned yellow and a copious red precipitate formed as the oxygen gas was vigorously evolved. Eventually, the entire solution became yellow and a sizable quantity of the red solid lay at the bottom of the tube. The yellow solution was decanted into the side arm, and the red solid was washed several times until the solution over the red solid was no longer colored. In this extraction process, a pale yellow solid crystallized from the yellow solution in the side arm. AHF and any volatiles were eventually removed in a dynamic vacuum. The product in the side arm was pale yellow. The product in the original reactor was reddish brown. X-ray powder photography showed the yellow solid to be a mixture of KAsF$_6$ and KAgF$_4$. The KAgF$_4$ pattern was rather weak in the powder photograph relative to that of KAsF$_6$, but unambiguously characteristic of the Ag(III) salt. A Raman
spectrum was obtained on the same 0.5 mm X-ray quartz capillary which clearly demonstrated the presence of the AgF$_4^-$ anion$^9$ together with the AsF$_6^-$ anion$^{10}$ (see Figure 8.1). X-ray powder photography showed the reddish brown solid to contain AgF$_2$ as the only microcrystalline phase.

In a separate experiment to find out the reaction yield, AgF (0.0692 g, 0.5454 mmole) and KF (0.0958 g, 1.649 mmole) were loaded into the side arm and 0.2463 g (1.115 mmole) O$_2$AsF$_6$ was loaded into the main tube of the reactor. This time, the KF + AgF solution was poured into the O$_2$AsF$_6$ solution instead. After the reaction, 0.1814 g yellow solid, a mixture of KAsF$_6$ and KAgF$_4$, was obtained. In a second T-shaped FEP reactor, about 1 ml AHF was condensed on to this yellow mixture. There was some solvolysis of KAgF$_4$ and some red solid precipitated (probably AgF$_3$). The supernatant solution was yellow. BF$_3$ was admitted into the reactor to precipitate$^{11}$ AgF$_3$ and the solution was agitated by vibrating the tube. Bright red solid AgF$_3$ precipitated. The solution was cooled to saturate the solution with BF$_3$. BF$_3$ was added until the supernatant solution was colorless and all Ag(III) had precipitate as AgF$_3$. The AgF$_3$ in AHF was then agitated for over 12 hrs to convert$^{11}$ AgF$_3$ to Ag$_3$F$_8$. The colorless supernatant solution was decanted and the reddish brown solid was washed repeatedly to ensure that all the side products, KAsF$_6$ and KBF$_4$, were washed away. X-ray powder photography showed the red brown solid was mainly Ag$_3$F$_8$. From the weight of the reddish brown Ag$_3$F$_8$ obtained, the yield of KAgF$_4$ from the interaction of AgF + 2O$_2$AsF$_6$ in excess KF was calculated to be nearly 23%.

8.2.3.6. reaction with AgF$_2$ in basic AHF
Inside the DRILAB, AgF2 (0.0722 g, 0.4950 mmole) and KF (0.0609 g, 1.048 mmole) and a Teflon-coated magnetic stirring bar were loaded into the main tube of a ½" FEP reactor. O2AsF6 (0.1227 g, 0.5554 mmole) was loaded into the reactor's side arm. AHF, treated with K2NiF6, was further dried over O2AsF6 in another FEP reactor. About 2 ml AHF in total was condensed on to the KF + AgF2 mixture and the O2AsF6 separately. With the KF + AgF2 solution being stirred very vigorously, the O2AsF6 solution was gradually added. A very fast reaction took place with oxygen evolution and the KF + AgF2 solution quickly turned yellow. After all the O2AsF6 solution had been added and there was no more gas evolution, the solution was left to stir for another 30 min. The resultant solution had an intense yellow color, and there was still an abundant reddish brown sediment. The yellow solution was decanted into the side arm, and the reddish brown solid was repeatedly washed until the HF solution condensed on to it was no longer colored yellow. AHF was then removed under a dynamic vacuum, and the solid products were vacuum-dried. The solid product in the side arm was yellow, and that in the main tube was reddish brown. X-ray powder photography showed that the yellow product was a mixture of KAgF4 and KAsF6 with a strong pattern of KAgF4, and the reddish brown solid was still AgF2. The weight of the unreacted AgF2 was 0.0422 g (0.2893 mmole). Based on the amount of AgF2 that was consumed, the yield of KAgF4 was estimated to be ~42%.

8.2.3.7. reaction of O2AsF6 with AgF2 in neutral AHF

The reaction is described in detail in Chapter 10. Reacting three parts of AgF2 with one part of O2AsF6 (O2AsF6 slightly in excess) produces (AgF2)3AsF6.
8.2.3.8. reaction with Ag$^{2+}$ in AHF

Inside the DRILAB, AgFAsF$_6$ (0.1353 g, 0.4284 mmole) was loaded into the side arm and O$_2$AsF$_6$ (0.0947 g, 0.4287 mmole) into the main tube of an FEP reactor. AHF (~1.5 ml) in total was condensed on to AgFAsF$_6$ and O$_2$AsF$_6$ in approximately equal amounts. The dissolution of AgFAsF$_6$ in AHF produced a small quantity of black solid and a blue solution. The O$_2$AsF$_6$ solution was poured slowly into the blue AgFAsF$_6$ solution. There was no noticeable reaction. After all the O$_2$AsF$_6$ solution had been transferred, the mixed solution was still blue, and the quantity of the black solid did not change visibly. There appeared to be no change even after the mixture was agitated for over 12 hrs. At the end, the clear blue solution was decanted into the main tube, and the remaining black solid was washed several times by condensing HF back into the side arm. After removing HF and any volatiles through the soda lime tower, a pale green solid was obtained from the blue solution. X-ray powder photography showed the pale green solid to be a mixture of AgFAsF$_6$ and O$_2$AsF$_6$. 0.0151 g black solid was retrieved from this experiment. The black solid was later characterized to be (AgF$_2$)$_3$AsF$_6$ (see Chapter 10).

8.2.3.9. interaction with (AgF$_2$)$_3$AsF$_6$ in AHF

This is essentially the same reaction described in the section above. In this case, the black (AgF$_2$)$_3$AsF$_6$ was produced as AgFAsF$_6$ disproportioned in a solvolytic reaction with the AHF. There seemed to be no change either in the amount or in the appearance of the black solid as it was agitated with O$_2$AsF$_6$ solution for over 12 hrs.
8.2.4. The oxidation chemistry of Ag$^{2+}$

8.2.4.1. reaction with $O_2$ in acid rich AHF

This experiment was initially designed to catalyze the reaction of $O_2$, AsF$_5$ and F$_2$ in the acid-rich HF with AgAsF$_6$ acting as a catalyst. In the DRILAB, AgFAsF$_6$ (0.0556 g, 0.1761 mmole), together with a Teflon-coated magnetic stirring bar, was loaded into the main tube of a $\frac{1}{2}$" T-shaped FEP reactor. AsF$_5$ (~1 ml) and HF (~2 ml) were condensed into the main tube. The molar ratio of AsF$_5$ to HF in this AsF$_5$/HF mixture was approximately 1:10. Upon warming up to room temperature, a blue solution was obtained and there was no residual solid. The reactor was then pressurized with F$_2$ to achieve a total pressure of 1500 torr and the solution was vigorously agitated for ~$\frac{1}{2}$ hr to ensure that any Ag(I) present in the solution would be converted to Ag(II). F$_2$ was then removed under a dynamic vacuum at -196°C. The reaction temperature was then maintained at around -80°C. The AsF$_5$/HF solution was stirred very vigorously with the stirring bar. A mixture of $O_2$ and F$_2$ in 10:7 ratio was admitted into the reactor. A steady pressure drop was noticed initially and a white solid precipitated. Upon warming up to ~60°C, the white solid started to disappear and oxygen was evolved from the solution. The reactor was pressurized with this gas mixture to achieve a total pressure of ~2.5 atm. The volume of the reactor was approximately 30 ml. Therefore, there were ~1.8 mmole $O_2$ and ~1.3 mmole F$_2$ inside the reactor. With 2 to 4 hrs of vigorous stirring, the solution turned completely colorless and there was a large quantity of white solid in the solution. This indicated that all the Ag$^{2+}$ had been reduced in the oxidation of $O_2$ to $O_2^+$ as $O_2$AsF$_6$ at -80°C.

In a similar experiment, a less acidic condition was employed. Inside the DRILAB, AgAsF$_6$ (0.0450 g, 0.142 mmole) was loaded into the reactor. AsF$_5$
I, (-6.5 mmole) and AHF (-2 ml) were condensed into the reactor. The molar ratio of AsF₅ to HF in this AsF₅/HF mixture was approximately 1:20. Upon warming up to room temperature, a blue solution was obtained and there was no residual solid. As in the previous reaction, this blue solution was treated with 2 atm F₂; the F₂ was then removed under a dynamic vacuum. The reaction temperature was maintained at around -80°C. The AsF₅/HF solution was stirred very vigorously with the stirring bar. A mixture of ~3.6 mmole O₂ and ~1.8 mmole F₂ was admitted into the reactor. The blue color of the solution became paler and a white solid precipitated. The reaction was run for 12 hrs and the solution always stayed pale blue. At the end of the reaction, all the white solid disappeared with gas evolution upon warming the solution to room temperature. HF and volatiles were removed and a blue-green solid was obtained. X-ray powder photography showed it was only AgFAsF₅. AgFAsF₅ was quantitatively recovered.

8.2.4.2. Reaction of AgFAsF₅ with Cl₂ in acid rich AHF

In the DRILAB, AgFAsF₆ (0.1175 g, 0.372 mmole) was loaded into the main tube of the T-shaped FEP reactor. AsF₅ (~0.4 ml, ~5.5 mmole) was condensed on to AgFAsF₆ first and then AHF (~1.5 ml) was condensed over it. Upon warming up to room temperature, a deep blue solution was obtained and there was no residual solid. This blue solution was treated with 2 atm F₂; the F₂ was then removed under a dynamic vacuum. The deep blue solution was warmed up to -60°C and kept at this temperature during the reaction. Cl₂ (~0.465 mmole) was admitted into the reactor. Shortly after, the deep blue solution turned blue-green and finally emerald green. Meanwhile, a large quantity of white solid precipitated from the solution. The agitation of the solution was continued until there appeared to be no more change. The emerald green
solution was decanted into the side arm which had been cooled down prior to the decantation. This emerald green solution in the side arm became much paler as HF, probably together with AsF₅, was distilled back to the main tube to wash the white solid. Therefore, the white solid was only washed once. HF, AsF₅ and other volatiles were removed at -60°C. As HF, AsF₅ and other volatiles were being removed, part of the solution became very pale green and gradually turned pale yellow. A yellow solid started to form as the liquid level decreased. The solution in the vicinity of the yellow solid was pale yellow although the rest of the solution was still green. A sizable quantity of yellow solid was produced when all the liquid had been removed. When this yellow solid was warmed up to room temperature from -60°C, it appeared that the yellow solid was quickly decomposing and vaporizing. Even with the reactor valve closed off from the vacuum line, this decomposition was still very rapid. The yellow solid was apparently unstable at room temperature. Its decomposition produced a small amount of white residue. The reaction vessel was evacuated at 10⁻³ torr for several hours. The weight of the decomposition residue was 0.0201 g. The white byproduct of the oxidation reaction in the main tube was shown to be AgAsF₆ by X-ray powder photography and weighed 0.0849 g, which was somewhat less than the calculated yield of 0.1104 g.

8.3. Results and Discussion

8.3.1. The stability of O₂AsF₆

In the DRILAB where the temperature is higher than ambient temperature, O₂AsF₆ on the walls of the Pyrex container is observed to dissociate and recombine in the cooler region of the container. In a mass spectroscopy study on the thermal decomposition of dioxygenyl salts by Young et al., small mass
peaks of $O_2^+$ were observed from $O_2AsF_6$ when evacuated to $10^{-6}$ torr. The $O_2^+$ peaks could have derived from $O_2F$ as well as $O_2$ itself. The observation here are consistent with the $O_2AsF_6$ being in thermal equilibrium with $O_2F$ and $AsF_5$:

$$O_2AsF_6 \leftrightarrow O_2F + AsF_5 \quad (1)$$

The $O_2F$ is known to be thermodynamically unstable with respect to $O_2$ and $1/2F_2$ but the constant illumination by fluorescent lighting of the DRILAB would probably provide enough photons for the formation of $O_2F$:

$$O_2 + 1/2F_2 \rightarrow^{hv} O_2F \quad (2)$$

A small loss of $O_2AsF_6$ was observed from the dissolution in AHF. This occurred even when the HF was pretreated with a separate sample of $O_2AsF_6$. The loss of $O_2AsF_6$ was more severe when $K_2NiF_6$ was used to dry the AHF, therefore in work with the $O_2^+$ salts the preferred "drying" agent for the AHF was $O_2AsF_6$. There must be some reductive interaction between $O_2AsF_6$ and the reaction container to account for the slight consumption of $O_2AsF_6$ over and above that required for the identified oxidations. This consumption of some $O_2AsF_6$ leads to formation of some $AsF_5$ and the solutions are, as a consequence of this, somewhat acidic:

$$\text{container surface} + O_2AsF_6 \rightarrow \text{container surface fluoride} + O_2 + AsF_5 \quad (3)$$

8.3.2. The oxidation chemistry of $O_2AsF_6$
\( \text{O}_2\text{AsF}_6 \) reacts with alkali metal fluoride through a displacement reaction and generates the gaseous basic fluoride, \( \text{O}_2\text{F} \) radical, which dissociates into \( \text{O}_2 \) and \( \text{F}_2 \):

\[
\text{NaF} + \text{O}_2\text{AsF}_6 \xrightarrow{\text{AHF}} \text{NaAsF}_6 + \text{O}_2\text{F} \rightarrow \text{NaAsF}_6 + \text{O}_2 + \frac{1}{2}\text{F}_2 \quad (4)
\]

This displacement of the base, \( \text{O}_2\text{F} \), occurs whenever a strong fluorobase is present. \( \text{AgF} \) and any alkali fluoride must interact in this way.

\( \text{O}_2\text{AsF}_6 \) is found to oxidize \( \text{IrF}_5^- \) quantitatively, liberating \( \text{IrF}_6^- \):

\[
\text{KIrF}_6 + \text{O}_2\text{AsF}_6 \xrightarrow{\text{AHF}} \text{KAsF}_6 + \text{IrF}_6 + \text{O}_2 \quad (5)
\]

The electron affinity of \( \text{IrF}_6^- \) has been estimated at \( \leq 160 \text{ kcal/mol} \) (6.9 eV)\(^{13}\). Also, no dioxygenyl salt has been observed\(^8\) from the interaction of \( \text{IrF}_6^- \) and several atmosphere of \( \text{O}_2 \) at room temperature. \( \text{O}_2\text{PtF}_5 \) is found to be quite soluble in AHF and can be recrystallized quantitatively from AHF. This indicates that \( \text{O}_2^+ \) is incapable of oxidizing \( \text{PtF}_6^- \) in AHF solution at least at \( \sim 20^\circ \text{C} \). The electron affinity of \( \text{PtF}_6 \) has been estimated at 182 kcal/mol (7.9 eV), approximately 1 eV higher\(^{13}\) than \( \text{IrF}_6^- \).

\( \text{O}_2\text{AsF}_6 \) interacts with \( \text{AgF} \) in AHF to produce \( \text{AgFAsF}_6 \) at 70 - 75% yield:

\[
\text{AgF} + \text{O}_2\text{AsF}_6 \xrightarrow{\text{AHF}} \text{AgFAsF}_6 + \text{O}_2 \quad (6)
\]

\( \text{AgF}_2 \) is produced as the major byproduct in this reaction. The reaction proceeds differently, depending on whether the \( \text{O}_2\text{AsF}_6 \) solution is poured into the \( \text{AgF} \).
solution or vice versa. When the $\text{O}_2\text{AsF}_6$ solution was poured into the $\text{AgF}$ solution, $\text{AgF}_2$ was generated first and the blue solution characteristic of solvated $\text{Ag}^{2+}$ appeared later. When the $\text{AgF}$ solution was poured into the $\text{O}_2\text{AsF}_6$ solution instead, that solution became blue immediately and $\text{AgF}_2$ began to precipitate only as the concentration of $\text{Ag}^{(II)}$ increased and $\text{O}_2^+$ decreased.

Since $\text{O}_2\text{AsF}_6$ is recovered almost quantitatively from the AHF solution (the slight loss being attributable to oxidation of the container surface) and since the solution is colorless (therefore significant production of the strongly absorbing red radical$^{14}$ $\text{O}_2\text{F}$ cannot occur) the ionization of the salt is likely to be complete:

$$\text{O}_2\text{AsF}_6 \xrightleftharpoons{\text{AHF}} {\text{O}_2}^+ (\text{solv}) + \text{Ag}^{2+}(\text{solv}) \quad (7)$$

When a strong base such as $\text{AgF}$ is present, however, $\text{O}_2\text{F}$ is displaced and this can act effectively as a fluorine atom source. The oxidation of $\text{Ag(I)}$ to $\text{Ag(II)}$ can be brought about in that way:

$$\text{Ag}^+ + \text{O}_2\text{F} \rightarrow \text{O}_2 + \text{AgF}^+ \quad (8)$$

as well as by interaction with $\text{O}_2^+$:

$$\text{Ag}^+ + \text{O}_2^+ + \text{F}^- \rightarrow \text{AgF}^+ + \text{O}_2 \quad (9)$$

But either way, the high $\text{F(HF)}_n$ concentration, existing in the $\text{AgF}$-rich solution, ensures precipitation of $\text{Ag}^{(II)}$ as $\text{AgF}_2$: 
AgF⁺ + F(HF)ₙ⁻ → AgF₂ + nHF  \hspace{1cm} (10)

Addition of AgF to the O₂AsF₆ solution ensures that the reaction mixture is not basic (i.e., not rich in F(HF)ₙ⁻) until near the end of the interaction. For the reverse reaction of addition of the O₂AsF₆ solution to the AgF solution, the reacting mixture is strongly basic at the outset and becomes less so as the mixing proceeds. The late appearance of AgF₂ in the former and its early appearance in the latter is therefore easily understood.

