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

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Ph.D. Thesis

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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, BC_x ($6 > x \geq 3$), have been prepared using BCl_3 and C_6H_6 at $800\text{ }^\circ\text{C}$ - $1000\text{ }^\circ\text{C}$, and C_xN ($14 > x \geq 5$) have been synthesized using $\text{C}_5\text{H}_5\text{N}$ and Cl_2 at $680\text{ }^\circ\text{C}$ - $986\text{ }^\circ\text{C}$. 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 $\text{C}_8\text{K}(\text{NH}_3)_{1.1}$ has been prepared by reacting C_8K with gaseous NH_3 at $20\text{ }^\circ\text{C}$. The carbon sub-lattice is hexagonal: $a = 2.47\text{ \AA}$, $c = 6.47\text{ \AA}$. The smaller a parameter and lower conductivity compared to C_8K are attributed to the diminution of the electron transfer from K to the conduction band as a consequence of the solvation of K by NH_3 .

A simplified liquid phase method for synthesizing Li-graphite intercalation compounds has been developed. The synthesis of a novel lamellar mixed conductor, $\text{C}_x^+\text{Li}_2\text{N}^-$, has been attempted.

The stability and conductivity of $(\text{BN})_3\text{SO}_3\text{F}$ have been studied. $(\text{BN})_3\text{SO}_3\text{F}$ has been shown to be metallic with a specific conductivity of $1.5\text{ S}\cdot\text{cm}^{-1}$. The relatively low conductivity compared to $\text{C}_{8.3}\text{SO}_3\text{F}$ is attributed to the low mobility of holes in the BN sheets.

F_2 , in the presence of Lewis acids, oxidizes Xe to Xe(II) in the dark to produce $XeFAsF_6$ in WF_6 or anhydrous HF (AHF), or in liquid AsF_5 at $-65\text{ }^\circ\text{C}$. However, O_2 is not oxidized by F_2 /Lewis acid under similar conditions. Xenon solvated in AHF is oxidized by F_2 in the dark to form XeF_2 at $20\text{ }^\circ\text{C}$. The probable mechanistic and thermodynamic reasons for these observations are proposed.

O_2^+ in AHF has been shown to be a very powerful oxidizer, able to oxidize IrF_6^- to IrF_6 , Ag^+ to Ag^{2+} , and in basic AHF, $Ag(II)$ to $Ag(III)$ in AgF_4^- . The oxidizing power of Ag^{2+} in AHF has been assessed thermodynamically, and shown to be comparable to that of O_2^+ in AHF.

Two new AgF^+ salts, $AgFW_2O_2F_9$ and " $AgFWOF_5BF_3$ ", have been synthesized. They have small, temperature-independent paramagnetism similar to that of known chain polymer $(Ag-F)_n^{n+}$ salts. The crystal structure of $AgW_2O_2F_9$ has been solved. Crystals of $AgFW_2O_2F_9$ and " $AgFWOF_5BF_3$ " have been obtained.

The pseudo-trifluorides $(AgF_2)_3MF_6$ ($M = As, Au, Sb, Pt$) have been prepared and the crystal structure of $(AgF_2)_3AsF_6$ has been solved. These pseudo-trifluorides are isostructural. They are a new type of AgF^+ salt, with a formulation of $(AgF^+)_2AgF_4^-MF_6^-$.

To my wife, Lindsay,

*A rose is a rose
more than a rose
in a lover's hands
in the beloved's eyes*

Preparation and Characterization of Novel Graphite-like Materials

AND

Some High Oxidation State Fluorine Chemistry

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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-NH₃-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 S₂O₆F₂ was used to prepare a BN intercalation compound, (BN)₃SO₃F. 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 O₂⁺ and Ag²⁺. Their utility as powerful oxidizers in preparing other high oxidation state fluorine compounds is discussed. And the oxidizing power of solvated Ag²⁺ 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 $(\text{AgF}_2)_3\text{MF}_6$, 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°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_2NiF_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-Pennwalt, 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 F_2 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 π 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 ($E_g = -0.04\text{V}$ band gap)¹. 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 Marinkovic² and Hirai³. 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).²