As anticipated, the reaction between O₂AsF₆ and AgAsF₆ avoids the F⁻ rich environment and thus produces AgFAsF₆ quantitatively and cleanly:

\[ \text{AgAsF}_6 + \text{O}_2\text{AsF}_6 \xrightarrow{\text{AHF}} \text{Ag(AsF}_6)_2 + \text{O}_2 \]  \hspace{1cm} (11.1)

\[ \text{Ag(AsF}_6)_2 \xrightarrow{\text{evac}} \text{AgFAsF}_6 + \text{AsF}_5 \]  \hspace{1cm} (11.2)

In neutral AHF, O₂AsF₆ oxidizes AgF₂ rapidly to generate a novel material (AgF₂)₃AsF₆, in which the average silver oxidation state is 2½. Reaction 6 proceeds quantitatively. Detailed discussion is given in Chapter 10.

\[ 3\text{AgF}_2 + \text{O}_2\text{AsF}_6 \xrightarrow{\text{AHF}} (\text{AgF}_2)_3\text{AsF}_6 + \text{O}_2 \]  \hspace{1cm} (12)

Under basic conditions in the presence of KF, O₂AsF₆ is able to oxidize Ag(I) in AgF or Ag(II) in AgF₂ to Ag(III) in anionic AgF₄⁻ ideally as follows:

\[ \text{AgF} + 3\text{KF} + 2\text{O}_2\text{AsF}_6 \xrightarrow{\text{AHF}} \text{KAgF}_4 + 2\text{KAsF}_6 + 2\text{O}_2 \]  \hspace{1cm} (13)
The yield of KAgF$_4$ from the interaction of O$_2$AsF$_6$ with AgF + KF is quite low, its presence in the mixed product, however, being clearly confirmed by the vibrational data (see Figure 8.1). The reaction yield from the interaction of O$_2$AsF$_6$ with AgF + KF is quite satisfactory, being as high as 42%. Since some AgF$_4^-$ is probably solvolyzed by HF to generate AgF$_3$ and F(HF)$_n^-$. This presents a lower limit on AgF$_4^-$ formation. This is only the second time that the oxidation of Ag in lower oxidation states to Ag(III) has been achieved at ambient temperature. AgF$_4^-$ has been previously prepared$^9$ at room temperature in basic HF using KrF$_2$. The synthesis of KAgF$_4$ ordinarily requires the fluorination a mixture of KCl or KNO$_3$ and AgNO$_3$ at 350 - 400°C, the treatment with F$_2$ being carried out for several times$^{15}$. The yield of reaction 13 and 14 is probably also diminished by the loss of O$_2^+$ in combining with F$^-$ to generate O$_2$F radical, decomposition of which, to O$_2$ and F$_2$, wastes oxidizing capability. The reaction yield of the oxidation of AgF to AgF$_4^-$ is particularly low because it involves the extra step to oxidize Ag(I) to Ag(II) during which the oxidizing power of O$_2^+$ can also be lost in combining with F$^-$ to form O$_2$F. The oxidation reaction may proceed from AgF$_2$ as follows:

$$\text{AgF}_2 + 2\text{KF} + \text{O}_2\text{AsF}_6 \xrightarrow{\text{AHF}} \text{KAgF}_4 + \text{KAsF}_6 + \text{O}_2$$

(14)

$$\text{AgF}_2 + \text{F(HF)}_n^- \Leftrightarrow \text{AgF}_3^- + n\text{HF}$$

(15.1)

$$\text{AgF}_3^- + \text{F(HF)}_n^- \Leftrightarrow \text{AgF}_4^{2^-} + n\text{HF}$$

(15.2)

$$\text{AgF}_3^- + \text{O}_2^+ \rightarrow \text{AgF}_3 + \text{O}_2$$

(15.3)
There is no detectable interaction between solvated Ag\(^{2+}\) cation and O\(_2\)AsF\(_6\) in acidic HF. Neither is there interaction between (AgF\(_2\))\(_3\)AsF\(_6\) and O\(_2\)AsF\(_6\).

8.3.3. The oxidation chemistry of solvated Ag\(^{2+}\)

It has been demonstrated that cationic Ag(II) is capable of oxidizing Xe at ordinary pressure and temperature\(^5\). The initial attempt to oxidize O\(_2\) with cationic Ag(II) under similar conditions failed even though the first ionization potentials of O\(_2\) and Xe are the same. In Chapter 7 it has been argued that the apparent ionization potential of the solvated Xe in AHF is probably lower because of the impact of the solvent cage. Recently, William Casteel has discovered\(^6\) that the cationic Ag(II) is able to oxidize O\(_2\) at temperatures below -60°C when the AHF solution is highly acidic in AsF\(_5\):

\[
\text{Ag(AsF}_6\text{)}_2 + \text{O}_2 \xrightarrow{\text{AsF}_5/\text{AHF}} \text{O}_2\text{AsF}_6(s) + \text{AgAsF}_6(s) \tag{16}
\]

In this study, the possible catalytic property of Ag(II) for the reaction system O\(_2\), AsF\(_5\) and F\(_2\) has been explored (reaction 17). With vigorous stirring, in a solution in which the volume ratio of AsF\(_5\)/HF is approximately 1:2, Ag(II) was found to be completely reduced to Ag(I) in the oxidation of O\(_2\), the blue solution rapidly becoming paler and eventually colorless in 2-4 hours at -78°C. Simultaneously colorless AgAsF\(_6\) and O\(_2\)AsF\(_6\) precipitate. Therefore, the
forward reaction can essentially go to completion under strongly acidic conditions. Under less acidic conditions, the blue solution quickly becomes paler but does not become completely colorless. Unfortunately, even with very good mixing solid AgAsF\(_6\) cannot be converted back to Ag(II) by F\(_2\) at -78°C, and oxygen uptake ceases when all Ag(II) has been consumed.

In the study of the fluorination of AgAsF\(_6\) under very acidic condition, the conversion of AgAsF\(_6\) to Ag(II) by F\(_2\) is unsuccessful until the temperature reaches ~0°C. AgAsF\(_6\) alone is of low solubility in neutral AHF. It seems that high concentration of AsF\(_5\) in AHF, and therefore high concentration of AsF\(_6^−\), further suppresses the solubility of the AgAsF\(_6\). The failure of the fluorination below 0°C must therefore be a consequence of exceedingly low concentration of Ag(I) ion in solution. The concentration of F\(_2\) must also be low. This inability to regenerate Ag(II) in solution from the solid AgAsF\(_6\) at low temperatures prevents reaction 17 to take place in a catalytic manner.

\[
O_2 + AsF_5 + F_2 \xrightarrow{Ag(II)/AsF_6/AHF} O_2AsF_6
\]  

(17)

The powerful oxidizing property of cationic Ag(II) as a one-electron oxidizer can be utilized in making other high oxidation state species. The reduced Ag(I) being in the form of low solubility AgAsF\(_6\) renders cationic Ag(II) a clean reagent in some syntheses.

All attempts to generate and preserve Cl\(_2^+\) in highly acidic media have thus far been unsuccessful\(^\text{16,17}\). The interaction\(^\text{18}\) of Cl\(_2\) and IrF\(_6\), although providing some evidence of Cl\(_2^+IrF_6^−\) as the intermediate product, quickly degrades via Cl\(_3^+\) salts to the pentafluoride of iridium, Ir\(_5\)F\(_{20}\). The relative poor F\(^−\) acceptor strength of the latter is responsible for this failure. Employing Ag\(^{2+}\)
as the oxidizing reagent provides a rational synthetic route to make Cl$_2^+$. AsF$_6^-$ may be able to stabilize Cl$_2^+$ because of the remarkable stability of AsF$_6^-$ (in contrast with that of IrF$_6^-$).

A blue solution of Ag(AsF$_6$)$_2$, with very high concentration of AsF$_5$, interacts with Cl$_2$ rapidly at -60°C. The solution quickly became blue-green and finally emerald green. Simultaneously, colorless AgAsF$_6$ precipitated. Upon removal of AHF at -60°C, this green solution became paler and the lower part of the solution gradually turned pale yellow as a yellow solid precipitated. The yellow solid proved to be unstable at higher temperatures and decomposed with loss of volatiles. A white residue was eventually obtained but has not yet been identified. It was not $^{19}$ ClF$_2^+$AsF$_6^-$. By analogy to Br$_2^+$ and I$_2^+$, the Cl$_2^+$ is expected$^{17}$ to have a strong visible absorption at around 400 nm which could give it green color. The first step in the reaction is probably the oxidation of Cl$_2$ to Cl$_2^+$ (reaction 18), and the green color of the solution may therefore be characteristic of Cl$_2^+$ in AHF. Cl$_2^+$ may only be stable under highly acidic conditions. Decomposition could proceed according to reaction 19 as AsF$_5$ is being removed together with AHF. The observed yellow solid answers the description$^{20}$ of Cl$_3^+$AsF$_6^-$, which is known to dissociate into Cl$_2$, ClF, and AsF$_5$ at ordinary temperatures (reaction 20).

$$\text{Cl}_2 + \text{Ag(AsF}_6\text{)}_2 \xrightarrow{\text{AsF}_5/\text{AHF}} \text{Cl}_2^+\text{AsF}_6^- + \text{AgAsF}_6(\text{s})$$  \hspace{1cm} (18)

$$\text{Cl}_2^+\text{AsF}_6^- \rightarrow \text{Cl}_3^+\text{AsF}_6^- + \text{ClF} + \text{AsF}_5$$  \hspace{1cm} (19)

$$\text{Cl}_3^+\text{AsF}_6^- \rightarrow \text{Cl}_2 + \text{ClF} + \text{AsF}_5$$  \hspace{1cm} (20)
The vibrational frequency of Cl$_2^+$ in the gas phase$^{21}$ has been determined at 645.3 cm$^{-1}$. A Raman spectroscopy study at low temperature on the green solution may be able to confirm whether Cl$_2^+$ is present or not. The white residue also needs to be identified to fully understand the reaction process.

8.3.4. Assessing the relative oxidizing powers of O$_2^+$ and Ag$_2^+$ in AHF

The 2nd ionization potential$^{22}$ of Ag, 21.49 eV, is the highest among any of the non-alkali metals. It is even higher than the 2nd I.P. of Xe (21.21 eV). The covalent interaction between Ag$_2^+$ and solvent molecules, such as HF, must be weakened by the strongly antibonding effect of the d$^9$ configuration. But because of the high charge and small cationic size, the solvation energy must still be high. It should be noted that Ag$_2^+$ is remarkably soluble in very acidic HF even at -78°C, probably owing to this high solvation energy. It has been demonstrated that Ag$_2^+$(solv) is a powerful oxidizer both in water$^{23}$ and in HF. But the electron affinity of Ag$_2^+$(solv) must be very much lower than the 2nd ionization potential of the gas because of the high solvation energy.

The lower limit of IP(Ag$^+$(solv)$\rightarrow$Ag$_2^+$(solv)) can be evaluated from the Born-Haber cycle given in Figure 8.2 where $E_{\text{solv}}$, and $U_L$ stand for the solvation energy and the lattice energy, respectively.

$$O_2(g) + Ag^{2+}(\text{solv}) + 2AsF_6^-(\text{solv}) \xrightarrow{\Delta H} \text{AgAsF}_6(s) + O_2\text{AsF}_6(s)$$

$$\Delta H_1$$

$$O_2^+(\text{solv}) + Ag^+(\text{solv}) + 2AsF_6^-(\text{solv}) \xrightarrow{\Delta H_2}$$

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\[ \Delta H_1 = \text{IP}(O_2(g) \rightarrow O_2^+(g)) - E_{\text{solv}}(O_2^+(g)) - \text{IP}(\text{Ag}^+(\text{solv}) \rightarrow \text{Ag}^{2+}(\text{solv})) \]

\[ \Delta H_2 = -U_L(\text{AgAsF}_6) - U_L(O_2\text{AsF}_6) + E_{\text{solv}}(O_2^+(g)) + E_{\text{solv}}(\text{Ag}^+(g)) \]

\[ \Delta H = \text{IP}(O_2(g) \rightarrow O_2^+(g)) - \text{IP}(\text{Ag}^+(\text{solv}) \rightarrow \text{Ag}^{2+}(\text{solv})) + E_{\text{solv}}(\text{Ag}^+(g)) - U_L(\text{AgAsF}_6) - U_L(O_2\text{AsF}_6) \]

Figure 8.2. Born-Haber Cycle for the oxidation of \( O_2 \) by \( \text{Ag}^{2+} \)

The \( T\Delta S \) term is negative for the reaction going from the gaseous and liquid states to the solid state. This negative \( T\Delta S \) term makes the forward reaction unfavorable at higher temperature. Because reaction proceeds as written below at -60\(^\circ\)C but is reversed above that temperature, \( \Delta H \) must be negative for \( \Delta G \) to be negative below -60\(^\circ\)C, but the value of \( \Delta H \) must also be small. The lattice energy can be estimated within \(-5 \text{ kcal/mole} \) for each of \( \text{AgAsF}_6 \) and \( O_2\text{AsF}_6 \). Therefore, from the calculated \( U_L(O_2\text{AsF}_6) \) (131 kcal/mol) and \( U_L(\text{AgAsF}_6) \) (140 kcal/mol)\(^{24} \), and the ionization potential of gaseous \( O_2 \) (280 kcal/mol), we have

\[ \Delta H = 280 - 131 - 140 - \text{IP}(\text{Ag}^+(\text{solv}) \rightarrow \text{Ag}^{2+}(\text{solv})) + E_{\text{solv}}(\text{Ag}^+(g)) < 0 \]

\[ \therefore \text{IP}(\text{Ag}^+(\text{solv}) \rightarrow \text{Ag}^{2+}(\text{solv})) > E_{\text{solv}}(\text{Ag}^+(g)) + 9 \quad \text{(kcal/mol)} \]

This indicates that the oxidation of \( O_2 \) by solvated \( \text{Ag}(\text{II}) \) in highly acidic HF at low temperatures is lattice energy driven as the high \( \text{IP}(O_2(g) \rightarrow O_2^+(g)) \) is offset by the lattice energy released from the formation of solid \( \text{AgAsF}_6 \) and \( O_2\text{AsF}_6 \). It
may be possible to reliably estimate $E_{\text{solv}}(\text{Ag}^+(\text{g}))$ from a set of solubility studies. If so this will provide a lower limit for IP(\text{Ag}^+(\text{solv}) \rightarrow \text{Ag}^{2+}(\text{solv})).

The upper limit of IP(\text{Ag}^+(\text{solv}) \rightarrow \text{Ag}^{2+}(\text{solv})) can be evaluated from the oxidation of Ag$^+$\text{(solv)} to Ag$^{2+}$\text{(solv)} by O$^2+$\text{(solv)} at room temperature. When the AgF solution is poured into the O$_2$AsF$_6$ solution, the solution rapidly becomes blue, indicating that the oxidation of Ag$^+$\text{(solv)} to Ag$^{2+}$\text{(solv)} by O$^2+$\text{(solv)} is very favorable at room temperature:

\[
\text{O}_2^+(\text{solv}) + \text{Ag}^+(\text{solv}) \xrightarrow{\Delta H} \text{Ag}^{2+}(\text{solv}) + \text{O}_2(\text{g})
\]  

(21)

\[
\Delta H = -\text{IP(O}_2(\text{g}) \rightarrow \text{O}_2^+(\text{g})) + E_{\text{solv}}(\text{O}_2^+(\text{g})) + \text{IP}(\text{Ag}^+(\text{solv}) \rightarrow \text{Ag}^{2+}(\text{solv}))
\]

\[
= -\text{IP(O}_2(\text{g}) \rightarrow \text{O}_2^+(\text{solv})) + \text{IP}(\text{Ag}^+(\text{solv}) \rightarrow \text{Ag}^{2+}(\text{solv}))
\]

As a consequence of its higher charge, the standard entropy, $S^\circ$, for Ag$^{2+}$\text{(solv)} must be smaller than that for Ag$^+$\text{(solv)}, but only by a small amount. The sign of the entropy change for this reaction must be positive. The entropy of gaseous O$_2$ can be used to set the upper limit for the entropy change for reaction 21 although the actual entropy change must be smaller than $S^\circ(\text{O}_2(\text{g}))$ (49 e.u.). At room temperature (295 K), the T\Delta S term is then smaller than 14 kcal/mol.

\[\Delta G = \Delta H - T\Delta S < 0; \quad \Delta H < T\Delta S < 14\]

\[\therefore \quad \text{IP(\text{Ag}^+(\text{solv}) \rightarrow \text{Ag}^{2+}(\text{solv})) < IP(\text{O}_2(\text{g}) \rightarrow \text{O}_2^+(\text{solv})) + 14 \text{ (kcal/mol)}\]

Ag$^{2+}$\text{ (solv)} has been found to be capable of oxidizing IrF$_6^-$\text{ (solv)} in acidic HF at room temperature$^{25}$, although the reaction appears to reach an equilibrium
and does not go to completion unless the oxidation product IrF$_6$ is removed. In comparison, the oxidation of IrF$_6^{\text{-}}$(solv) to IrF$_6$(solv) by O$_2^+$(solv) is very fast and complete at room temperature. It should be noted that in the latter reaction the entropy term is more favorable due to the generation of gaseous O$_2$. Therefore, IP(Ag$^+$(solv)$\rightarrow$Ag$^{2+}$(solv)) is probably comparable to IP(O$_2$(g)$\rightarrow$O$_2^+$(solv)) with 

$[\text{IP(O}_2\text{(g)$\rightarrow$O}_2^+\text{(solv)}] + 14\] \text{kcal/mol being the upper limit.}$

It may be possible to evaluate the solvation energy of O$_2^+$ in HF from a set of solubility studies. Once $E_{\text{solv}}(\text{O}_2^+(\text{g}))$ is known, we have

$$\text{IP(O}_2\text{(g)$\rightarrow$O}_2^+\text{(solv)}\right) = \text{IP(O}_2\text{(g)$\rightarrow$O}_2^+\text{(g)} - E_{\text{solv}}(\text{O}_2^+(\text{g}))}$$

The electron affinity of PtF$_6$ (7.9 eV) is 1 eV higher$^{13}$ than IrF$_6$ (-6.9 eV). PtF$_6$ and IrF$_6$$^{26}$, or PtF$_6^-$ and IrF$_6^-$$^{27}$ are comparable in size. Because of the similarity in size the solvation energies for the hexafluorides are probably close, as are also for those of the anions. For the following reaction:

$$\text{O}_2^+(\text{solv}) + \text{IrF}_6^{\text{-}}(\text{solv}) \xrightarrow{\Delta H} \text{IrF}_6(\text{solv}) + \text{O}_2(\text{g}) \quad (22)$$

\[
\Delta H = -\text{IP(O}_2\text{(g)$\rightarrow$O}_2^+(\text{g})} + E_{\text{solv}}(\text{O}_2^+(\text{g})) + \text{EA(IrF}_6) + E_{\text{solv}}(\text{IrF}_6^-) - E_{\text{solv}}(\text{IrF}_6)
\]

\[
= -\text{IP(O}_2\text{(g)$\rightarrow$O}_2^+\text{(solv})} + \text{EA(IrF}_6) + E_{\text{solv}}(\text{IrF}_6^-) - E_{\text{solv}}(\text{IrF}_6)
\]

As for the reaction 21, the entropy of gaseous O$_2$ can be used to set the upper limit for the entropy change for reaction 22 since the actual entropy change is probably smaller than $S^0(O_2(\text{g}))$ (49 e.u.). At room temperature (295 K), the $T\Delta S$ term is then smaller than 14 kcal/mol.
\[ \Delta G = \Delta H - T \Delta S < 0; \quad \Delta H < T \Delta S < 14 \]

\[ \therefore \text{IP}(\text{O}_2(g) \rightarrow \text{O}_2^+(\text{solv})) > \text{EA}(\text{IrF}_6^-) + \text{E}_{\text{solv}}(\text{IrF}_6^-) - \text{E}_{\text{solv}}(\text{IrF}_6) - 14 \\
> 146 + \text{E}_{\text{solv}}(\text{IrF}_6^-) - \text{E}_{\text{solv}}(\text{IrF}_6) \quad \text{(kcal/mol)} \]

The upper limit for \( \text{IP}(\text{O}_2(g) \rightarrow \text{O}_2^+(\text{solv})) \) can then be reasonably set at [169 + \( \text{E}_{\text{solv}}(\text{IrF}_6^-) - \text{E}_{\text{solv}}(\text{IrF}_6) \)] kcal/mol.

**8.4. Conclusions**

It has been demonstrated that \( \text{O}_2^+ \) cation in AHF is a very powerful one-electron oxidizer, capable of oxidizing \( \text{IrF}_6^- \) to \( \text{IrF}_6 \), and \( \text{Ag}^+ \) to cationic \( \text{Ag}^2+ \). It can even oxidize \( \text{Ag(I)} \) and \( \text{Ag(II)} \) to \( \text{Ag(III)} \) in anionic \( \text{AgF}_4^- \) under basic conditions, or oxidize \( \text{Ag(II)} \) to \( (\text{AgF}_2)_3\text{MF}_6 \).

The remarkable oxidizing power of solvated cationic \( \text{Ag}^2+ \) in acid-rich HF has been assessed with thermodynamic considerations. The upper and lower limits in \( \text{kcal/mol} \) of the oxidizing power of solvated \( \text{Ag}^2+ \) have been defined:

\[ \text{E}_{\text{solv}}(\text{Ag}^+(g)) + 9 < \text{IP}(\text{Ag}^+(\text{solv}) \rightarrow \text{Ag}^2+(\text{solv})) < \text{IP}(\text{O}_2(g) \rightarrow \text{O}_2^+(\text{solv})) + 14 \]

Once the solvation energies of \( \text{Ag}^+ \) and \( \text{O}_2^+ \) in AHF are assessed, the oxidizing power of solvated \( \text{Ag}^2+ \) can be more quantitatively placed. An interaction of \( \text{Ag}^2+ \) and \( \text{Cl}_2 \) in AHF may proceed via a \( \text{Cl}_2^+ \) salt but it is unstable at ordinary temperatures.
8.5. References


8 Jha, N.K., Ph.D. Thesis, Univ. of British Columbia (1966)


14 Turner, J.J., Endeavour, 1968, 27(100), 42.


The powder photograph shows AgAsF$_5$ to be face-centered cubic, $a = 7.74\,\text{Å}$, $Z = 4$, Unit cell Volume = $463.7\,\text{Å}^3$. The lattice energy could be slightly higher due to polarization.

Lucier, G., unpublished results, U.C. Berkeley, 1992


Figure 8.1. Raman spectrum of a mixture of KAgF$_4$ and KAsF$_6$
Chapter 9

Compounds of Ag(I, II) with Complex Oxyfluorotungstate Anions

9.1. Introduction

Recently, several AgF+ salts with simple fluorometallate counter anions have been prepared\textsuperscript{1,2,3,4,5}. AgFAsF\textsubscript{6} and AgFBF\textsubscript{4} were synthesized by either reacting AgF\textsubscript{2} with the corresponding Lewis acid AsF\textsubscript{5} and BF\textsubscript{3} or by fluorinating AgAsF\textsubscript{6} and AgBF\textsubscript{4}\textsuperscript{1,2,3}. AgFlrF\textsubscript{6} was also prepared by fluorinating AgIrF\textsubscript{6}\textsuperscript{5}. AgFAuF\textsubscript{6} and AgFAuF\textsubscript{4} were prepared through metathesis reactions with AgFAsF\textsubscript{6}\textsuperscript{4}. In these compounds the AgF+ cation exists as a one-dimensional chain (AgF)\textsubscript{n}\textsuperscript{n+}. Single crystal structure analysis has shown that AgFAsF\textsubscript{6} and AgFlrF\textsubscript{6} are very alike structurally\textsuperscript{1,5}. (AgF)\textsubscript{n}\textsuperscript{n+} in AgFAsF\textsubscript{6} and AgFlrF\textsubscript{6} is a zigzag chain with F ligands symmetrically bridging Ag(II) in the chain, the Ag-F bond distances in the chain in both compounds being 2.00 Å within the experimental error. Interestingly, the (AgF)\textsubscript{n}\textsuperscript{n+} chains in AgFBF\textsubscript{4} are linear\textsuperscript{3}, the Ag-F bond distance again being 2.00 Å.

In this study, two new AgF+ salts with complex oxyfluorotungstates have been synthesized and single crystal growth of both compounds has been successfully achieved. One AgF+ salt has a dimeric W\textsubscript{2}O\textsubscript{2}F\textsubscript{9}− anion and the other has a complex anion formed by WOF\textsubscript{5}− with BF\textsubscript{3}. The structures of these two new AgF+ salts are inherently interesting as they are the first AgF+ salts containing irregularly shaped anions as the counter anions. The impact of the irregular anion shape on the cation geometry is a primary interest but the nature of the interaction of WOF\textsubscript{5}− with BF\textsubscript{3} is also of same significance.

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The relative stabilities of the AgF⁺ salts and the failure to prepare AgFWOF₅ will be discussed in the context of the Lewis acid character of the (AgF)ₙⁿ⁺ cation.

9.2. Experimental

9.2.1. Materials

The preparation of WOF₄ was as previously described⁶, ⁷. The sublimation product was checked by Raman spectroscopy and X-ray powder photography and was found to be free of detectable contaminants. WF₆ was treated with KF to minimize the HF impurity before use in the reaction. Quartz wool, dried in the oven, was used as the source of SiO₂.

9.2.2. Preparation of AgWOF₅

Inside the DRILAB, WOF₄ (0.3149 g, 1.142 mmole) and AgF (0.1680 g, 1.324 mmole) were loaded, respectively, into the side arm and the main tube of a prepassivated T-shaped Teflon-FEP reactor. AHF (~1.5 ml) was condensed on to the AgF and WOF₄ in approximately equal amounts. Both solids dissolved in AHF upon warming to room temperature to give colorless solutions. To avoid the formation of AgW₂O₂F₉ during the reaction, the WOF₄ solution was decanted into the AgF solution in the main tube of the reactor. White solid AgWOF₅ immediately began to precipitate out as the two solutions were mixed. This solution was agitated for a few minutes to ensure complete mixing. The supernatant solution was decanted thoroughly into the main tube, the white solid being thoroughly drained of solution. To avoid solvolysis of AgWOF₅ to AgW₂O₂F₉, the white solid was washed. The AHF was removed under dynamic vacuum and the AgWOF₅ was vacuum-dried for several hours. Raman
spectroscopy confirmed that it was mainly AgWO\textsubscript{5}, containing only a small amount of AgW\textsubscript{2}O\textsubscript{2}F\textsubscript{9} (see Figure 9.1).

### 9.2.3. Preparation of KW\textsubscript{2}O\textsubscript{2}F\textsubscript{9}

The reaction was originally designed to prepare KWOF\textsubscript{5}. Inside the DRILAB, KF (0.0720 g, 1.239 mmole) and WOF\textsubscript{4} (0.2335 g, 0.8465 mmole) were loaded, respectively, into the side arm and the main tube of a prepassivated T-shaped Teflon-FEP reactor. AHF (~1.5 ml) was condensed onto the KF and WOF\textsubscript{4}. The KF solution was decanted into the WOF\textsubscript{4} solution in the main tube of the reactor, and a white solid immediately precipitated. This solution was agitated for a short time. The supernatant solution was decanted into the side arm. The white solid was washed about 3 times by condensing HF back from the side arm. It appeared that the quantity of the white solid in the main tube was decreasing rather quickly in the process of washing with AHF. The residual AHF was removed under a dynamic vacuum from the white solid which was vacuum-dried for several hours. Raman spectroscopy showed that it was KW\textsubscript{2}O\textsubscript{2}F\textsubscript{9} (see Figure 9.2).

### 9.2.4. Synthesis and crystal structure of AgW\textsubscript{2}O\textsubscript{2}F\textsubscript{9}

#### 9.2.4.1. Preparation of AgW\textsubscript{2}O\textsubscript{2}F\textsubscript{9}

Inside the DRILAB, AgF (0.0715 g, 0.5628 mmole) and WOF\textsubscript{4} (0.3127 g, 1.134 mmole) were loaded, respectively, into the side arm and the main tube of a prepassivated T-shaped Teflon-FEP reactor. AHF (~1.5 ml) was condensed on to the AgF and WOF\textsubscript{4}. The AgF solution was decanted into the WOF\textsubscript{4} solution in the main tube of the reactor. White solid AgW\textsubscript{2}O\textsubscript{2}F\textsubscript{9} immediately began to precipitate as the two solutions were mixed. This solution was agitated for a
short time. The supernatant solution was decanted into the side arm. The white solid was washed several times by condensing HF back from the side arm. The AHF was removed under dynamic vacuum and the AgW₂O₂F₉ was vacuum-dried for several hours.

9.2.4.2. Crystal growth

The following synthesis was originally intended to grow crystals of AgWO₂F₅. A small amount of AgWO₂F₅ (35.0 mg, 0.0869 mmole) was loaded into the main tube of a prepassivated T-shaped FEP reactor. AHF (~2 ml) was condensed on to the white AgWO₂F₅ solid. The solution was gently agitated, but most of the white solid remained. About two-thirds of the clear supernatant solution was carefully decanted into the side arm. Subsequently, a small quantity of AHF was distilled from the main tube into the side arm to make the solution in the side arm under-saturated. The main tube was then cooled down to ~3°C below room temperature to slowly condense back HF from the side arm. Cube-like colorless crystals of suitable size for single X-ray crystallography study were obtained in the side arm over a period of 6-12 hrs. Towards the very end, the main tube was cooled down to 0°C to remove the last bit of HF from the side arm. To avoid violent boiling of the HF, it was removed by bleeding slowly through a valve to a dynamic vacuum. A very small residue of orange-yellow solid (probably AgF) formed on the bottom of the side arm where the last of the HF solution had been. The crystals were vacuum-dried for several hours under a dynamic vacuum of 10⁻³ torr.

9.2.4.3. Structural determination of AgW₂O₂F₉
Crystals were manipulated in a dry argon atmosphere in the Drilab on a prepassivated Teflon sheet. The selected crystal was mounted in a diam. 0.5 mm quartz capillary the narrow end of which had been further drawn down to a long tapered end. The crystal was wedged into the fine tip of the capillary by gently tapping the capillary. The quartz capillary was then flame sealed.

Precession photographs indicated the monoclinic P2₁/c space group and yielded approximate cell dimensions, β being very close to 90°. Data collection was carried out on an Enraf-Nonious CAD-4 diffractometer at room temperature. Automatic peak search and indexing procedures yielded the same monoclinic cell seen in the precession photographs, with β equal to 90.2°. The final cell parameters and specific data collection parameters for this data set are given in Table 9.1. The positional and thermal parameters are listed in Table 9.2, and inner-atomic distances and bond angles in Table 9.3 (a) and (b). Since the data appeared to suffer from severe absorption and the morphology of the crystal was not well defined, a semi-empirical correction (EAC) was first applied and then DIFABS was used on the corrected data set¹⁰.

*Table 9.1. Crystal data and details of the structure determination and refinement for AgW₂O₂F₉.*

<table>
<thead>
<tr>
<th>Formula, mol wt</th>
<th>AgW₂O₂F₉, 678.57 a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>temperature</td>
<td>295 K</td>
</tr>
<tr>
<td>a₀</td>
<td>10.402 Å</td>
</tr>
<tr>
<td>b₀</td>
<td>12.307 Å</td>
</tr>
<tr>
<td>c₀</td>
<td>13.639 Å</td>
</tr>
<tr>
<td>β</td>
<td>90.2°</td>
</tr>
<tr>
<td>V</td>
<td>1746.0 Å³</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/c (No. 14)</td>
</tr>
</tbody>
</table>
dealed.

Crystal size 0.25 · 0.18 · 0.17 mm; colorless
Wavelength (Mo Kα) 0.71069 Å
Diffractometer Enraf-Nonious CAD4, graphite monochromator
Scan range ±h, k, l
Scan angle 0.60 + 0.35 · tanθ
Data collected Independent 3054
Intensity standards (0-18), (0-6-5), (-317); measured every 1 hour of X-ray exposure time. Over the data collection period no decrease in intensity was observed.
orientation 3 reflections were checked after every 200 measurements. Crystal orientation was redetermined if any of the reflections were offset by more than 0.10 degree from their predicted positions. Reorientation was not needed during data collection.

Absorption correction ψ-scans, 4 hkl,
Structure solution Multan
Refinement Full matrix least squares, 254 parameters
Weighting scheme 1/σ²
Extinction correction \( F_{\text{corr}} = F_{\text{obs}} \cdot (1 + g \cdot l) \), \( g = 6.3 \times 10^{-8} \)
R, R' 0.0367
wR 0.0341
Goodness-of-fit 1.181

9.3. Attempted synthesis of AgFWOF₅

9.3.1. Fluorination of AgWOF₅

Inside the DRILAB, AgWOF₅ (0.121 g, 0.3005 mmole) was loaded into the side arm of a prepassivated T-shaped Teflon-FEP reactor. AHF (~1 ml) was condensed on to the AgWOF₅. Most of the white solid remained in the solution even with vigorous agitation. The reactor was pressurized to 1500 torr with F₂. The solution was continuously agitated and was periodically cooled down in
order to dissolve more F_2 in the solution. In a few minutes, the white solid appeared to be turning brown and the solution became quite cloudy. Small, fibrous crystallites appeared. These greenish bronze crystallites were voluminous and had a metallic luster. When agitation of the mixture was halted, a dark brown layer of solid quickly formed on the bottom of the tube and the voluminous bronze-luster crystallites floated in HF solution. At the end of the reaction, these crystallites turned into a film which stuck to the reactor wall upon removal of the HF under dynamic vacuum. The metallic bronze film and the dark brown solid was vacuum-dried for several hours. X-ray powder photography showed the brown solid to be AgF_2.

In attempts to grow the bronze crystals from the fluorination of AgWOF_5, less AgWOF_5 (35 mg) was used. The solution was not agitated and was left undisturbed until it appeared that all the white AgWOF_5 had been consumed. Invariably, dark brown AgF_2 was formed on the bottom of the solution and bronze, fibrous crystals formed in the solution. The AHF was removed by bleeding slowly through a valve to a dynamic vacuum. But the bronze crystals always formed a strongly adherent film on the reactor wall upon the removal of HF. No crystals were found in such films. Fluorination at 0°C only produced AgF_2 more quickly probably as a consequence of the greater solubility of the F_2 in AHF at this lower reaction temperature.

9.3.2. Interaction of WOF_4 and F_2 in AHF

Inside the DRILAB, WOF_4 (0.0742 g) was loaded into a prepassivated one arm Teflon-FEP reactor. AHF (~2 ml) was condensed on to the WOF_4. Upon warming to room temperature, WOF_4 dissolved completely to give a colorless solution. The reactor was then pressurized with F_2 to a total pressure
of over 1200 torr. The solution was continuously agitated for over 12 hrs. The solution was occasionally cooled down to dissolve more F\textsubscript{2} in the solution, and then vigorously agitated as it warmed up to room temperature. The solution remained colorless throughout the reaction. AHF and F\textsubscript{2} were removed under a dynamic vacuum and a white solid was retrieved. X-ray powder photography confirmed the white solid to be WOF\textsubscript{4}.

9.4. Synthesis of "AgFWOF\textsubscript{5}BF\textsubscript{3}"

9.4.1. Reaction of AgWOF\textsubscript{5}, BF\textsubscript{3}, and F\textsubscript{2} in AHF

Inside the DRILAB, AgWOF\textsubscript{5} (0.0703 g, 0.145 mmole) was loaded into the side arm of a prepassivated T-shaped Teflon-FEP reactor. AHF (~1 ml) was condensed on to the AgWOF\textsubscript{5}. The reactor was pressurized to about 1100 torr with BF\textsubscript{3}. With vigorous agitation, nearly all the white AgWOF\textsubscript{5} dissolved in the HF in the presence of BF\textsubscript{3}, and the solution appeared to become somewhat turbid. After the solution settled down, it became clear and there was a small amount of white precipitate. Enough F\textsubscript{2} was introduced into the reactor to achieve a total pressure of 1500 torr. The solution quickly turned blue and a blue solid started to form from the blue solution. The solution was continuously agitated for another 30 min. after it appeared that there was no more F\textsubscript{2} uptake. The blue supernatant solution was decanted into the main tube of the reactor and the blue solid was washed 2 to 3 times by condensing back HF. AHF and the volatiles were then removed under a dynamic vacuum and the blue product was vacuum-dried for several hours under a vacuum of 10\textsuperscript{-3} torr. The blue color of the product appeared to be lighter than that of AgFBF\textsubscript{4}. The X-ray powder pattern of the blue product showed a new phase with a marked resemblance to that of AgFBF\textsubscript{4} (this new phase will be hereafter referred to as the BLUE PHASE.
or the BLUE MATERIAL). The X-ray powder data with indexing are given in Table 9.4.

Table 9.4. X-ray powder data (Cu Kα, Ni filter) for the blue phase, orthorhombic cell with a = 6.77 Å, b = 6.60 Å, c = 11.78 Å, V = 526.1 Å³, possible space group Imm2.

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9.4.2. Reaction of AgBF₄, WOF₄, and F₂ in AHF

Inside the DRILAB, WOF₄ (0.0606 g, 0.220 mmole) and AgBF₄ were loaded, respectively, into the side arm and the main tube of a prepassivated T-shaped Teflon-FEP reactor. AHF (~1.5 ml) was condensed on to the WOF₄ and AgBF₄ in approximately equal amounts. The clear solution of WOF₄ was decanted into the AgBF₄ solution and AHF was condensed back into the main tube to rinse off any residual WOF₄ in the main tube. A small amount of BF₃ (~0.1 mmole) was admitted into the reactor. Enough F₂ gas was then introduced into the reactor to achieve a total pressure of 1500 torr. With vigorous stirring,
the solution quickly turned blue. A blue solid started to form in the solution, and
the amount of the white AgBF$_4$ quickly diminished. The solution was agitated for
another 30 min. after all the AgBF$_4$ had been consumed and there appeared to
be no more F$_2$ uptake. The blue supematant solution was decanted into the
main tube of the reactor and the remaining blue solid was washed several times
by condensing back HF. AHF and the volatiles were then removed under a
dynamic vacuum and the blue product was vacuum-dried for several hours. X-
ray powder photography showed the product to be the same blue phase as
prepared in Section 9.4.1.

9.4.3. The stability of "AgFWOF$_5$BF$_3$" in neutral AHF
The blue material was freshly made from the reaction described in Section
9.4.1. After the AHF, BF$_3$ and F$_2$ were removed from the reaction and the blue
material had been vacuum-dried, fresh AHF was condensed on to the blue
material under vacuum. As the HF was warming to room temperature, the blue
material quickly decomposed to give a dark brown solid. The colorless
supematant solution was decanted into the other arm of the reactor and the dark
brown solid was washed a few times. After the AHF was removed under a
dynamic vacuum, a white solid was obtained from the supematant solution. X-
ray powder photography showed the dark brown solid to be AgF$_2$ and the white
solid to be WOF$_4$.

9.4.4. Crystal growth of "AgFWOF$_5$BF$_3$"
Inside the DRILAB, AgBF$_4$ (12.7 mg, 0.0652 mmole) and WOF$_4$ (18.1
mg, 0.0656 mmole) were loaded into the main tube of a prepassivated Teflon-
FEP reactor. The main FEP tube was drawn down at about 2 cm from the end of
the tube to make a narrow neck. AHF (about 1 ml) was added on to this solid mixture just so that the level of HF was in the middle of the narrow neck. This was to reduce the surface area of the solvent in order to slow down the diffusion of F₂ into the solution. About 25 torr BF₃ (about 0.0721 mmole) and 100 torr F₂ (0.2883 mmole) were introduced into the reactor. The bottom part of the solution where the white AgBF₄ solid was kept at 0°C with an ice bath to reduce the solubility of AgBF₄ in AHF. Blue crystals slowly formed on the reactor wall between the AHF surface and the solid AgBF₄. The reaction was left undisturbed until it appeared that all of the AgBF₄ had been consumed. The supernatant solution was decanted into the side arm, care being taken to avoid disturbing the crystals. AHF and volatiles were then removed by bleeding them slowly through a valve to a dynamic vacuum, this slow removal was managed to avoid violent boiling of the HF. The crystals were then vacuum dried for several hours in a dynamic vacuum of 10⁻³ torr. In the crystal growth work, when the FEP tubes were not drawn down and no low temperature condition was employed, the crystals obtained were usually very small with no well-defined morphology. In one instance, those tiny crystals were left undisturbed in the solution for one week but they did not grow into larger crystals.