In this experimental work, low-temperature synthetic routes have been devised to yield material which may be thermodynamically unstable. These materials are BC₃⁴, BC₂N⁵, C_xN⁵, and PC_x. The principle of this low-temperature route is illustrated by the following two reactions:

$$\Delta G^\circ = +12.13 \text{ kcal/mol graphite}$$

$$\Delta G^\circ = -27.92 \text{ kcal/mol graphite}$$

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 sp^2 hybridized form. Thus graphite can be made at moderate temperatures, as can highly doped graphite.

BC_3 , a metallic material, is synthesized⁴ via the interaction of BCl_3 and benzene (also see Chapter 3); and BC_2N , a semiconductor, is synthesized⁵ via the interaction of BCl_3 and CH_3CN . 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 sp^2 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 N_2 , 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 sp^2 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:

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_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 $CaCl_2$. 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 C_xN 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/cm^3 , compares very well with the known density of graphite, 2.27 g/cm^3 .

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 C_xN 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 HCl 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 C_5N occurs at 680°C and drops to $C_{13.5}N$ at 986°C .

Table 2.1. The Composition of the C_xN materials (in ratio to nitrogen)

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

2.3.1.2. Gas phase IR study of the self decomposition of C₅H₅N and the interaction of C₅H₅N 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 C_xN 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 observed⁶. 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 spectrum⁶. 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 detected⁶ 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 ClCN⁶, 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:

With increasing Cl_2 concentration in the gas mixture, the HCN signal was depressed, and finally nearly disappeared, whereas the ClCN signal became more and more pronounced (see Figure 2.5). In addition, part of the cyanogen was converted to ClCN 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.

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 (l_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_xN 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 π^* 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, , projecting out of the sheet rather than in a

planar, trigonal configuration in the matrix, $\begin{array}{c} \text{C} \\ | \\ \text{C}-\text{N}-\text{C} \end{array}$, 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

RXN TEMP ($^{\circ}\text{C}$)	l_c ($\text{\AA}$)	a ($\text{\AA}$)	density (g/cm^3)
680	---	---	2.1
731	---	---	2
773	---	---	2.01
832	3.52	2.40	2
868	3.52	2.41	1.97
946	3.46	2.39	1.95
986	3.43	2.41	1.93

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 C_xN materials decrease slightly with increasing reaction temperature. There are two major competing factors influencing the density. On one hand, C_xN 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 C_xN 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 C_xN 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 $\sim 10^{-4}$ per carbon atom. It is the extremely high mobility of the free charge carriers which gives graphite a relatively high conductivity. In the C_xN 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 C_xN 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 C_xN 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 graphite⁷. Secondary peaks are fitted at 285.6 - 285.8 eV to account for the broadening and the asymmetry of the principal C-1s peak⁸. 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 C_xN 986 °C to 22.1% in the C_xN 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 nitride⁷. They can be assigned to nitrogen in the sp^2 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 environments⁷ (Table 2.4), it

may be assigned to pyridine-like nitrogen, , 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 C_xN 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 C_xN materials prepared at different temperatures.

XPS also shows that nearly all the chlorine present in the C_xN samples synthesized at 680 °C and 868 °C is covalently bonded (Cl-2p_{1/2} peak at 201 eV)⁷. 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)⁷. 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

	C-1s		
Rxn Temperature	680 °C	868 °C	986 °C
B.E. (eV)	284.8	284.9	284.6
Area (%)	37.0	41.0	52.6
B.E. (eV)	285.7	285.8	285.6
Area (%)	40.9	38.8	32.0
B.E. (eV)	288.2	288.6	288.7