When AgWOF₅ was used as the starting material with BF₃ and F₂ to grow crystals of "AgFWOF₅BF₃", in the first few hours all the solid AgWOF₅ gradually dissolved and the solution turned blue. Crystals then started to form in the blue solution. Because of their rapid formation here, the crystals were very small and they tended to grow into each other and formed aggregates.

Crystals obtained from each of these two reaction routes were ground into powder and loaded into the 0.5 mm quartz capillary for powder X-ray diffraction studies. X-ray powder photographs of each sample confirmed that the crystals
were the same material and identical to the microcrystalline product from the same reactions.

9.4.4.1. Structural determination

A blue crystal of suitable size was mounted in a 0.5 mm quartz capillary with the end drawn out into a narrower capillary. Unlike the AgFBF$_4$ crystal$^5$, the transmitted light was not markedly anisotropic to polarized light. Preliminary work with precession photography gave approximate cell parameters in agreement with those derived from the X-ray powder data. Crystal imperfection (twinning) and the failure to fix an ideally imperfect crystal in a capillary have so far frustrated a full structure determination of the material.

9.5. Synthesis of AgFW$_2$O$_2$F$_9$

9.5.1. Reaction of AgWOF$_5$, WOF$_4$, and F$_2$ in AHF

Inside the DRILAB, AgWOF$_5$ (0.0836 g, 0.2076 mmole) and WOF$_4$ (0.0608 g, 0.2204 mmole) were loaded into the side arm of a prepassivated T-shaped Teflon-FEP reactor. AHF (~1 ml) was condensed on to this mixture. Enough F$_2$ gas was introduced into the reactor to achieve a total pressure of 1500 torr. The solution was vigorously agitated. A lavender solid started to form in the solution very quickly and the amount of the white solid diminished. The mixture was continuously agitated for 2-3 hours. When signs of F$_2$ uptake had ceased, the supernatant solution was decanted into the main tube and the lavender product was washed several times by distilling back AHF from the main tube. AHF and F$_2$ were then removed under a dynamic vacuum, and the lavender product was vacuum-dried for several hours. X-ray powder photography showed it to be free of the starting materials. The X-ray powder pattern of this
new phase was somewhat complex and has not been indexed (this new phase will be henceforth referred to as the LAVENDER PHASE). X-ray powder data are given in Table 9.5.

Table 9.5. X-ray powder data (Cu Kα, Ni filter) for the lavender AgFW₂O₂F₉

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9.5.2. Crystal growth

AgFW2O2F9 seems slightly soluble in AHF although the solution is not obviously colored. Single crystals, as purple plates, were obtained by slow evaporation of the HF solution.

Crystal growth of AgFW2O2F9 from slow fluorination of the corresponding Ag(I) salts was also studied. AgW2O2F9 (30 mg, 0.044 mmole) was used by itself, or in combination with a small amount of WOF4 (4 mg, 0.0145 mmole). In another case, AgWO5F (23.5 mg, 0.0584 mmole) and WOF4 (18.1 mg, 0.0656 mmole) with WOF4 in excess of 1:1 ratio were used as the starting materials. The amount of AHF was usually 1 - 1.5 ml. In some cases, the solution was cooled down to 0°C with an ice bath. Slow fluorination in these reactions invariably led to the formation of dark brown AgF2.

9.5.3. Interactions of AgW2O2F9, F2 in the presence of BF3 in AHF

Inside the DRILAB, AgW2O2F9 (0.0723 g, 0.107 mmole) was loaded into the side arm of a prepassivated T-shaped Teflon-FEP reactor. AHF (~1 ml) was condensed on to the AgW2O2F9. A small amount of BF3 (~0.1 mmole) was admitted into the reactor. Enough F2 was then introduced into the reactor to bring the total pressure to 1500 torr. With vigorous agitation, the solution turned purple in about 2 minutes and a lilac solid started to form in the solution. The solution was continuously agitated for ~30 min. after it appeared that all the AgW2O2F9 had been consumed. The supernatant solution was light blue and was decanted into the main tube, making sure as much as possible that the liquid on the lilac solid had drained away. The lilac solid was not washed by condensing back AHF as BF3 would be more soluble at lower temperature and it
would interact with the lilac material. AHF and F₂ were removed under a
dynamic vacuum and the lilac product was vacuum-dried for several hours. A
very small quantity of byproduct from the supernatant solution was milky white.
The lilac material was shown by X-ray powder photography to be a mixture of the
lavender AgFW₂O₂F₉ and the blue phase "AgFWOF₅BF₃".

In a similar experiment, after the reaction had proceeded to produce the
lilac product in the presence of BF₃, the lilac product was washed by condensing
AHF back on to it. The lilac product quickly turned blue in the cold distilled-back
HF. X-ray powder photography showed the blue product to be the blue phase
"AgFWOF₅BF₃".

9.6. Results and discussions

9.6.1. AgW₂O₂F₉

Crystals of AgW₂O₂F₉ were grown through the solvolysis of AgWOF₅ in
AHF via the following reaction:

\[ \text{AgWOF}_5 + n\text{HF} \xrightarrow{\text{AHF}} \text{AgW}_2\text{O}_2\text{F}_9 + \text{AgF(HF)}_n \]  (1)

The low solubility of AgW₂O₂F₉ and the high solubility of AgF combine to
comeplete the conversion of the AgW₂O₂F₉ as represented in equation (1).

The structure of AgW₂O₂F₉ has been solved. The coordination
environments of tungsten and silver in the AgW₂O₂F₉ structure are shown in
Figure 9.3 (a), (b) and Figure 9.4 (a), (b). There are two crystallographically
independent AgW₂O₂F₉ units in the structure and the bond lengths and angles
are slightly different in these two units (see Table 9.3 (a) and (b)). The dumbbell-
shaped W₂O₂F₉⁻ anions are bridged by fluorine atoms, F5 and F15. The oxygen
ligands are trans to the bridging F (Fₜ). The tungsten atoms are in distorted octahedral environments with the bond distances falling into three categories: (a) tungsten to nonbridging fluorines (Fₙₙ), 1.831 - 1.880 Å, (b) tungsten to bridging fluorines (Fₜ), 2.080 - 2.124 Å, (c) tungsten to oxygens, 1.636 - 1.672 Å. The variations in bond distances in the same group arise probably because of the interaction of fluorine atoms and oxygen atoms with silver atoms. The Fₙₙ-W-Fₜ angles are in the range of 80.5° - 83.5°. This angle, significantly smaller than 90°, is probably due to the high repulsive impact of the oxygen ligand and the weak repulsive effect of the distant nonbridging fluorine ligands. The oxygen and bridging fluorine ligands are in essentially linear array, with the O-W-Fₜ angles being 177.7° - 179.1°. The W₁-F₅-W₄ bridging angle is 163.6°, and W₂-F₁₅-W₃ is 152.3°. The appreciable bending of the latter appears to be a result of the coulombic attraction between silver atoms and the nonbridging fluorine ligands (see Figure 9.3 (a) (b)). This also explains why the two sets of nonbridging fluorines in the anion are not staggered, but rather eclipse one another. The coordination environments around the silver atoms are quite irregular.

There are some common features between the structure of AgW₂O₂F₉ and that of WOF₄. In the crystal structure of WOF₄ reported by Edwards and Jones¹¹ the oxygen atom was misassigned as the bridging atom even though the vibrational data clearly showed non bridging W=O group. The overall feature is still correct once bridging fluorines are properly assigned. WOF₄ is tetrameric in the structure with four corner-sharing distorted octahedra bridged through fluorine. The W-Fₜ-W bridging angle being 173°. The bond lengths are comparable to those in W₂O₂F₉⁻ and notably the nonbridging fluorines are also bent away from the oxygen ligands.
9.6.2. Fluorination of AgWOF₅

The fluorination of AgWOF₅ invariably leads to the formation of dark brown AgF₂ together with some light, voluminous, bronze-luster material:

\[
\text{AgWOF}_5 + F_2 \xrightarrow{\text{AHF}} \text{AgF}_2 + \text{bronze material} \quad (2)
\]

The light bronze material may have metallic character and needs to be identified.

So far, the known AgF⁺ salts have a stable "hard" counter anions, such as BF₄⁻, AsF₆⁻, IrF₆⁻, and AuF₆⁻. The AgF⁺ cation is probably a strong Lewis acid and the conjugate Lewis base AgF₂ correspondingly weak. It should be noted that the strongest Lewis acid SbF₅ effectively takes both F⁻ from AgF₂ to make Ag(SbF₅)₂ whereas the corresponding Ag(AsF₆)₂ salt has never been prepared. Evidently Ag²⁺ captures F⁻ to generate the polymeric (Ag-F)ₙ⁺ ion from all but the poorest fluorobase anions. The fluorination of AgBF₄ in the absence of or with an insufficient amount of BF₃ even leads to the formation of AgF₂. The washing of AgFBF₄ with AHF also produces some AgF₂. BF₃ is a relatively weak acid, and its conjugate Lewis base BF₄⁻ is correspondingly stronger, hence the ready conversion of AgFBF₄ to AgF₂ as BF₃ is removed from the equilibrium mixture in AHF:

\[
\text{AgFBF}_4 \xrightarrow{\text{AHF}} \text{AgF}_2 + \text{BF}_3 \quad (3)
\]

The failure to prepare AgFWOF₅ and the instability of AgFW₂O₂F₉ and "AgFWOF₅BF₃" in neutral HF appear to be consequences of the Lewis acidity of AgF⁺ cation. WOF₅⁻ appears to be too strong a Lewis base for AgF⁺, or WOF₄
is a weaker acid than AgF⁺. In contrast, the dimeric anion W₂O₂F₉⁻ and the complex anion (WO₅BF₃)⁻ appear to be able to stabilize the AgF⁺ cation.

9.6.3. "AgFWOF₅BF₃"

The blue material which probably has the formulation of "AgFWOF₅BF₃" is synthesized in the following reactions:

\[
\text{AgWOF}_5 + \text{BF}_3 + \frac{1}{2}\text{F}_2 \xrightarrow{\text{AHF}} \text{AgFWOF}_5\text{BF}_3
\] (4)

\[
\text{AgBF}_4 + \text{WO}_4 + \frac{1}{2}\text{F}_2 \xrightarrow{\text{AHF}} \text{AgFWOF}_5\text{BF}_3
\] (5)

Although the AgWOF₅ solid is only sparingly soluble in HF, it dissolves on addition of BF₃. Subsequent fluorination quickly produces the blue material which has a paler blue than AgFBF₄².

Raman data are consistent with the presence of both BF₄⁻ and WOF₅⁻ anions (see Figure 9.5). The results of variable temperature magnetic susceptibility measurement on the blue material, however, are very similar to those of the known AgF⁺ salts (see Figure 9.6). The low value of the temperature-independent paramagnetism indicates that the blue material is also an AgF⁺ salt. It is therefore possible that WOF₅⁻ and BF₃ form a complex anion like (WO₅BF₃)⁻ with a fluorobridged structure [OF₄W-F-BF₃]⁻ which could be consistent with the Raman spectra. The bridging role of F in the (WO₄)₄ tetramer indicates that a fluorine ligand is more likely to bridge to BF₃ than is the oxygen ligand of WOF₅⁻. A good quality structural study should settle this matter definitively.
The X-ray powder pattern has been indexed with an orthorhombic unit cell, \(a = 6.77 \text{ Å}, b = 6.60 \text{ Å}, \text{ and } c = 11.78 \text{ Å}\). The unit cell volume is 526.1 \(\text{Å}^3\). The average of the \(a\) and \(b\) parameters is 6.68 Å, very close to the \(a\) value (6.69 Å) of the tetragonal AgFBF₄. And the \(c\) parameter is approximately three times that of AgFBF₄ (4.00 Å). Consequently, the line positions of many of the corresponding \((hk0)\), \((hk3)\), and \((hk6)\) reflections of "AgFWOF₅BF₃" and AgFBF₄ are close to each other, giving rise to the similarity between the X-ray powder photographs. The systematic absence condition, \(h + k + l = 2n\), appears to hold for the reflections in the powder data, indicating that the orthorhombic cell is possibly body-centered. The probable space group is Im\(\text{mm}2\). It is difficult to deduce more information from the powder data at this stage. Crystal growth has been achieved by slow fluorination in reaction (7). Preliminary work with precession photograph confirms that the indexing of the powder data is correct. Suitable single crystals have been obtained for crystallographic work.

The disintegration of the blue material into AgF₂, BF₃, and WOF₄ upon washing with AHF is akin to the similar solvolysis of AgFBF₄:

\[
\text{AgFWOF}_5\text{BF}_3 \xrightarrow{\text{AHF}} \text{AgF}_2 + \text{BF}_3 + \text{WO}_4
\]

(6)

Thus the combined WOF₅⁻, BF₃ (probably as the fluorobridged anion [OF₄W-F-BF₃⁻]) is able to stabilize AgF⁺, which WOF₅⁻ alone is not, but the complex anion is evidently extensively solvolyzed by AHF.

9.6.4. AgFW₂O₂F₉

AgFW₂O₂F₉ has been produced via the following reactions in HF solutions:
AgWOF$_5$ + WOF$_4$ + 1/2F$_2$ $\xrightarrow{\text{AHF}}$ AgFW$_2$O$_2$F$_9$  \hspace{1cm} (7)

For reaction (7) to be effective, the ratio of WOF$_4$ to AgWOF$_5$ needs to be in excess of 1:1. This fluorination of AgW$_2$O$_2$F$_9$ thus needs some WOF$_4$ present.

With vigorous agitation, the reaction proceeded quickly. Fluorination of AgW$_2$O$_2$F$_9$ without excess WOF$_4$ present quickly produced some AgF$_2$.

Evidently excess fluoroacid is required in the AHF to prevent AgF$_2$ formation. Clearly WOF$_4$ must diminish the hydrofluoride anion concentration:

$$F(\text{HF})_n^- + 2\text{WOF}_4 \Leftrightarrow \text{W}_2\text{O}_2\text{F}_9^- + n\text{HF}$$ \hspace{1cm} (8)

Attempts to grow crystals from similar routes using slow fluorination have been unsuccessful, even when there was excess WOF$_4$ present. Invariably, AgF$_2$ was produced instead.

It has been found in the study of AgFBF$_4$ that the presence of a small amount of BF$_3$ in the fluorination of AgBF$_4$ helps to suppress the formation of AgF$_2$. In the fluorination of AgW$_2$O$_2$F$_9$, addition of a small amount of BF$_3$ helped to produce the lavender AgFW$_2$O$_2$F$_9$ although some "AgFWOF$_5$BF$_3" was also generated during the reaction.

AgW$_2$O$_2$F$_9$ + F$_2$ $\xrightarrow{\text{BF}_3/\text{AHF}}$ AgFW$_2$O$_2$F$_9$  \hspace{1cm} (9)

In the same reaction, when the solution was cooled down making BF$_3$ more soluble in the AHF, the lilac product was very quickly converted to the blue "AgFWOF$_5$BF$_3" via the interaction with BF$_3$:
It is possible that AgFW2O2F9 can also be prepared from the metathesis reaction between AgFAsF6 and KW2O2F9:

\[ \text{AgFW}_{2}\text{O}_2\text{F}_9 + \text{BF}_3 \xrightarrow{\text{AHF}} \text{AgFWOF}_5\text{BF}_3 + \text{WO}_4 \] (10)

At the same time as this work was carried out, Dr. Hagiwara and his coworkers in Kyoto University\textsuperscript{13} also synthesized AgFW2O2F9. They prepared it from the stoichiometric interaction of AgF2 and WOF4. The reaction was found to be very sluggish and was attributed to the low solubility of AgF2 in AHF. Attempts by Hagiwara et al to prepare AgFWOF5, Ag(WOF5)(W2O2F9), or Ag(W2O2F9)2 from the interaction of AgF2 and WOF4 were unsuccessful, the only new phase detected being AgFW2O2F9.

The magnetic data for AgFW2O2F9 indicate weak temperature independent paramagnetism at low and high fields from room temperature down to about 30K (see Figure 9.7). This weak temperature independent paramagnetism is very similar to that of other known AgF\textsuperscript{+} salts\textsuperscript{3}. Therefore the lavender material can be reasonably formulated as AgFW2O2F9, and not the structural isomer Ag(WOF5)2. The latter would be a simple one-electron paramagnet obedient to the Curie-Weiss law as observed\textsuperscript{3,14} for Ag(AuF4)2 and Ag(AgF4)2. It was also shown by Hagiwara et al from Raman and IR vibrational data that the lavender material contains the dimeric anion W2O2F9\textsuperscript{−} and not WOF5\textsuperscript{−}.
The magnetic behavior below 30 K is not yet understood. A crystal structure may provide a basis for understanding it.

It appears probable that the lilac crystalline solid AgFW₂O₂F₉ contains the (Ag-F)ₙ⁺ one-dimensional cation and the anion W₂O₂F₉⁻ but a crystal structure of AgFW₂O₂F₉ is needed to settle these conclusions definitively.

9.7. Conclusions

Two new AgF⁺ salts containing oxyfluorotungstate anions appear to be preparable. This is the first time that an AgF⁺ salt with complex anions such as the F bridged W₂O₂F₉⁻ have been prepared. Single crystals of these two new compounds have been obtained, therefore definitive structure are likely to be available in due course. The structure of AgW₂O₂F₉ has been solved and the anion W₂O₂F₉⁻ shown to a fluorine bridged species with the W=O bonds trans to the bridging F ligand.

Evidently (AgF)ₙ⁺ chain polymer can be stabilized by [OF₄W-F-WF₄O]⁺ and [OF₄W-F-BF₃]⁺ but not by [OWF₅]⁺, thus WOF₄ in this context is an inferior fluoroacid to BF₃ since BF₄⁻ stabilizes the (AgF)ₙ⁺ cation. Thus BF₄⁻, W₂O₂F₉⁻, WO₅BF₃⁻ are comparable, and weaker fluorobase than WOF₅⁻.
9.8. References

6 Wilson, W.W., Christe K.O., Inorg. Syn. 12, 37
Table 9.2. Positional parameters and their estimated standard deviations for AgW₂O₂F₉.

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**Table 9.3 (p.4)** Intramolecular bond angles in Ag₂O₂F₂.
Figure 9.1. Raman spectrum of AgWOF₅, region 1 and 2
Figure 9.2. Raman spectrum of KW$_2$O$_2$F$_9$, region 1 and 2
Figure 9.3 (a) Tungsten (W1 and W4) coordination environment in AgW$_2$O$_2$F$_9$
Figure 9.3 (b) Tungsten (W2 and W3) coordination environment in AgW₂O₂F₉.
Figure 9.4 (a) Silver (Ag1) coordination environment in AgW2O2F9
Figure 9.4 (b) Silver (Ag2) coordination environment in AgW2O2F9
Figure 9.5. Raman spectrum of AgFWOF$_5$BF$_3$, region 1 and 2
Figure 9.6. Magnetic susceptibility data for AgFWOF$_5$BF$_3$
Figure 9.7. Magnetic susceptibility data for AgFW₂O₂F₉
Chapter 10

Pseudo-trifluoride $(AgF_2)_3MF_6$: Syntheses and Structures

10.1. Introduction

It has been widely observed in these laboratories that $AgFAsF_6$, in the absence of $AsF_5$ in excess of that required to form $AgFAsF_6$, interacts with the AHF solvent to produce a black solid, usually in small quantity. This black product appeared to be identical to a black solid obtained by Žemva and et al when one equivalent of $AsF_5$ was added to pure $AgF_3$ in AHF. It was also detected by its distinctive X-ray powder pattern as a major product of the interaction between $Ag_2F_5$ and $AsF_5$. Indeed, this black solid phase was found to be present in many reactions in which $Ag(II)$ or $Ag(III)$ fluorides were involved in interaction with $AsF_5$ in AHF. It was also observed as an impurity product in the oxidation of $AgF$ by $O_2AsF_5$ (see Chapter 8). A dark blue solid obtained when a large excess of $O_2AuF_6$ was allowed to react with $AgFBF_4$ also appeared to be isomorphous with the black solid phase.

The X-ray powder photographs of the black solid showed a clear relationship at the outset to those of rhombohedral binary trifluorides, notably that of $RuF_3$. But, the black solid was always mixed with other phases such as $AgAsF_6$, and as a consequence an unambiguous set of diffraction data characteristic of the phase was not readily obtainable. In this study, the black solid was obtained in high purity when $AgFAsF_6$ solution and the product of the interaction of it with AHF were treated with $O_2AsF_6$ in AHF. The X-ray powder pattern was successfully indexed on a monoclinic distortion of a trifluoride-like cell. In combination with analytical data and the chemistry associated with this
black solid, a pseudo-trifluoride structure of composition \((\text{AgF}_2)_3\text{AsF}_6\) was derived. Successful attempts to grow single crystals provided a definitive structure determination of \((\text{AgF}_2)_3\text{AsF}_6\).

It had been observed by Žemva and Bartlett\(^3\) that \(\text{AgFA}_\text{S}_\text{F}_6\) in interaction with successive aliquots of \(\text{AsF}_5\)-free AHF yielded a mixture of the black solid and \(\text{AgAsF}_6\) (colorless) in a disproportionation associated with solvolysis by AHF (reaction 1). The black solid was shown, chemically, to contain \(\text{Ag(III)}\) as it yielded bright red \(\text{AgF}_3\) when titrated with \(\text{AsF}_5\) (reaction 2). The black solid was also obtained by fluorinating \(\text{AgFA}_\text{S}_\text{F}_6\) (reaction 3) and from interaction of \(\text{AgF}_2\) with \(\text{AgFA}_\text{S}_\text{F}_6\) (reaction 4) in reactions apparently related to (1).

\[
4\text{AgFA}_\text{S}_\text{F}_6 \xrightarrow{\text{AHF}} (\text{AgF}_2)_3\text{AsF}_6 + \text{AgAsF}_6 + 2\text{AsF}_5 \tag{1}
\]

\[
(\text{AgF}_2)_3\text{AsF}_6 + \text{AsF}_5 \xrightarrow{\text{AHF}} \text{AgF}_3 + 2\text{AgFA}_\text{S}_\text{F}_6 \tag{2}
\]

\[
3\text{AgFA}_\text{S}_\text{F}_6 + \frac{1}{2}\text{F}_2 \xrightarrow{\text{AHF}} (\text{AgF}_2)_3\text{AsF}_6 + 2\text{AsF}_5 \tag{3}
\]

\[
2\text{AgF}_2 + 2\text{AgFA}_\text{S}_\text{F}_6 \xrightarrow{\text{AHF}} (\text{AgF}_2)_3\text{AsF}_6 + \text{AgAsF}_6 \tag{4}
\]

In this study, an efficient systematic approach using \(\text{O}_2^+\) salts to the synthesis of \((\text{AgF}_2)_3\text{AsF}_6\) was found and has been applied to the preparation of other \((\text{AgF}_2)_3\text{MF}_6\) (\(M = \text{As, Au, Sb, Pt}\)). The structures of \((\text{AgF}_2)_3\text{MF}_6\) salts will be discussed.

10.2. Experimental

10.2.1. Materials
O₂AsF₆, O₂PtF₆, O₂AuF₆, and O₂Sb₂F₁₁ were prepared by literature methods⁴,⁵,⁶. CuF₂ (Aldrich, Milwaukee, WI) was used as received. AgFBF₄ was prepared⁷ by fluorinating AgBF₄ in the presence of BF₃. The reactants were checked by X-ray powder photography and each powder pattern was entirely attributable to each reagent. AgF₂ was produced by fluorinating AgF in AHF solution.

10.2.2. Synthesis of (AgF₂)₃AsF₆

10.2.2.1. From the disproportionation of AgFAAsF₆

Pure (AgF₂)₃AsF₆ was obtained initially, in this work, from the disproportionation of AgFAAsF₆ (0.1353 g, 0.4284 mmole) in AHF (~1.5 ml) in the presence of O₂AsF₆. The experimental detail has been described in Chapter 8. Any Ag(I) formed by disproportionation in the solvolysis to produce (AgF₂)₃AsF₆ is oxidized by O₂AsF₆ to Ag²⁺ in the solution. O₂AsF₆ and AgFAAsF₆ (as the acid solubilized Ag(AsF₆)₂) were easily washed away by decantation to leave high purity (AgF₂)₃AsF₆ (0.0151 g, 0.02410 mmole). (AgF₂)₃AsF₆ was obtained from AgFAAsF₆. The extent of the disproportionation under the stated condition therefore amounts to approximately 22.5% (0.0241x4/0.4284).

10.2.2.2. Interaction of O₂AsF₆ with AgF₂ in AHF

Inside the DRILAB, AgF₂ (0.0693 g, 0.4751 mmole) and O₂AsF₆ (0.0368 g, 0.1666 mmole) were loaded, respectively, into the side arm and the main tube of a prepassivated T-shaped Teflon-FEP reactor. AHF was further dried over O₂AsF₆ in a separate FEP reactor. AHF (~1.5 ml) was condensed on to approximately equimolar amounts of AgF₂ and O₂AsF₆ in separate arms of the reactor. The O₂AsF₆ solution was poured slowly into the AgF₂ suspension in

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AHF in the side arm. Oxygen evolution was immediately observed as the $O_2AsF_6$ solution was added and a black solid was produced. After the gas evolution had ceased, the solution was agitated for about another 30 min. The supernatant solution was decanted into the main tube. The black solid was washed with back-distilled AHF about 5 times, to the point when the black solid no longer settled quickly, but remained several minutes in suspension in the AHF. This was a signal that soluble salts had been largely removed by the multiple washing. AHF and volatiles were removed under a dynamic vacuum and the black solid was vacuum-dried under dynamic vacuum of $10^{-3}$ torr for several hours. The X-ray powder pattern was completely indexed on the basis of a primitive monoclinic cell (see Section 10.2.6.1). The theoretical yield of $(AgF_2)_3AsF_6$ was 0.0992 g based on the amount of the limiting reagent AgF$_2$. 0.0950 g was observed. Some of the black solid was surely lost in the multiple washing by decantation steps. Evidently the oxidation of AgF$_2$ by O$_2AsF_6$ was quantitative since no AgF$_2$ was detected in the X-ray photograph.

10.2.3. Attempted synthesis of $(CuF_2)_3AsF_6$

10.2.3.1. Interaction of $O_2AsF_6$ with CuF$_2$

In the DRILAB, CuF$_2$ (0.0649 g, 0.6391 mmole) and O$_2AsF_6$ (0.0478 g, 0.2164 mmole) were loaded, respectively, into the side arm and the main tube of an FEP reactor. AHF (~1.5 ml in total) was condensed on to CuF$_2$ and O$_2AsF_6$. The white CuF$_2$ solid did not appear to dissolve in AHF. The O$_2AsF_6$ solution was poured slowly into the side arm. There was no apparent reaction. The amount of the white CuF$_2$ solid appeared to remain the same, and there was no oxygen evolution. This mixture was agitated for several hours without any evident change. One equivalent of AsF$_5$ (0.6391 mmole) was admitted into the
reactor. Approximately half of the white CuF₂ solid dissolved in the solution. Upon adding another equivalent of AsF₅, all the CuF₂ dissolved to give a colorless solution without any oxygen evolution. This solution was agitated for another several hours without any change. After HF and other volatiles were removed under dynamic vacuum, a white solid (0.2000 g) remained in the side arm. An X-ray powder photograph showed the pattern of O₂AsF₆ and a second, predominant pattern. The latter was identical to that of the white solid obtained by George Lucier and identified by him as CuFAsF₆. The theoretical yield of CuFAsF₆ was 0.1765 g. Therefore, the total weight of CuFAsF₆ and O₂AsF₆ in the side arm should have been 0.2146 g (0.0067 g O₂AsF₆ remained in the main tube). This weight was fairly close to the measured value 0.2009 g. The slight weight loss from that anticipated is probably a consequence of some loss of O₂AsF₆ by reductive interaction with the container.

10.2.4. Synthesis of (AgF₂)₃PtF₆

10.2.4.1. Interaction of O₂PtF₆ with AgF in AHF

This reaction was initially designed to synthesize AgFPtF₆. In the DRILAB, AgF (0.0348 g, 0.2743 mmole) and O₂PtF₆ (0.0948 g, 0.2779 mmole) were loaded, respectively, into the side arm and the main tube of a prepassivated T-shaped Teflon-FEP reactor. AHF (~1.5 ml) was condensed on to the AgF and O₂PtF₆ in approximately equal amounts. The O₂PtF₆ solution had an intense yellow color and about half of the O₂PtF₆ remained as solid in contact with the solution. The AgF solution was poured slowly into the O₂PtF₆ solution. A very fast reaction took place with oxygen evolution and a dark brown precipitate formed. The precipitate, when settled, appeared to be reddish brown. When visible gas evolution had ceased, the solution was still yellow. The
supernatant yellow solution was decanted into the side arm and the reddish brown solid was repeatedly washed until the AHF was no longer colored. AHF and any oxygen were eventually removed under dynamic vacuum, leaving behind a dark red solid in the side arm and a reddish brown solid in the main tube. The dark red solid weighed 0.0247 g and was shown by X-ray powder photography to be very crystalline cubic \( \text{O}_2\text{PtF}_6 \). The reddish brown solid weighed 0.0903 g and was not very crystalline. The diffraction lines in the powder photograph were broad and not well defined. The poorly crystalline powder pattern was not convincingly indicative of an isomorph of \((\text{AgF}_2)_3\text{AsF}_6\), although similar to it. The reddish color probably came from some tetrameric \( \text{PtF}_5 \) generated during the reaction. The reaction was not complete as there was some \( \text{O}_2\text{PtF}_6 \) left even though there was a slight deficiency of \( \text{O}_2\text{PtF}_6 \) at the onset, as required to complete the oxidation of the silver. This reaction should be repeated with more AHF solvent and a longer reaction period.

10.2.4.2. Interaction of \( \text{O}_2\text{PtF}_6 \) with \( \text{AgF}_2 \) in AHF

This reaction was carried out by George Lucier in these laboratories. \( \text{O}_2\text{PtF}_6 \) and \( \text{AgF}_2 \) in 1:3 ratio were used in the reaction. The weight of the black-brown product indicated a quantitative reaction in making \((\text{AgF}_2)_3\text{PtF}_6\). The material was of poor crystallinity as the reflection lines were generally broad and again although similar, the powder pattern was not convincingly of an isomorph of \((\text{AgF}_2)_3\text{AsF}_6\).

10.2.4.3. Interaction of \( \text{O}_2\text{PtF}_6 \) with \( \text{AgFBF}_4 \) in AHF

Inside the DRILAB, \( \text{AgFBF}_4 \) (0.0583 g, 0.2728 mmole) and \( \text{O}_2\text{PtF}_6 \) (0.1003 g, 0.2941 mmole) were loaded, respectively, into the side arm and the
main tube of the FEP reactor. AHF (~1.5 ml in total) was condensed on to the AgFBF₄ and O₂PtF₆. AgFBF₄ did not seem to dissolve in HF. The O₂PtF₆ dissolved to some extent to give a yellow solution. The O₂PtF₆ solution, with the solid O₂PtF₆ churned up, was poured into the side arm in small portions. Vigorous gas evolution took place immediately and a nearly black solid, with reddish brown tint, was precipitated. The reaction appeared to have finished before all of the O₂PtF₆ solution was added. After all the O₂PtF₆ solution had been added into the side arm, the solution in the side arm was yellow. This solution was agitated for ~30 minutes to ensure that all the AgFBF₄ had reacted. The supernatant solution was then decanted into the main tube and the solid in the side arm was repeatedly washed with HF until the solution was colorless. HF and other volatiles were removed in a dynamic vacuum. A nearly black solid (red-brown tint) was obtained in the side arm and a deep red solid in the main tube. The deep red solid was found to be very crystalline O₂PtF₆. X-ray powder photographs of the nearly black solid were sharp and indicative of good microcrystallinity. Its pattern closely resembled that of (AgF₂)₃AsF₆. The weight of the recovered black-brown solid was 0.0817 g (0.109 mmole), a little higher than the calculated yield of 0.0679 g (0.0909 mmole) for (AgF₂)₃PtF₆.

10.2.5. Synthesis of (AgF₂)₃AuF₆

10.2.5.1. Interaction of O₂AuF₆ with AgF₂ in neutral AHF

Inside the DRILAB, O₂AuF₆ (0.0943 g, 0.2750 mmole) was loaded into the main tube of a prepassivated ½" T-shaped Teflon-FEP reactor and AgF₂ (0.1143 g, 0.7836 mmole) into the side arm. AHF (~2 ml) was condensed on to O₂AuF₆. The O₂AuF₆ dissolved to some extent to give a yellow solution. In the beginning, the AgF₂ solid was tapped into the O₂AuF₆ solution slowly. But the
reaction appeared to be very sluggish, oxygen evolution being very slow.
Therefore, the AgF₂ was added into the O₂AuF₆ solution all at once. HF was
condensed into the side arm to rinse down any residual AgF₂. The reaction was
agitated for over 12 hrs with a mechanical tapping device. The solution remained
yellow and the solid in the main tube became dark brown. The supernatant
yellow solution was decanted into the side arm and the product was washed with
HF until the solution was colorless. HF and other volatiles were removed in a
dynamic vacuum. The dark brown product gave an X-ray powder diffraction
pattern which was predominantly that of AgF₂, with a weak pattern very like that
of (AgF₂)₃AsF₆ and therefore probably that of (AgF₂)₃AuF₆. The orange yellow
solid in the side arm was shown by X-ray powder photography to be O₂AuF₆.
The weight of the dark brown solid was 0.1686 g and that of the unreacted
O₂AuF₆ was 0.0336 g (0.0980 mmole). From the difference in the weight of
O₂AuF₆ before and after the reaction, the weight of the reaction product
(AgF₂)₃AuF₆ was calculated to be 0.1325 g. The total weight of (AgF₂)₃AuF₆
and the unreacted AgF₂ in the main tube should accordingly be 0.1754 g, which
is slightly greater than that actually obtained: 0.1686 g.

10.2.5.2. Interaction of O₂AuF₆ with AgF₂ in acidic AHF

Inside the DRILAB, O₂AuF₆ (0.1458 g, 0.4251 mmole) was loaded into
the main tube of a prepassivated ½" T-shaped Teflon-FEP reactor and AgF₂
(0.1432 g, 0.9817 mmole) into the side arm. AHF (~2 ml) was condensed on to
the O₂AuF₆. The O₂AuF₆ dissolved to some extent to give a yellow solution.
BF₃ (~0.14 mmole) was admitted into the reactor to render the HF solution acidic
and convert the AgF₂ to AgFBF₄. The AgF₂ solid was tapped into the O₂AuF₆
solution slowly. There was gas evolution as the AgF₂ solid fell into the O₂AuF₆
solution and black material started to precipitate. Some of the HF was condensed over to the side arm to rinse down AgF₂ into the O₂AuF₅ solution. As the cold BF₃-saturated HF was poured back into the O₂AuF₅ solution, the color of the O₂AuF₅ solution turned blue probably from dissolution of the AgF₂. Upon agitation, the blue color faded. This color alteration was repeated in the condensing-rinsing-agitating cycle. The reaction mixture was agitated for ~12 hrs. The supernatant yellow solution was decanted into the side arm and the product was washed with HF until the solution was colorless. HF and other volatiles were removed in a dynamic vacuum. The reaction product was black with a brown tint in reflected light and the washed-over product in the side arm was orange-yellow. X-ray powder photography showed the brown tinted black solid to be mainly (AgF₂)₃AuF₅. The other lines in the pattern were attributable to AgFAuF₆. The weight of the solid was 0.2447 g, close to the theoretical yield of 0.2449 g. The weight of the unreacted O₂AuF₅ was 0.0396 g, in slight excess of that anticipated to remain after the oxidation, which was 0.0336 g.

10.2.6. Synthesis of (AgF₂)₃SbF₆

Inside the DRILAB, AgFBF₄ (0.1634 g, 0.7647 mmole) and a mixture of O₂SbF₅ and O₂Sb₂F₁₁ (0.1619 g), which is mainly O₂Sb₂F₁₁, were loaded, respectively, into the side arm and the main tube of the FEP reactor. AHF (~1.5 ml in total) was condensed on to the AgFBF₄ and O₂SbF₆/O₂Sb₂F₁₁. The O₂SbF₆/O₂Sb₂F₁₁ dissolved completely to give a colorless solution. The O₂SbF₆/O₂Sb₂F₁₁ solution was poured into the side arm in small portions. Vigorous gas evolution took place immediately and a nearly black solid, with reddish brown tint, was precipitated. Meanwhile, the solution in the side arm gradually turned blue. The reaction appeared to have finished before all of the
O$_2$SbF$_6$/O$_2$Sb$_2$F$_{11}$ solution was added. After all the O$_2$SbF$_6$/O$_2$Sb$_2$F$_{11}$ solution had been added into the side arm, the reactor was agitated for ~10 minutes to ensure that all the AgFBF$_4$ had reacted. The blue supernatant solution was then decanted into the main tube and the solid in the side arm was repeatedly washed with HF until the solution was colorless. HF and other volatiles were removed in a dynamic vacuum. A nearly black solid (red-brown tint) was obtained in the side arm. X-ray powder photographs of the nearly black solid were sharp and indicative of good microcrystallinity. Its pattern closely resembled that of (AgF$_2$)$_3$AsF$_6$. The weight of the recovered black-brown solid was 0.0633 g (0.1306 mmole).

10.2.7. The structural arrangement in (AgF$_2$)$_3$MF$_6$

10.2.7.1. Structure determination of (AgF$_2$)$_3$AsF$_6$

10.2.7.1.1. X-ray powder diffraction study of (AgF$_2$)$_3$AsF$_6$

The close resemblance of the X-ray powder photograph of (AgF$_2$)$_3$AsF$_6$ to that of a trifluoride, typified by the rhombohedral$^8$ RuF$_3$ suggested that (AgF$_2$)$_3$AsF$_6$ was a pseudo-trifluoride, Ag$_3$MF$_{12}$, and its structure a lower-symmetry distortion of the RuF$_3$ type structure. By applying various distortions to the rhombohedral structure, the powder pattern was initially indexed successfully with a pseudo-triclinic unit cell based on a slightly distorted rhombohedral cell with $a = 5.61\ \text{Å}$, $b = c = 5.69\ \text{Å}$, $\alpha = 55.28^\circ$, $\beta = \gamma = 55.28^\circ$, and $V = 114.0\ \text{Å}^3$. For comparison, the cell parameters for bimolecular rhombohedral RuF$_3$ are $a = 5.41\ \text{Å}$ and $\alpha = 54.67^\circ$. This initial indexing, with three unknowns implied that the true symmetry was probably monoclinic. A monoclinic cell was derived from the pseudo-triclinic one and from this, the cell with $\beta$ closest to 90° was selected: $a = 5.61\ \text{Å}$, $b = 5.25\ \text{Å}$, $c = 7.80\ \text{Å}$, $\beta = 96.49^\circ$, $V = 228.0\ \text{Å}^3$, possible space group
P2/m. The unit cell volume of the monoclinic cell doubled that of the bimolecular pseudo-rhombohedral cell, and contained the formula unit \((\text{AgF}_2)_3\text{AsF}_6\). The calculated \(1/d^2\) values and intensities of reflections based on the parameters obtained from the single crystal structure (see Section 10.2.7.1.3) are in excellent agreement with those observed (Table 10.1).