Area (%)	22.1	20.2	15.4
N-1s			
Rxn Temperature	680 °C	868 °C	986 °C
B.E. (eV)	401.0	401.1	400.9
Area (%)	43.7	35.0	46.2
B.E. (eV)	398.5	398.3	398.4
Area (%)	24.5	21.9	22.3
B.E. (eV)	402.0	401.7	402.0
Area (%)	29.2	40.1	28.9
B.E. (eV)	405.2	405.3	404.7
Area (%)	2.5	3.0	1.4
B.E. (eV)			406.3
Area (%)			1.4

Table 2.4. N-1s peaks in different environments⁷

Compounds	B.E. (eV)
C ₅ H ₅ N	398.6
(C ₆ H ₅)NH ₂	399.2
(C ₆ H ₅)CN	399
(C ₄ H ₁₂)NH ₂	398.7
(C ₆ H ₅)N=N(C ₆ H ₅)	399.9
Me ₄ N ⁺ Cl ⁻	402.1
EtNH ₃ ⁺ Cl ⁻	401
Me ₃ NO	402.8

MeNO ₂	406
PhNO ₂	405.7

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 C₅N 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 π^* and σ^* states in the conduction band. The π^* and σ^* positions of carbon are 286.7 eV and 295 eV, respectively. And the π^* and σ^* 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 sp² hybridization and have planar-trigonal coordination in a graphite-like network. The π^* position of nitrogen agrees with the assignment of the XPS peaks at around 400.0 - 402.2 eV to sp² 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±0.7}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 PCl₃ was used (reaction 9). Thermodynamics evaluation indicates that the reaction temperature has to be above 1200 °C to reduce PCl₃ to

elemental P by hydrogen. It was found that the maximum content of phosphorus was only ~2 at.%, and some of that phosphorus was present as second phase particles of red phosphorus rather than substitution of carbon atoms.

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.

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)₂.

Unfortunately, these C_xN 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_xN 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 sp² 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_xN 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

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Figure 2.1. Schematic drawing of the CVD apparatus

Figure 2.2. The composition of the C_xN 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 C_xN thin film deposited at 680°C

Figure 2.7 (b) XPS spectra of C_xN thin film deposited at 868°C

Figure 2.8. EELS spectra of the C_xN material deposited at 680 °C: core-loss regions (K-edge) of carbon and nitrogen.

Figure 2.9. The composition of the C_xP 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, Lowell¹ 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 Marinkovic².

In 1986, this laboratory³ reported the synthesis, by chemical vapor deposition (CVD), of a novel graphite-like boron-carbon (B/C) material that had an approximate stoichiometry of BC₃ via the interaction of benzene and BCl₃ at ~800 °C. The equation below represents the reaction to produce ideal BC₃:

A structural model proposed for this graphite-like BC₃ 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 Kertesz⁷ 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 Bogy⁸.

The novel aspects of graphite-like B/C, C/N, and B/C/N materials have been briefly discussed in an earlier preliminary report⁹. 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 statically¹⁰ 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 benzene¹¹, and approximately 5 torr (at -78 °C) for BCl₃¹². 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 $25\text{ }^{\circ}\text{C}$) was delivered by helium at the flow rate of $10\text{ cm}^3\text{ min}^{-1}$ into the fused silica tube maintained at temperatures between $25\text{ }^{\circ}\text{C}$ and $950\text{ }^{\circ}\text{C}$ 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 $830\text{ }^{\circ}\text{C}$ 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 method¹⁴. 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 Hérol¹⁵. 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.

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 Jong¹⁶ has reported that carbon and silica (SiO₂) react to produce SiC and CO at 900 °C when the partial pressure of CO is below 10⁻⁵ atm, and since Jeffes and Alcock¹⁷ 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 BCl₃ and benzene between 800 °C and 1000 °C had similar features. Prominent absorptions peaks from HCl and unreacted benzene and BCl₃ 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 BCl₃ and benzene at 910 °C

Wavenumbers (cm ⁻¹)	Intensity	Peak Assignment ^{18, 19}	Literature Value (cm ⁻¹)
3100	w	C ₆ H ₆ , $\nu_{12}^{\text{CH}}(\text{E}_{1\text{u}})$	3099
3044	w	C ₆ H ₆ , $\nu_{13} + \nu_{16}(\text{E}_{1\text{u}})$	3045