**Table 10.1.** X-ray powder data (Cu Kα radiation, Ni filter) for \((\text{AgF}_2)_3\text{AsF}_6\). The calculated \(1/d^2\) values and intensities of reflections are based on the parameters obtained from the structure analysis on a perfectly disordered single crystal: \(a = 5.6045, b = 5.2567, c = 7.8061\AA, \beta = 96.594^\circ, V = 228.5\AA^3, Z = 1, \) space group P2/c.

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10.2.7.1.2. Crystal growth of \((\text{AgF}_2)_3\text{AsF}_6\)

The reaction vessels for crystal growth were usually constructed of 3/8" FEP tubing, Teflon tees, and Teflon valves with Kel-F tips. Approximately 1 cm away from the sealed end of the side arm, a restriction was made by pinching the FEP tubing halfway under heat. The purpose of this restriction was to slow down the diffusion of \(\text{F}_2\) during crystal growth. Typically, \(\text{AgFAsF}_6\) (in excess by 15 - 20\%) was loaded into the main arm of the FEP reactor, and the other starting materials such as \(\text{AgF}_2\) or \(\text{AgFBF}_4\) were loaded into the side arm. 1 to 2 ml AHF was condensed onto \(\text{AgFAsF}_6\). This gave a blue solution and a small
amount of black solid. After the black solid had settled, the blue solution was
carefully decanted into the side arm. F₂ was then admitted into the reactor until
the total pressure was about 1000 torr. The reactor was then left undisturbed for
about one week for crystal growth. During crystal growth, the blue solution
usually became much paler, sometimes almost colorless, the solid starting
materials on the bottom such as AgF₂ or AgFBF₄ slowly diminished as the
highly reflective black crystallites grew, from solution, on the reactor wall. At the
end of the crystal growth, the solution was carefully decanted back into the main
arm and the crystals were left behind in the side arm. AHF and any remaining F₂
were removed under a dynamic vacuum and the black solid was vacuum-dried
under dynamic vacuum of 10⁻³ torr for several hours.

The multi-faceted, highly reflective, jet black (AgF₂)₃AsF₆ crystallites
were roughly cubical. The crystals were usually very small, and often did not
have good morphology for they tended to form aggregates. Even those crystals
which appeared to be single crystals with smooth, well-defined facets commonly
turned out to be twins or multiple crystals as shown by Laue and precession
photographs. Various crystal growth conditions with different reactor designs,
partial pressures, concentrations, reaction time, or temperatures were employed.
Neutral compounds such as LiAsF₆ and KBF₄ were sometimes added to the HF
to modify its solvent properties. A single crystal of (AgF₂)₃AsF₆ was eventually
obtained from the reaction of AgFBF₄, AgFAsF₆, and F₂ with a small amount of
KBF₄ present in the HF.

10.2.7.1.3. Crystal structure determination of (AgF₂)₃AsF₆

Crystals were manipulated in a dry argon atmosphere in the Drilab on a
prepassivated Teflon sheet. The selected crystal was mounted in a 0.5 mm
diam. quartz capillary the narrow end of which had been further drawn down to a long taper. The crystal was wedged into this fine tapered tip by gently tapping the capillary. The quartz capillary was then flame sealed. Preliminary Laue and precession photographs indicated monoclinic Laue symmetry and yielded cell dimensions close to those derived from the X-ray powder data (see Section 10.2.7.1.1).

The crystal used for data collection was then transferred to the Enraf-Nonius CAD-4 diffractometer and centered in the beam. Automatic peak search and indexing procedures yielded the same monoclinic cell as derived from the X-ray powder diffraction data and precession photographs. Testing showed that the cell was indeed primitive and that there was no superlattice present. The final cell parameters and specific data collection parameters for this data set are given in Table 10.2. The positional and thermal parameters of the atoms are given in Tables 10.7.-10.9. The intramolecular distances and angles are given in Tables 10.10.-10.11.

The 1463 raw intensity data were converted to structure factor amplitudes and their esds by correction for scan speed, background and Lorentz and polarization effects. No correction for crystal decomposition was necessary. Inspection of the azimuthal scan data showed a variation $I_{\text{min}}/I_{\text{max}}=0.82$ for the average curve. An empirical correction based on the observed variation was applied to the data as a first approximation. After solution of the structure and assignment of the correct space group, an empirical correction$^9$ was made to the data based on the combined differences of $F_{\text{obs}}$ and $F_{\text{calc}}$ following refinement of all atoms with isotropic thermal parameters ($\text{Corr}(\text{max})=1.32, \text{Tmin}=0.79$, no theta dependence). Inspection of the data was at first interpreted as yielding no systematic absences, but later inspection based on the structure solution
revealed an apparent absence for h0l, l\neq2n. The choice of the centric group P2/c was eventually confirmed by the successful solution and refinement of the structure. Removal of systematically absent data and averaging of redundant data (R1=4.3% for observed data) left 670 unique data in the final data set.

The structure was solved by Patterson methods in space group P(-1) of the original powder data indexing (q.v.) following poor refinements in monoclinic space groups. Refinement and elucidation of additional atoms proceeded via standard least-squares and Fourier techniques. Examination of the triclinic model demonstrated the correct monoclinic space group, P2/c, and refinement continued in that group with a completely disordered model for one Ag and the As, and partial occupancy for one of the fluorine sites.

The final residuals for 40 variables refined against the 213 data for which F^2>2.5\sigma(F^2) were R=2.44%, wR=2.89% and GOF=1.06. The R value for all 670 data was 15.2%. (This very large value is in part an artifact of the way that reflections with negative measured intensities are treated in calculation of RALL. In part it is due to the fact that only 15 reflections with l=2n+1 are "observed" in the data set.)

The quantity minimized by the least squares program was \Sigma w(|F_{ol}-|F_{cl}|)^2, where w is the weight of a given observation. The p-factor, used to reduce the weight of intense reflections, was set to 0.03 throughout the refinement. The analytical forms of the scattering factor tables for the neutral atoms were used and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion.

Inspection of the residuals ordered in ranges of \sin\theta/\lambda, |F_{ol}|, and parity and value of the individual indexes showed no unusual features or trends, other than those caused by the strong pseudo-translation of 1/2c in the structure. The
largest peak in the final difference Fourier map had an electron density of 0.78 e⁻/Å³, and the lowest excursion -1.06 e⁻/Å³. There was no indication of secondary extinction in the high-intensity low-angle data.

Table 10.2. Crystal and Data parameters for disordered (AgF)₂(AgF₄)(AsF₆).

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<th>Formula, mol. wt.</th>
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</tr>
</thead>
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<td>Temperature</td>
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<tr>
<td>a</td>
<td>5.6045(6) Å</td>
</tr>
<tr>
<td>b</td>
<td>5.2567(6) Å</td>
</tr>
<tr>
<td>c</td>
<td>7.8061(8) Å</td>
</tr>
<tr>
<td>β</td>
<td>96.594(9)°</td>
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<td>Space Group</td>
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<tr>
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<tr>
<td>d(calc)</td>
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<td>μ(calc)</td>
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<tr>
<td>Size</td>
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<tr>
<td>Monochromator</td>
<td>Highly-oriented graphite (2θ = 12.2)</td>
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<tr>
<td>Detector</td>
<td>Crystal scintillation counter, with PHA.</td>
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<tr>
<td>Reflections measured</td>
<td>+/-H, + K, +/-L</td>
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<td>Horiz. aperture = 2.3 + 1.0 tanθ mm</td>
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<tr>
<td>Independent</td>
<td>670</td>
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</table>
Intensity standards | (116),(42-2),(132); measured every 1 hours of x-ray exposure time. Over the data collection period no significant decrease in intensity was observed.
Orientation | Three reflections were checked after every 200 measurements. Crystal orientation was redetermined if any of the reflections were offset by more than 0.10 degree from their predicted positions. Reorientation was not needed during data collection.

[a] Unit cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 24 reflections with 2θ between 26° and 34°.

[b] In this and all subsequent tables the esd's of all parameters are given in parentheses, right-justified to the least significant digit(s) of the reported value.

10.2.7.2. The Structures of (AgF₂)₃AuF₆, (AgF₂)₃SbF₆, and (AgF₂)₃PtF₆.

The X-ray powder diffraction photographs indicate that the other (AgF₂)₃MF₆ (M = Au, Pt, Sb) compounds are isostructural to (AgF₂)₃AsF₆. Their powder X-ray diffraction data have been indexed, using the cell parameters of (AgF₂)₃AsF₆ as the initial starting values. Their cell dimensions are very similar to those of (AgF₂)₃AsF₆ (Table 10.3). The dark blue solid obtained by William Casteel from the interaction of O₂AuF₆ and AgFBF₄ can therefore be identified as (AgF₂)₃AuF₆. The X-ray powder diffraction data and indexing for (AgF₂)₃MF₆ (M = Au, Pt, Sb) are given in Table 10.4 -10.6. The calculated 1/d² and the observed values are in excellent agreement for (AgF₂)₃AuF₆ and (AgF₂)₃SbF₆. The reflection intensities, Icalc, were calculated with only metal atoms in the structure and assuming that the Ag in AgF₄⁻ and the M in MF₆⁻ are also
disordered as in \((\text{AgF}_2)_3\text{AsF}_6\). The X-ray powder photograph of \((\text{AgF}_2)_3\text{PtF}_6\) clearly shows that it is also related to the other \((\text{AgF}_2)_3\text{PtF}_6\) salts although the indexing of the powder pattern is, however, yet incomplete. It is possible that some of the observed reflections (most weak or very weak) may belong to an impurity phase.

Table 10.3. A comparison of cell dimensions for \((\text{AgF}_2)_3\text{MF}_6\) (\(M = \text{As, Au, Sb, Pt}\)).

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<tr>
<th></th>
<th>((\text{AgF}_2)_3\text{AsF}_6)</th>
<th>((\text{AgF}_2)_3\text{AuF}_6)</th>
<th>((\text{AgF}_2)_3\text{PtF}_6^a)</th>
<th>((\text{AgF}_2)_3\text{SbF}_6)</th>
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<td>(c) (Å)</td>
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<td>(\beta) (°)</td>
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<td>(V) (Å(^3))</td>
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*The indexing of \((\text{AgF}_2)_3\text{PtF}_6\) is not complete.

Table 10.4. X-ray powder data (Cu K\(\alpha\) radiation, Ni filter) for \((\text{AgF}_2)_3\text{AuF}_6\), monoclinic cell with \(a = 5.660\) Å, \(b = 5.240\) Å, \(c = 7.788\) Å, \(\beta = 97.53^\circ\), \(Z = 1\), \(V = 229.0\) Å\(^3\), possible space group P2\(/c\).

*The reflection intensities, \(I_{\text{calc}}\), were calculated with only metal atoms in the structure.
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Table 10.5. X-ray powder data (Cu Kα radiation, Ni filter) for (AgF₂)₃SbF₆, monoclinic cell with a = 5.699 Å, b = 5.267 Å, c = 7.830 Å, β = 97.21°, Z = 1, V = 233.2 Å³, possible space group P2/c.

*The reflection intensities, Icalc, were calculated with only metal atoms in the structure.
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Table 10.6. X-ray powder data (Cu Kα radiation, Ni filter) for (AgF₂)₃PtF₆, monoclinic cell with \( a = 5.689 \) Å, \( b = 5.250 \) Å, \( c = 7.807 \) Å, \( β = 97.70° \), \( Z = 1 \), \( V = 231.1 \) Å³, possible space group P2/c.

*The reflection intensities, \( I_{calc} \), were calculated with only metal atoms in the structure.

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221
10.3. Results and Discussion

10.3.1. The structures of (AgF₂)₃MF₆ salts

The crystal structure of the AsF₆⁻ salt was solved on a perfectly disordered single crystal (Figure 10.1 - 10.6). The lattice parameters are: a = 5.6045(6), b = 5.2567(6), c = 7.8061(8)Å, β = 96.594(9)°, V = 228.5Å³, Z = 1, space group P2/c. The structure shows that the material is composed of zigzag (AgF)ₙ⁺⁺ chains enclosing anion arrays of alternating inclined planar and octahedral anions AgF₄⁻ and AsF₆⁻ running along the c axis (Figure 10.6). Therefore, the material should be formulated as (AgF⁺)₂AgF₄⁻AsF₆⁻.

Each F ligand of AsF₆⁻ makes a long bridging contact, F···Ag, with one of the six surrounding Ag species, as shown in Figure 10.1 - 10.2. The three Ag species are of two types. Two are Ag(II) each of which is linearly coordinated by 2 F ligands, each shared with another Ag(II) atom, thus generating the (Ag-F)ₙ⁰⁺⁺ chains which run parallel to c. Each of the Ag(II) species also makes four long-bridge Ag···F contacts, equatorial to the chain axis, to the four closest anions (Figure 10.4). The other Ag species is Ag(III) which is in an approximately square
F ligand environment, appropriate for an AgF$_4^-$ anion (Figure 10.1, 10.2, 10.5). Interaction of this with AsF$_6^-$ above and below it are at long Ag···F interatomic distances roughly perpendicular to the AgF$_4^-$ plane.

The refined model has Ag-F chains which are well behaved, with Ag1 {an Ag(II) species} on the inversion center at the origin and F1 on the two-fold axis at 0, y, 1/4. The Ag-F distance is 2.003(4) Å, which is essentially identical with that in the other known AgF$^+$ salts. The F-Ag-F angle is therefore 180° and the Ag-F-Ag angle is 153.9(11)°. Each Ag1 is in additional contact with four other fluorine atoms from the anions, at distances of 2.336(17) Å and 2.316(17) Å, forming a tetragonally compressed octahedral environment (Figure 10.4).

The refined model of the anions, however, is less well behaved. While Figure 10.1, 10.2, and 10.5 show alternating Ag and As atoms, the two sites are in fact equivalent (related by the pseudo c-glide), and each atom is included at half occupancy. Each of the two site is coordinated at short distance by four fully-occupied equatorial fluorine positions (2xF2 and 2xF3) and by two half-occupancy axial fluorine position (2xF4). (The distance between two neighboring F4 positions is 1.01 Å). The coordination is nearly octahedral. But because of the inherently longer M-F distance$^{10}$ in AgF$_4^-$ of 1.89 Å compared with that$^{11}$ in AsF$_6^-$ of 1.715 Å, the distances to F2 and F3 (1.80Å) are longer than the distance to F4 (1.72Å). The former is identical to the average of AgF$^-$ and AsF$_6^-$ M-F distances. The large apparent thermal motion of the anion fluorine ligands must be a consequence of the anion disorder.

The diffraction data indicate that within a given chain of anions the AsF$_6^-$ and AgF$_4^-$ are in ordered alternating sequence along c axis with the axial fluorines (F4) of the AsF$_6^-$ forming long coordination bonds (2.61Å) to the open faces of the planar AgF$_4^-$ (Figure 10.5). But any given anion array is not in
registry with the equivalent anion arrays in neighboring cells (Figure 10.6). The intensities of reflections calculated for X-ray powder diffraction using the positional parameters from this perfectly disordered crystal structure are in excellent agreement with the observed intensities (Table 10.1), indicating that \((\text{AgF}_2)_3\text{AsF}_6\) prepared in polycrystalline form is also disordered.

Including the \([\text{AgF}_4]^\text{−}\) anion, the fluorine-bridged Ag-F assembly can be viewed as a \((\text{AgF}_2)_3^+\) cage for the \(\text{MF}_6^-\) anion (Figure 10.1, 10.2). It should also be noted that all the metal atoms are in pseudo-octahedral environments, with each F ligand coordinated to only two metal atoms. It is for these reasons that the diffraction characteristics are so like those of a trifluoride. It is possible that this rather close-packed structure type one of highly favorable lattice energy since it is generated in disproportionation of \(\text{AgFAsFs}\) in HF solution, and has several structural relatives in which the \(\text{AsFs}^-\) is substituted by other \(\text{MF}_5^-\).

The other \((\text{AgF}_2)_3\text{MF}_6\) salts \((M = \text{Au, Sb, Pt})\) appear to be isostructural with \((\text{AgF}_2)_3\text{AsF}_6\). The lattice parameters of these salts, derived from X-ray powder diffraction data, are very close to those of \((\text{AgF}_2)_3\text{AsF}_6\). The general trend of the unit cell volume increase (Table 10.3) is similar to that found in the other salts of these anions (Table 10.12) although the differences in volume are smaller than occurs in the salts listed in Table 10.12.

**Table 10.12.** A comparison of formula unit volume (FUV) of the salts of \(\text{AsF}_6^-\), \(\text{AuF}_6^-\), \(\text{PtF}_6^-\), and \(\text{SbF}_6^-\).

<table>
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<th></th>
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<td>K\text{AuF}_6</td>
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<tr>
<td>K\text{SbF}_6</td>
<td>130.7</td>
<td>17</td>
<td>Cs\text{SbF}_6</td>
<td>148.8</td>
<td>18</td>
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</table>
10.3.2. Reactions and chemistry

The AgF\(^+\) cation appears to be unstable in neutral AHF. AgFAFsF\(_6\) is invariably solvolized by neutral AHF and undergoes disproportionation to generate Ag(I) which precipitates as AgAsF\(_6\) and AgF\(_4^-\) which occurs in the precipitate of (AgF\(_2\))\(_3\)AsF\(_6\). Part of this insolubility of Ag(II) in the AHF must be due to the favorable bonding in the square planar AgF\(_4^-\) species. Addition of AsF\(_5\) to this mixture produces a blue solution of Ag\(^{2+}\)\((\text{solv})\). We can write the following equation to represent the equilibrium products:

\[
4\text{AgF}^+\text{(solv)} + 4\text{AsF}_6^- \overset{\text{AHF}}{\rightarrow} (\text{AgF}_2)_3\text{AsF}_6 + \text{AgAsF}_6 + 2\text{AsF}_5
\]  

(5)

Diminishing the AsF\(_5\) concentration has the effect of producing more disproportionation. At high AsF\(_5\) concentration the AgF\(_4^-\) species is unstable with respect to AgF\(_3\), which in any case interacts with Ag(I) to yield Ag(II). The other driving forces for this unexpected disproportionation of Ag(II) must be the very high lattice energy of (AgF\(_2\))\(_3\)AsF\(_6\) and the solvation of AsF\(_5\) by HF.

In the experiment to study the interaction of AgFAFsF\(_6\) and O\(_2\)AsF\(_6\) (Chapter 8), as the O\(_2\)AsF\(_6\) solution was added to the AgFAFsF\(_6\) solution which already contained the disproportionation products from equilibrium 1, any Ag(I) formed by disproportionation would be oxidized by O\(_2\)AsF\(_6\) back to Ag(II) as the acid solubilized Ag(AsF\(_6\))\(_2\) (see Chapter 8).

\[
\text{AgAsF}_6 + \text{O}_2\text{AsF}_6 \overset{\text{AHF}}{\rightarrow} \text{Ag(AsF}_6)_2 + \text{O}_2
\]  

(6)
As the O$_2$AsF$_6$ and Ag(AsF$_6$)$_2$ can be easily washed away, (AgF$_2$)$_3$AsF$_6$ was obtained in high purity. This provided reliable X-ray powder data for a successful indexing.

The crystal growth of (AgF$_2$)$_3$AsF$_6$ was finally achieved by using the following reaction schemes (reaction 7 - 9, 3 - 4) devised based on the disproportionation of AgFAsF$_6$ in HF (equilibrium 5). AgF$_2$, or AgFBF$_4$ was used to scavenge AsF$_5$ on the right side of the equilibrium (5) to yield AgFAsF$_6$.

Presence of AgF$_2$ or AgFBF$_4$ therefore ensured less acidic conditions, necessary for the preservation of AgF$_4^+$. F$_2$ would also fluorinate AgAsF$_6$ on the right side of the equilibrium (5) back to AgFAsF$_6$. By converting the byproducts on the right side to the starting material AgFAsF$_6$, the equilibrium was constantly shifted to the right, which allowed for the slow growth of single crystals of (AgF$_2$)$_3$AsF$_6$.

Reactions 7 and 8 yielded jet black crystals of (AgF$_2$)$_3$AsF$_6$ with smooth well-defined facets. A single crystal suitable for structure analysis was finally obtained with a small amount of KBF$_4$ present in solution from reaction 8. The crystals obtained from reaction 9 were in general of poor quality. And the crystals obtained from reaction 3 were of very small size. The crystal growth in reaction 4 did not appear to proceed. Probably, reaction 4 was too slow under the room temperature crystal growth conditions.

\[
\text{AgFAsF}_6 + 2\text{AgF}_2 + 1/2\text{F}_2 \xrightarrow{\text{AHF}} (\text{AgF}_2)_3\text{AsF}_6 \quad (7)
\]

\[
\text{AgFAsF}_6 + 2\text{AgFBF}_4 + 1/2\text{F}_2 \xrightarrow{\text{AHF}} (\text{AgF}_2)_3\text{AsF}_6 + 2\text{BF}_3 \quad (8)
\]

\[
\text{AgAsF}_6 + 2\text{AgF}_2 + \text{F}_2 \xrightarrow{\text{AHF}} (\text{AgF}_2)_3\text{AsF}_6 \quad (9)
\]
\[ 3\text{AgFAsF}_6 + \frac{1}{2}\text{F}_2 \xrightarrow{\text{AHF}} (\text{AgF}_2)_3\text{AsF}_6 + 2\text{AsF}_5 \]  
(3)

\[ 2\text{AgF}_2 + 2\text{AgFAsF}_6 \xrightarrow{\text{AHF}} (\text{AgF}_2)_3\text{AsF}_6 + \text{AgAsF}_6 \]  
(4)

A more efficient synthesis of \((\text{AgF}_2)_3\text{AsF}_6\) was achieved via the interaction of \(\text{AgF}_2\) and \(\text{O}_2\text{AsF}_5\). In spite of the fact that the solubility of \(\text{AgF}_2\) is very low in AHF, the reaction of \(\text{AgF}_2\) and \(\text{O}_2\text{AsF}_5\) in 3:1 ratio with \(\text{O}_2\text{AsF}_6\) slightly in excess (reaction 10) is quantitative and very facile, the net reaction being:

\[ 3\text{AgF}_2 + \text{O}_2\text{AsF}_6 \xrightarrow{\text{AHF}} (\text{AgF}_2)_3\text{AsF}_6 + \text{O}_2 \]  
(10)

The similar reaction between \(\text{AgF}_2\) and \(\text{O}_2\text{PtF}_6\) to make \((\text{AgF}_2)_3\text{PtF}_6\) is also facile although the product is very poor in crystallinity. Interestingly, the reaction between \(\text{AgF}_2\) and other \(\text{O}_2\text{MF}_6\) \((\text{M} = \text{Au, Sb})\) seems to be very slow. In the reaction of \(\text{AgF}_2\) and \(\text{O}_2\text{AuF}_6\), acidifying AHF with BF\(_3\) appears to promote the oxidation reaction, probably because of the greater solubility of the \(\text{AgF}\text{BF}_4\) salt.

Reactions which were initially designed to synthesize \(\text{AgFAuF}_6\), and \(\text{AgFPtF}_6\), via the interaction between \(\text{AgF}\) and the corresponding \(\text{O}_2\text{AuF}_6\), and \(\text{O}_2\text{PtF}_6\) salts, produced \((\text{AgF}_2)_3\text{AuF}_6\), and \((\text{AgF}_2)_3\text{PtF}_6\) respectively, as the major products but poorly crystalline pentafluorides of Au and Pt could also be present. The interaction between \(\text{AgF}\) and \(\text{O}_2\text{AsF}_6\) is cleaner and produced \(\text{AgFAsF}_6\) in yields of up to 75\% (see Chapter 8). This could be a consequence of the high solubility of AsF\(_5\) relative to AuF\(_5\) and PtF\(_5\) in the AHF.

\[ 3\text{AgF} + 4\text{O}_2\text{MF}_6 \xrightarrow{\text{AHF}} (\text{AgF}_2)_3\text{MF}_6 + 4\text{O}_2 + 3\text{MF}_5 \]  
(11)
\[ M = \text{Au, Pt} \]

A more generally satisfactory and efficient route to crystalline \((\text{AgF}_2)_3\text{MF}_6\) \((M = \text{As, Au, Pt, Ru, Sb})\) was discovered with \(\text{AgFBF}_4\) in place of \(\text{AgF}_2\):

\[
3\text{AgFBF}_4 + \text{O}_2\text{MF}_6 \xrightarrow{\text{AHF}} (\text{AgF}_2)_3\text{MF}_6 + 3\text{BF}_3 + \text{O}_2 \quad (12)
\]

\[ M = \text{As, Au, Pt, Sb} \]

This reaction scheme works very well probably because \(\text{AgFBF}_4\) is slightly soluble in HF and the other products of the reaction are gaseous \(\text{BF}_3\) and \(\text{O}_2\).

Pure, crystalline \((\text{AgF}_2)_3\text{SbF}_6\) was prepared (reaction 13) via the interaction of \(\text{AgFBF}_4\) with a mixture of \(\text{O}_2\text{SbF}_6/\text{O}_2\text{Sb}_2\text{F}_{11}\) which was predominantly \(\text{O}_2\text{Sb}_2\text{F}_{11}\). A small portion of \(\text{AgFBF}_4\) is lost in making the byproduct \(\text{Ag}(\text{SbF}_6)_2\) in this reaction. \(\text{Ag}(\text{SbF}_6)_2\) was easily washed away with HF.

\[
7\text{AgFBF}_4 + 2\text{O}_2\text{Sb}_2\text{F}_{11} \xrightarrow{\text{AHF}} 2(\text{AgF}_2)_3\text{SbF}_6
\]

\[ + \text{Ag}(\text{SbF}_6)_2 + 7\text{BF}_3 + 2\text{O}_2 \quad (13) \]

The variable temperature magnetic susceptibility measurements on \((\text{AgF}_2)_3\text{AsF}_6\), done by George Lucier\(^{19}\), show a small temperature independent paramagnetism at least down to 60 K where the impact of small amounts of paramagnetic and ferromagnetic impurities becomes relatively large. This magnetic behavior, which is like that of a metallic system, is essentially identical in magnitude and its temperature independence to that of the other known \(\text{AgF}^+\) salts\(^{20}\). Magnetic measurements also show that repeated washing of
(AgF$_2$)$_3$AsF$_6$ with AHF resulted in some solvolysis to produce some AgF$_2$ and an unidentified product that is strongly diamagnetic below 63 K.

Attempts to synthesize the Cu analog, (CuF)$_3$AsF$_6$, through the interaction of CuF$_2$ and O$_2$AsF$_6$ were unsuccessful. CuFAuF$_4$, as described by Müller$^{21}$, contains linear (CuF)$_n^{n+}$ chains. And square planar CuF$_4^-$ also exists in the compound CsCuF$_4$ prepared by Hoppe$^{22}$. Therefore, it appears plausible that a trifluoride-like (CuF)$_2$CuF$_4$MF$_6$ analogous to (AgF)$_2$AgF$_4$MF$_6$ could also be prepared. It does seem likely that the CuF$_4^-$ species is very much less favorable energetically relative to CuF$_2$ than AgF$_4^-$ relative to AgF$_2$. This correlates with the very high third ionization energy of Cu, which is actually the highest among the coinage metals$^{23}$. Formation of Cu(III) fluorocomplexes requires more extreme reaction conditions$^{24}$.

10.4. Conclusion

A new class of pseudo-trifluoride silver compounds, (AgF$_2$)$_3$MF$_6$ (M = As, Au, Sb, Pt), has been established. The "black solid phase" frequently observed in the fluorochemistry of Ag(II) in AHF has been conclusively identified as (AgF$_2$)$_3$MF$_6$, and its frequent occurrence can be attributed to its very favorable lattice energy associated with the close packing evident in the pseudo-trifluoride structure. The crystal structure of (AgF$_2$)$_3$AsF$_6$ has been determined which showed that this material is a new (AgF)$_n^{n+}$ salt with a formulation best represented as (AgF$_{n+}$)$_2$AgF$_4^-$AsF$_6^-$. The X-ray powder diffraction data shows that the other (AgF$_2$)$_3$MF$_6$ salts are isostructural with (AgF$_2$)$_3$AsF$_6$. Efficient synthetic routes to (AgF$_2$)$_3$MF$_6$ of high purity and crystallinity have been established using O$_2^+$ salts. It is also clear that similar materials such as (AgF$_2$)$_3$MF$_6$ (M = Nb, Ta) can probably also be synthesized using analogous
methods. These new materials also exhibited the same small temperature-independent paramagnetism of the other known (AgF)$_n^{n+}$ salts.
10.5. References

9 N. Walker and D. Stuart, Acta Crystallographica, A39, 159 (1983), as used by the program DIFABS in MolEN.
### Table 10.7. Positional Parameters and Their Estimated Standard Deviations for (AgF₂)₃AsF₆.

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<td>0.000</td>
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<td>0.500</td>
<td>0.500</td>
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<tr>
<td>F1</td>
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</tr>
<tr>
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<td>0.485(4)</td>
<td>0.326(4)</td>
<td>0.185(2)</td>
<td>2.8(4)*</td>
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</table>

* Starred atoms were included with isotropic thermal parameters.
** Double-starred atoms are present at site occupancy = 1/2.

The thermal parameter given for anisotropically refined atoms is the isotropic equivalent thermal parameter defined as: $(4/3) [a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$ where $a, b, c$ are real cell parameters, and $\beta(i,j)$ are anisotropic betas.

### Table 10.8. Anisotropic Thermal Parameters - B's for (AgF₂)₃AsF₆.

<table>
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<tr>
<th>Name</th>
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<th>B(2,2)</th>
<th>B(3,3)</th>
<th>B(1,2)</th>
<th>B(1,3)</th>
<th>B(2,3)</th>
<th>Beqv</th>
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<td>1.34(5)</td>
<td>1.58(4)</td>
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<td>AS</td>
<td>B(1,1)</td>
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<td>B(3,3)</td>
<td>-B(1,2)</td>
<td>B(1,3)</td>
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<td>(constrained)</td>
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<td>-1.1(5)</td>
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<td>1.0(4)</td>
<td>-2.2(4)</td>
<td>3.5(2)</td>
</tr>
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</table>

The form of the anisotropic temperature factor is:

$$
\exp[-0.25\{h^2a^2B(1,1) + k^2b^2B(2,2) + l^2c^2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) \\
+ 2klbcB(2,3)\}]. \text{where } a, b, \text{ and } c \text{ are reciprocal lattice constants.}
$$
Table 10.9. Root-Mean-Square Amplitudes of Anisotropic Displacement in Angstroms for \((\text{AgF}_2)_3\text{AsF}_6\).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Min.</th>
<th>Int'med.</th>
<th>Max.</th>
</tr>
</thead>
<tbody>
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<td>0.180</td>
</tr>
<tr>
<td>AS</td>
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</tr>
<tr>
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<td>0.166</td>
<td>0.212</td>
</tr>
<tr>
<td>F2</td>
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<td>0.188</td>
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</tr>
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<td>F3</td>
<td>0.103</td>
<td>0.222</td>
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Table 10.10. Intramolecular Distances for (AgF$_2$)$_3$AsF$_6$.

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<td>F2</td>
<td>2.336(17)</td>
</tr>
<tr>
<td>AG1</td>
<td>F3</td>
<td>2.316(17)</td>
</tr>
<tr>
<td>AS/AG2</td>
<td>F2</td>
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</tr>
<tr>
<td>AS/AG2</td>
<td>F3</td>
<td>1.806(14)</td>
</tr>
<tr>
<td>AS</td>
<td>F4</td>
<td>1.719(24)</td>
</tr>
<tr>
<td>AG2</td>
<td>F4</td>
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</tr>
<tr>
<td>F2</td>
<td>F3</td>
<td>2.510(21)</td>
</tr>
<tr>
<td>F2</td>
<td>F4</td>
<td>2.36(4)</td>
</tr>
<tr>
<td>F2</td>
<td>F4</td>
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</tr>
<tr>
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</tr>
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</tr>
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</tr>
<tr>
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</tr>
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</tr>
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</tr>
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</tr>
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<td>F4</td>
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</tr>
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</tr>
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</tr>
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<td>F3</td>
<td>F4</td>
<td>3.26(3)</td>
</tr>
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</table>
Table 10.11. Intramolecular Angles for (AgF$_2$)$_3$AsF$_6$:

<table>
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<th>ATOM 3</th>
<th>ANGLE</th>
</tr>
</thead>
<tbody>
<tr>
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<td>AG1</td>
<td>F1</td>
<td>180.00(0)</td>
</tr>
<tr>
<td>F1</td>
<td>AG1</td>
<td>F2</td>
<td>94.4(6)</td>
</tr>
<tr>
<td>F1</td>
<td>AG1</td>
<td>F2</td>
<td>85.6(6)</td>
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<tr>
<td>F1</td>
<td>AG1</td>
<td>F3</td>
<td>87.8(5)</td>
</tr>
<tr>
<td>F1</td>
<td>AG1</td>
<td>F3</td>
<td>92.2(5)</td>
</tr>
<tr>
<td>F2</td>
<td>AG1</td>
<td>F2</td>
<td>180.00(0)</td>
</tr>
<tr>
<td>F2</td>
<td>AG1</td>
<td>F3</td>
<td>92.4(7)</td>
</tr>
<tr>
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<td>F3</td>
<td>87.6(7)</td>
</tr>
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<td>AG1</td>
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</tr>
<tr>
<td>F2</td>
<td>AG2</td>
<td>F2</td>
<td>180.00(0)</td>
</tr>
<tr>
<td>F2</td>
<td>AG2</td>
<td>F3</td>
<td>88.2(9)</td>
</tr>
<tr>
<td>F2</td>
<td>AG2</td>
<td>F3</td>
<td>91.8(9)</td>
</tr>
<tr>
<td>F2</td>
<td>AG2</td>
<td>F4</td>
<td>93.2(8)</td>
</tr>
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<td>AG2</td>
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</tr>
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</tr>
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<td>86.7(9)</td>
</tr>
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<td>93.3(9)</td>
</tr>
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<td>AG2</td>
<td>F4</td>
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</tr>
<tr>
<td>F2</td>
<td>AS</td>
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</tr>
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<td>F4</td>
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<td>93.3(9)</td>
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<td>F4</td>
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</tr>
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<td>AG1</td>
<td>153.9(11)</td>
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<td>AS/AG2</td>
<td>137.2(9)</td>
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<tr>
<td>AS</td>
<td>F4</td>
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<td>127.3(13)</td>
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</tbody>
</table>
Figure 10.1 - Monocular view of the unit cell of the (AgF)₂AgF₄AsF₆ \( (\text{AgF}_2)_3\text{AsF}_6 \). View direction is roughly down \( \mathbf{a} \), with \( \mathbf{b} \) horizontal on the page. The central metal atom has been assigned to As to emphasizes the cage-like nature of the AsF₆⁻ environment.

*In all following figures the ellipsoids are scaled to represent the 75% probability surface*
Figure 10.2. Monocular view similar to Figure 10.1. View direction approximately down b.
Figure 10.3 - View of the \((\text{AgF})_2\text{AgF}_4\text{AsF}_6\) structure approximately down \(c\). The \(b\) axis is approximately vertical on the page.
Figure 10.4 - View of the Ag-F chain in (AgF)$_2$AgF$_4$AsF$_6$, including four long Ag-F contacts to show the approximate octahedral environment of Ag(II).
Figure 10.5. View of one AsF$_6^-$/AgF$_4^-$ chain in (AgF)$_2$AgF$_4$AsF$_6$, showing the grossly distorted octahedral environment of Ag(III).
Figure 10.6 - View of three neighboring AsF$_6^-$/AgF$_4^-$ chains showing that the anions AsF$_6^-$ and AgF$_4^-$ are in ordered alternating sequence along c axis but the anion array is not in registry with the equivalent anion arrays in neighboring cells. View direction is approximately down the [110].
Appendix:

Mnemonic Diagrams for Basic Thermodynamic Relationships

The thermodynamic relationships can be illustrated quite easily through the utilization of mnemonic diagrams. It remains of interest to further develop and improve such mnemonic diagrams. Recently, three dimensional mnemonic diagrams were presented by Phillips. Rodriguez and Brainhard worked on the improvement of mnemonic diagram which was originally developed by Callen. Based on the ongoing interest, the purpose of this study is to present new two-dimensional and three-dimensional mnemonic diagrams, a complete set of consistent and systematic rules, and the rationale behind the mnemonic diagrams. Moreover, some interesting symmetry properties among the thermodynamic relationships and the mathematical operations will be briefly discussed.

The two-dimensional mnemonic diagrams can be applied to one-component simple thermodynamic systems. Furthermore, its three-dimensional extension incorporates other conjugate variable pairs, the mole numbers \(N_i\)s and the chemical potentials \(\mu_i\)s \((i = 1, 2, \ldots, r)\). Thus the three-dimensional diagram completely covers all the relationships involving the mole numbers and the chemical potentials for the multi-component systems.

I. Legendre Transformations and the Construction of Mnemonic Diagrams

*I developed most of this work when I was an undergraduate. The text has undergone many revisions over the years. I therefore reserve copyright for the work in this appendix.*
It will be beneficial to first briefly review Legendre transformations. Provided that function \( f = f(X_1, \ldots, X_n) \) is a natural function of \( X_1, \ldots, X_n \), then

\[
\begin{align*}
df &= \sum_{i=1}^{n} Y_i dX_i, \quad \text{with} \quad Y_i = (\partial f / \partial X_i)_{X}
\end{align*}
\]

Let

\[
g = f - \sum_{i=r+1}^{n} Y_i X_i
\]

Then

\[
dg = \sum_{i=1}^{r} Y_i dX_i + \sum_{i=r+1}^{n} (-X_i) dY_i
\]

Therefore, \( g = g(X_1, \ldots, X_n, Y_{r+1}, \ldots, Y_n) \), the Legendre transform of \( f \), is a natural function of \( X_1, \ldots, X_n \) and the conjugate variables to \( X_{r+1}, \ldots, X_n \), namely \( Y_{r+1}, \ldots, Y_n \).