2886	w	HCl, ν	2886
994	s	$^{10}\text{BCl}_3$, ν_3	995
956	s	$^{11}\text{BCl}_3$, ν_3	956
672	s	C_6H_6 , $\nu_4^{\text{H}\perp}(\text{A}_{2\text{u}})$	671

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 ($\nu_3 = 3019 \text{ cm}^{-1}$ and $\nu_4 = 1306 \text{ cm}^{-1}$)¹⁹ 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 $^{\circ}\text{C}$ to 5.6:1 at 1000 $^{\circ}\text{C}$.

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

Deposition Temperature ($^{\circ}\text{C}$)	Bulk Composition (uncertainty: $\pm 10\%$)	Comments
800	B _{1.00} C _{3.08} O _{0.19} Cl _{0.02}	Si accumulated on surface of film.
830	B _{1.00} C _{3.57} O _{0.29} Cl _{0.03}	Si accumulated on surface of film.
830	B _{1.00} C _{3.30} O _{0.02} Cl _{0.02}	Si accumulated on surface of film. Slight non-uniformity of O content in the film.
900	B _{1.00} C _{3.00} O _{0.09} Cl _{0.004}	Si accumulated on surface of film.
910	B _{1.00} C _{4.10} O _{0.05} Cl _{0.005}	Si accumulated on surface of film.
1000	B _{1.0} C _{5.6} O _{0.1}	

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 sputtering²⁰.

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 (l_c) of the B/C material. The l_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 ($00l$) and (hkl) 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

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

Deposition Temperature (°C)	l_c (Å)	a (Å)
800	3.34 ± 0.02	-----
830	3.37 ± 0.02	-----
830	3.39 ± 0.02	-----
830	3.39 ± 0.02	-----
870	3.36 ± 0.02	-----
900	3.37 ± 0.02	2.47 ± 0.02
900	3.37 ± 0.02	2.49 ± 0.02
910	3.34 ± 0.02	-----
950	3.38 ± 0.02	2.47 ± 0.02
950	3.35 ± 0.02	2.46 ± 0.02
950	3.37 ± 0.02	2.45 ± 0.02
970	3.36 ± 0.02	2.48 ± 0.02
990	3.36 ± 0.04	2.48 ± 0.02
1000	3.38 ± 0.02	2.47 ± 0.02
1000	3.38 ± 0.02	2.48 ± 0.02
1000	3.38 ± 0.02	2.48 ± 0.02

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 (*hk*0) reflections. Streak-like (*00*l) reflections could be obtained by large angle tilt. The diffraction data is presented in Table 3.4. The indicated lattice parameters are $a \approx 2.4 \text{ \AA}$ and $c \approx 3.4 \text{ \AA}$. No general (*hk*l) 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

$d(\text{\AA})$	$hk0$ (rings)	$d(\text{\AA})$	$00l$ (streaks)
2.09	100	0.32	001
1.18	110	1.66	002
		1.12	003
		0.84	004

$$a \approx 2.4 \text{ \AA}, \quad c \approx 3.4 \text{ \AA}$$

EELS data was collected on the sample of B/C material deposited at 830 °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 π^* and σ^* 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 graphite⁹, h-BN⁹, diamond⁸, the B/C material deposited at 830 °C, and the C_xN material (Chapter 2) deposited at 680 °C.

Compound	π^* edges (K-edge) (eV)			σ^* edges (K-edge) (eV)		
	B	C	N	B	C	N
Graphite	-----	284.0	-----	-----	290.0	-----
h-BN	191.0	-----	397.5	197.5	-----	404.0
Diamond	-----	-----	-----	-----	288.9	-----
B/C (830 °C)	190.2	280.0	-----	198.2	290.9	-----
C/N (680 °C)	-----	286.7	401.4	-----	295	407.5

From the EELS data, the composition of this B/C sample deposited at 830 °C is BC_{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.

	B-1s				
	800	830	900	910	1000
B.E. (eV)	191.4	191.1	190.7	191.4	190.6
FWHM (eV)	1.4	1.4	2.4	1.5	2.4
Area (%)	61.2	79.4	28.3	45.0	32.4
B.E. (eV)	189.2	189.0	188.7	188.6	188.7
FWHM (eV)	2.1	1.8	2.1	3.0	1.6
Area (%)	15.6	10.4	25.8	32.3	26.7

B.E. (eV)	187.0	186.9	186.8	186.7	186.9
FWHM (eV)	1.8	1.6	1.9	1.4	1.8
Area (%)	11.4	3.4	27.9	17.1	22.7
B.E. (eV)	193.3	193.1	193.5	193.0	192.7
FWHM (eV)	2.7	1.8	3.2	1.4	2.0
Area (%)	11.8	6.8	18.0	5.6	18.2

C-1s					
	800	830	900	910	1000
B.E. (eV)	284.1	283.9	283.8	283.8	283.9
FWHM (eV)	1.4	1.4	1.4	1.7	1.4
Area (%)	82.2	90.2	47.4	57.5	53.4
B.E. (eV)	285.6	285.6	285.1	284.5	285.2
FWHM (eV)	1.8	1.3	3.0	3.5	2.1
Area (%)	8.2	2.0	28.8	24.2	22.4
B.E. (eV)	282.6	282.4	282.6	282.3	282.7
FWHM (eV)	1.1	1.2	1.5	1.1	1.5
Area (%)	5.9	3.8	12.4	6.9	12.2
B.E. (eV)	290.3	290.2	290.5	289.8	290.2
FWHM (eV)	1.8	1.5	3.1	4.7	2.7
Area (%)	3.7	4.0	6.3	11.4	4.8
B.E. (eV)	-----	-----	288.3	-----	287.5
FWHM (eV)	-----	-----	2.2	-----	2.4
Area (%)	-----	-----	5.7	-----	7.1

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)²¹. These peaks could be assigned to the boron atoms in the B/C materials with the local environment of ideal BC₃. 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

formed by boron atoms with oxygen impurity on the surface or to B-Cl bonds from incomplete reaction of BCl_3 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 BC_3 . 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-2p_{1/2} 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

Deposition Temperature (°C)	Apparent Density (g cm ⁻³)
870	2.17 ± 0.02
910	2.244 ± 0.006
950	2.122 ± 0.002
970	2.081 ± 0.006
990	2.170 ± 0.006
1000	2.13 ± 0.01

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 range²³. 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

Deposition Temperature (°C)	Thickness (μm)	Conductivity (S cm ⁻¹)
800	0.66 ± 0.03	5x10 ²
900	3.9 ± 0.1	8x10 ²
900	1.47 ± 0.09	1x10 ³
910	2.05 ± 0.07	8x10 ²
950	1.5 ± 0.3	9x10 ²
1000	0.634 ± 0.002	6x10 ²

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).

Wavenumbers (cm ⁻¹)	Intensity	Peak Assignment ¹⁸	Literature Value (cm ⁻¹)
2886	w	HCl, ν	2886
2348	m	CO ₂ , ν_3	2349
1827	w	COCl ₂ , $\nu_1(A_1)$	1827
994	m	¹⁰ BCl ₃ , ν_3	995
956	s	¹¹ BCl ₃ , ν_3	956
850	mw	COCl ₂ , $\nu_4(B_2)$	849
792	mw	CCl ₄ , ν_3	790
667	m	CO ₂ , ν_2	667

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 Lemay²⁴ 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)²⁵, 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^{3,9}. 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 readily²⁵. The deep blue $(SO_3F)_2$ 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 π^* and σ^* 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.

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Figure 3.1. Proposed structure of BC_3 .

Figure 3.2. IR spectrum of gaseous species collected from the reaction of BCl_3 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 CH_4 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 BC_{3.08}O_{0.19}Cl_{0.02}.