The macroscopic thermodynamics of equilibrium for simple systems can be described by the internal energy as a natural function of the extensive independent variables, \( E = (S, V, N_1, \ldots, N_r) \). The differential form of this fundamental energy formulation is as follows:

\[
dE = TdS - PdV + \sum \mu_i dN_i
\]

The Legendre transformations can be employed to change the dependence of \( E = E(S, V, N_1, \ldots, N_r) \) on its natural variables to that on their conjugates, respectively, thus resulting in a number of new auxiliary functions, such as enthalpy \( H \), Gibbs free energy \( G \), Helmholtz free energy \( F \) (the symbol \( A \) is also used), etc\(^{2,6} \). These new fundamental energy functions contain no more or less information about the system than the original one. The difference lies in terms of convenience under different circumstances. It has been observed that many of the important thermodynamic relationships fall into families of marked
algebraic symmetry\(^1\). It has also been noticed that the presence of certain superficial geometric symmetry could be utilized in determining the signs in the Maxwell relations\(^2\). These are, in fact, due to the restraint to which the Legendre transformations are to be carried out, and the consequential differential forms of the energy functions. Therefore, the construction of any mnemonic diagrams should be able to account for the Legendre transformations, the differential forms of the energy functions, and the symmetry properties present in a family of thermodynamic relationships.

Figure 1. a) A primitive diagram for the Legendre transformations among the energy functions. b) A primitive diagram for the differential form of the internal energy \(E\). c) The final version of the mnemonic diagram for simple thermodynamic systems, as a combination of diagrams in (a) and (b). d) The symmetry properties of the mnemonic diagram.

In the construction of the mnemonic diagrams, the arrows are used to indicate certain mathematical operations. The directions of the arrows are chosen to be as "from the positive position to the negative position \([+ \rightarrow -]\)". The diagram in Figure 1(a) reflects the Legendre transformations among the four energy functions. The arrows point towards the direction in which the quantity of energy decreases by the amount of the product term on the arrow. It is recognized that \(H\) has the largest value among four energy functions. Therefore \(H\) is placed at the upper left corner. The diagram in Figure 1(b) implies only the
differential form of the internal energy function, $E$. The internal energy $E$ at the corner is flanked by its natural variables, $S$ and $V$, on the adjacent edges. The arrows connect the conjugate variable pairs, implying the product of the differential of the natural variable with its conjugate variable and the signs for this individual product term. Combining the diagrams in Figure 1(a) and Figure 1(b), the final version of the mnemonic diagram is obtained, as shown in Figure 1(c). It not only contains the information about the Legendre transformations but also accounts for the differential forms of all the energy functions. The simple algebraic symmetry is reflected in the structure of this mnemonic diagram. Furthermore, it is recognized that the mathematical operations in the mnemonic diagram is symmetric with respect to the solid blackened diagonal, and antisymmetric with respect to the dashed blackened diagonal (see Figure 1(d)). The solid blackened diagonal will be thereafter called the symmetric line, and the dashed blackened diagonal the antisymmetric line. It will be shown later that this symmetry property is of great help in practice, especially in the Maxwell relations.

Now it should be obvious that the various mnemonic diagrams all originate from the differential form of the internal energy function and the Legendre transformations indirectly. This is why the mnemonic diagrams usually have the similar appearances no matter how they were developed. Hence, the final goal here is to construct better diagrams and formulate better rules to extract maximum possible information more easily.

II. The Two-dimensional Diagram

In practice, the mnemonic diagram in Figure 1(c) can be constructed with the following recommendation:
1. A two-dimensional square is first drawn. The energy functions \( H, G, F, E \) are placed, clockwise, at the four corners in a reversed alphabetic order \((H \rightarrow G \rightarrow F \rightarrow E)\), with \( H \) at the upper left corner.

2. Two arrows are drawn to connect the midpoints of the two pairs of parallel edges. The arrowheads should point away from \( H \).

3. The conjugate pairs of variables \( S, T; P, V \) are added to the starting and end points of the arrows, with \( P \rightarrow V \) for the vertical arrow and \( S \rightarrow T \) for the horizontal.

In the first and second steps, one should bear in mind that the value of \( H \) is the largest among the four energy functions. In the third step, it is always helpful if those natural variables with which one is more familiar are written down first in their positions. In this diagram, each energy function at the corner is flanked by its natural independent variables on the adjacent edges. The arrows indicate certain mathematical operations involving the conjugate pairs. The directions of the arrows, "from the positive position towards the negative position \([+ \rightarrow -]\)," provide a basis for a sign convention. This will be discussed in detail in the relevant parts.

Since the mnemonic diagram is constructed from the Legendre transformations and the differential form of the internal energy, it would only be natural to start with the Legendre transforms and the differential forms of the four energy functions in the derivation of basic thermodynamic relationships. The rules (in undersized characters) are recommended in the course of derivations.

A. The Legendre Transforms

1. A particular transformation travels along an edge to change one corner energy function into another corner function by the amount of the product of the conjugate pair on the arrow parallel to the edge.
2. It can be easily judged whether the Legendre transform is larger or smaller than the original one by inspecting the directions of the arrows (from "positive (large)" towards "negative (small)"). Whether to add or to subtract the product term can be thereby easily determined.

From the diagram in Figure 1(c), the following equations are obtained:

\[ H = G + ST \quad (1.1) \]
\[ G = F + PV \quad (1.2) \]
\[ F = E - ST \quad (1.3) \]
\[ E = H - PV \quad (1.4) \]

**B. The Differential Forms of the Energy Functions**

1. Start with the differentials of the adjacent natural variables. Travel along the arrows to form the products with their respective conjugates.

2. The sign of such products is **positive** if the travel direction is along that of the arrow, and **negative** if the travel direction is opposite to that of the arrow. Or the sign is **positive** if the starting natural variable is at the "positive position", and **negative** if the starting natural variable is at the "negative position".

3. The sum of these product terms yields the differential form of the energy function at the corner.

The four differential forms are obtained:

\[ dH = TdS + VdP \quad (2.1) \]
\[ dG = VdP - SdT \quad (2.2) \]
\[ dF = - SdT - PdV \quad (2.3) \]
\[ dE = TdS - PdV \quad (2.4) \]

**C. The Partial Derivatives of the Energy Functions**

Although it is straightforward to obtain the partial derivative terms from the differential forms, it can be made easier by using the diagram:
1. Start at a corner energy function. The result of the partial derivative of this energy function with respect to one adjacent natural variable can be found across the arrow, which is the natural variable's conjugate.

2. The subscript for this partial derivative is the another adjacent natural variable on the edge parallel to the arrow. The afore-mentioned sign convention still applies.

The following equations are obtained:

\[(\partial H/\partial S)_P = T \quad (3.1) \quad (\partial H/\partial P)_S = V \quad (3.2)\]
\[(\partial G/\partial P)_T = V \quad (3.3) \quad (\partial G/\partial T)_P = -S \quad (3.4)\]
\[(\partial F/\partial T)_V = -S \quad (3.5) \quad (\partial F/\partial V)_T = -P \quad (3.6)\]
\[(\partial E/\partial V)_S = -P \quad (3.7) \quad (\partial E/\partial S)_V = T \quad (3.8)\]

D. The Variational Principles and the Second Law

A useful form of the second law is the variational statement, i.e., the equilibrium state is the state at which the characteristic function of state has its global maximum or minimum. A complete set of variational principles have been derived from the mnemonic diagram developed by Li\textsuperscript{4}. The result can also be easily derived from this mnemonic diagram:

1. The energy function at the corner and its two adjacent variables form a corner triangle. The equilibrium state is the state at which one quantity in this triangle achieves its global maximum or minimum while the other two are held constant.

2. The "positive positions" indicate the maxima at equilibrium state, namely for S and P. Otherwise the minima are always implied (including for the four energy functions).

If the symbol "S" is used for any small variation away from the equilibrium state, then we have the following expressions:
(δS)_E, \ V \leq 0 \quad (4.1) \quad (δS)_H, \ P \geq 0 \quad (4.2)

(δP)_H, \ S \leq 0 \quad (4.3) \quad (δP)_G, \ T \geq 0 \quad (4.4)

(δT)_F, \ V \geq 0 \quad (4.5) \quad (δT)_G, \ P \geq 0 \quad (4.6)

(δV)_E, \ S \geq 0 \quad (4.7) \quad (δV)_F, \ T \geq 0 \quad (4.8)

(δH)_S, \ P \geq 0 \quad (4.9) \quad (δG)_P, \ T \geq 0 \quad (4.10)

(δE)_V, \ S \geq 0 \quad (4.11) \quad (δF)_T, \ V \geq 0 \quad (4.12)

E. The Maxwell Relations

Traditionally, the derivation of the Maxwell relations could be troublesome in the use of mnemonic diagrams. It is demonstrated here that the use of the symmetry properties gives a unique, clear-cut method:

1. Travel in a manner of continuous rotation among the four variables, and write down the first two for the partial derivative with the third as its subscript (as a constant).

2. The counterpart of this partial derivative can be found through the reflection of each variable with respect to the symmetric or antisymmetric line. That is, start at the another side of the symmetric or antisymmetric line, and travel in the counter direction on a one-to-one correspondence.

3. The Maxwell relation relating these two partial derivatives has positive sign when it is a symmetric reflection (the reference is the symmetric line), and negative if antisymmetric.

![Figure 2. Illustration of the symmetries contained in the Maxwell relations. The symmetries can also be observed directly from Fig.1(c) and Fig.1(d).](image-url)
Clearly \((P, T)\) and \((S, V)\) astride across the symmetric line, whereas \((P, S)\) and \((T, V)\) across the antisymmetric line (see Figure 2). The following Maxwell relations are obtained with the signs easily determined:

\[
\begin{align*}
(\partial P/\partial T)_V &= (\partial S/\partial V)_T, & (5.1) \\
(\partial P/\partial S)_V &= -(\partial T/\partial V)_S, & (5.2) \\
(\partial T/\partial P)_S &= (\partial V/\partial S)_P, & (5.3) \\
(\partial S/\partial P)_T &= -(\partial V/\partial T)_P. & (5.4)
\end{align*}
\]

III. The Three-dimensional Diagram and the Mole Numbers

The two-dimensional diagram can be easily modified to accommodate new variables, such as the mole numbers and their conjugates - the chemical potentials. Consequently, a three-dimensional mnemonic diagram is obtained, as shown in Figure 3. The arrow of the conjugate pair \(N_i \rightarrow \mu_i\) is added through the center of the diagram perpendicularly. The subscript \(i\) indicates the \(i\)th species present in the system, \(i = 1, 2, \ldots, r\). \(N_i \rightarrow \mu_i\) implies a mathematical operation involving only \((N_i, \mu_i)\) with all the other \(N_j's\) held constant, or a particular mathematical operation involving all \((N_j's, \mu_j's)\) summed over the subscript \(i\) when it is suitable. Now \(S, T, P, V, N_i, \mu_i\) are at the vertices of a regular octahedron. All the energy functions can, in addition to their original "natural" variables, have \(N_j's\) as their natural independent variables. It should be noted that different variable pairs can be put onto the three orthogonal arrows in lieu of \((P, V), (S, T),\) or \((N_i, \mu_i)\). And the resulting three-dimensional diagram shall be sufficient to cope with new situations.
Figure 3. A three-dimensional extension of the mnemonic diagram in Fig. 1c. The third dimension is achieved by incorporating the conjugate variable pairs, \( N_i \) and \( \mu_i \), i.e., adding the arrow, \( N_i \rightarrow \mu_i \), through the center of the two-dimensional diagram perpendicularly.

By analogy to the rules and the sign convention that have already been developed for the two-dimensional diagram, it is very easy to obtain the thermodynamic relationships involving \( N_i \) or \( \mu_i \). If all the \( N_i \)'s are to be held constant, it is clear that the same expressions will result just as those from the two-dimensional diagram.

The following are some of the thermodynamic relationships involving the mole numbers and the chemical potentials:

1. The partial derivative of an energy function with respect to \( N_i \) gives the chemical potential, with the other adjacent natural variables being held constant.

\[
(\frac{\partial H}{\partial N_i})_{S, P, N_j = \mu_j} \quad (6.1) \quad (\frac{\partial G}{\partial N_i})_{P, T, N_j = \mu_j} \quad (6.2) \\
(\frac{\partial F}{\partial N_i})_{T, V, N_j = \mu_j} \quad (6.3) \quad (\frac{\partial E}{\partial N_i})_{V, S, N_j = \mu_j} \quad (6.4)
\]

2. The differential form of an energy function includes, additionally, the summation term \( \Sigma \mu_i dN_i \). Start with \( dN_i \) to find its conjugate across the arrow and form the product, then sum over the subscript \( i \).

\[
dH = TdS + VdP + \Sigma \mu_i dN_i \quad (7.1) \quad dG = VdP - SdT + \Sigma \mu_i dN_i \quad (7.2) \\
dF = -SdT - PdV + \Sigma \mu_i dN_i \quad (7.3) \quad dE = TdS - PdV + \Sigma \mu_i dN_i \quad (7.4)
\]
3. Again the symmetry property can be utilized in deriving the Maxwell relations involving \( N_i \)
and \( \mu_i \). Note that besides all the variables directly involved in the permutations in the Maxwell relation,
one of the variables on the third arrow should be chosen with \( N_j/s (j \neq i) \) as additional constants for the
partial derivatives. From those Maxwell relations, the expressions for some partial molar quantities,
such as \( s_i \) and \( v_j \), are obtained (see Figure 4(a) and 4(b)).

\[
(\partial \mu / \partial T) P, N_i, j = - (\partial S / \partial N_i) T, P, N_j = - s_i \\
(\partial \mu / \partial P) T, N_i, j = (\partial V / \partial N_i) T, P, N_j = v_j
\]

Figure 4. a) The symmetries in the Maxwell relations involving \( S, T, N_i, \mu_i, P \) on the arrow perpendicular
to the \( (S, T, N_i, \mu_i) \) plane is chosen as the additional constant to get the partial molar \( s_i \) in eq.(8.1). b) The
symmetries in the Maxwell relations involving \( P, V, N_i, \mu_i \). In addition, \( T \) is a constant.

A. Extensive Functions and the Gibbs-Duhem Equation

A macroscopic property is extensive if it depends *linearly* on the size of
the system, and intensive if it is independent of the size of the system. Clearly,
the variables \( S, V, N_i/s \) and the four energy functions \( H, G, F, E \) are extensive;
whereas \( P, T, \mu_i/s \) are intensive. For instance:

\[
E(\lambda S, \lambda V, \lambda N_1, \ldots, \lambda N_P) = \lambda E(S, V, N_1, \ldots, N_P) \text{ for any } \lambda
\]
The three-dimensional diagram in Figure 3 can be easily modified to show the extensive characteristics of some macroscopic properties, as shown in Figure 5:

- The corresponding three-dimensional diagram when the size of the thermodynamic system is increased to \( \lambda \) times as large.
- The zero function \( \theta(P, T, \mu) \) is the Legendre transform of \( G \) by the summation \( \sum N_i \mu_i \).

From the rules for the derivation of the differential forms of the energy functions, the following is self-evident:

\[
d(\lambda E) = Td(\lambda S) - Pd(\lambda V) + \sum \mu_i d(\lambda N_i)
\]

Differentiation of this equation with respect to \( \lambda \) yields:

\[
E = TS - PV + \sum \mu_i N_i
\]

which is the same result as from Euler's theorem for the first-order homogeneous functions.

Four such equations can be derived from the following rules:

1. The corner energy function is the sum of the product term of its extensive natural variables (only) with their respective intensive conjugates.
2. The sign of the product term is positive if the extensive natural variable is at the "positive position", otherwise the sign is negative.

\[ H = TS + \sum \mu_j N_j \quad (9.1) \]
\[ G = \Sigma \mu_j N_j \quad (9.2) \]
\[ F = -PV + \sum \mu_j N_j \quad (9.3) \]
\[ E = TS - PV + \sum \mu_j N_j \quad (9.4) \]

Furthermore, from eq.(9.2) the Legendre transform of \( G(P, T, N_j) \) by the summation \( \Sigma \mu_j N_j \) is the Zero function \( 0(P, T, \mu_j) \),

\[ 0(P, T, \mu_j) = G - \Sigma \mu_j N_j \equiv 0 \quad (10) \]

which is a natural function of the intensive variables \( P, T, \mu_j \) (see Figure 5). The differential form of this Zero function can be simply written from the rules:

\[ d0(P, T, \mu_j) = VdP - SdT - \sum N_j d\mu_j \equiv 0 \quad (11) \]

which is the Gibbs-Duhem equation.

IV. Symmetries in the Thermodynamic Relationships

The symmetries present in the Maxwell relations are not unique to the Maxwell relations. This can be shown with a few examples.

With respect to the symmetric line, the reflection is \( S \leftrightarrow P \), \( V \leftrightarrow T \), \( E \leftrightarrow G \), but no changes for \( H \) and \( F \). With respect to the antisymmetric line, the reflection is \( S \leftrightarrow V \), \( P \leftrightarrow T \), \( H \leftrightarrow F \), but no changes for \( E \) and \( G \) (see Figure 1(c)). The signs in the corresponding mathematical operations are the same if it
is a symmetric reflection, and opposite if it is an antisymmetric reflection. Clearly, for the symmetric reflections, there are:

\[ H = E + PV \leftrightarrow H = G + ST \]
\[ G = F + PV \leftrightarrow E = F + ST \]
\[ dH = TdS + VdP \leftrightarrow dH = VdP + TdS \]
\[ dG = VdP - SdT \leftrightarrow dE = TdS - PdV \]

For the antisymmetric reflections, there are:

\[ E = H - PV \leftrightarrow E = F + ST \]
\[ H = E + PV \leftrightarrow F = E - ST \]
\[ dE = -PdV + TdS \leftrightarrow dE = TdS - PdV \]
\[ dH = TdS + VdP \leftrightarrow dF = -PdV - SdT \]

For the other thermodynamic relationships based on the Legendre transformations and the differential forms of the energy functions, the similar symmetry properties are expected.

V. Conclusions

It has been shown that the proposed two-dimensional and three-dimensional mnemonic diagrams provide an ideal basis for the derivation of the basic thermodynamic relations. The rationale and the rules for the construction of the mnemonic diagrams make this important first step much easier, more practical, and visually more comfortable. The recommended rules are basically complete, consistent, and systematic. In the sign convention, the directions of
the arrows provide a reference, i.e., the arrows point "from the positive position towards the negative position [+ \rightarrow -]." Therefore it is unnecessary to preassign some variables negative as most of the previous mnemonic diagram do\textsuperscript{1,3,4,6}, which usually makes the rules more complicated. Moreover, the symmetries of the mnemonic diagrams are utilized to distinguish the symmetric reflection from the antisymmetric reflection in the Maxwell relations. It should be mentioned that if users of the mnemonic diagrams would prefer the opposite of the as-defined directions of the arrows, all the arrows can be simply flipped and the rules correspondingly rephrased.

This is the first time that a rationale behind the construction of the mnemonic diagram has been provided. The understanding of such rationale ought to be considered as very important for people other than the initiators of those mnemonic diagrams to be able to use the diagrams to the full advantages. The existence of helpful symmetries among the mathematical operations is revealed through the structure of the mnemonic diagram. Although the proposed mnemonic diagram has the potential to accommodate many more thermodynamic properties, such as heat capacities, or account for more complicated thermodynamic relationships, it is probably best that one should develop his own methodology or even his own mnemonic diagram for his specific needs, following the continuation of the rationale provided here. Otherwise, the mounting intricacy will deprive the general use of a mnemonic diagram.
VI. References