Figure 3.5. EELS spectrum of the B/C material deposited at 830 °C: core-loss region (K-edge) of boron and carbon. The σ^* and π^* 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_3N , has generated much interest as a promising solid ionic conductor¹. The Li_3N sinters and single crystals have high Li-ion conductivity of the order $10^{-3} \Omega^{-1}cm^{-1}$ at ambient temperature². Li_3N is hexagonal with $a = 3.69 \text{ \AA}$, $c = 3.86 \text{ \AA}$ and space group $P6/mmm$.^{3, 4} The structure is lamellar as Li^+ and Li_2N^- layers stack upon each other with Li^+ cation in the Li^+ layer sitting right above the nominal N^{3-} anion in the Li_2N^- layer. The Li-ion conductivity is in the Li_2N^- layer as Li ions diffuse among the vacancies on the Li sites in the Li_2N^- 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_2N^- 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_2N^- 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 on⁵. 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 1955⁶. Since then, several synthetic methods have been developed for preparing Li-graphite intercalation compounds (GIC) of the first, second and higher stages^{7, 8, 9}. The stoichiometry and structure of the first stage Li GIC have been established⁷ as C_6Li , and space group P6/mmm with $a = 4.305 \text{ \AA}$ and $c = 3.706 \text{ \AA}$. 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 composition⁹ between $C_{12}Li$ and $C_{18}Li$.

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 reported⁷ 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_2C_2 . In the liquid phase synthesis, which was first investigated by Hérold⁸ and further developed by Fischer⁹, 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 $C_x^{+}Li_2N^{-}$ has been explored. Some other synthetic routes to make $C_x^{+}Li_2N^{-}$ 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, Li_2C_2 , using the same apparatus. The bulk of the product looked grayish white. X-ray powder photography showed it to be Li_2C_2 .

4.2.2. Preparation of Li_3N

Lithium nitride, Li_3N , 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 N_2 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 N_2 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 Li_3N with only traces of impurity. The Li_3N 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 C_6Li and 2nd stage $C_{12}Li$ was used in the nitriding. The reactor and condition were identical to those in the synthesis of Li_3N . The reactor was pressurized with 10 atm N_2 and the heating was ramped twice at the rate of $12^\circ C/min$ up to about $300^\circ C$. After the reactor was cooled down and excessive N_2 removed, it was opened the DRILAB. X-ray powder photography showed that the product after nitriding was mainly 2nd stage $C_{12}Li$ with some faint lines which appeared to belong to Li_3N .

In the second run, very pure 1st stage C_6Li 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 $C_{12}Li$ and Li_3N , and the pattern of the 1st stage C_6Li was absent.

4.2.4. Annealing of Li_3N /graphite or Li/graphite under N_2 atmosphere

Li_3N Powder and graphite powder were mixed in 1:1 molar ratio and pressed into pellets using a Wilmad evacuable 13 mm die. The pellet was loaded into the reactor for nitriding. About 4 atm. N_2 was added to the reactor. The reaction was run at $700^\circ C$ 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 N_2 removed, it was opened inside the DRILAB. Large clear colorless crystals were seen on the wall of the top part of the $\frac{1}{2}$ " 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 Li_2NCN .^{11, 12} X-ray powder photographs showed the red and white powders on the bottom of the reactor to be a mixture of Li_3N and Li_2NCN . In other experiments, the ratio of Li_3N to graphite used in making pellets was varied and reactions were heated from 2 to 4 days, but lithium cyanimide, Li_2NCN , was always a major product. When the reaction was heated at a lower temperature, 350 °C, for three days, the Li_3N /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. N_2 . 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 N_2 had been consumed. After the reactor was opened inside the DRILAB, clear crystals of Li_2NCN were seen on the wall of the cooled top part of the $\frac{1}{2}$ " tubing.

4.2.5. Interaction of Li_3N and graphite

This reaction was designed to investigate the interaction of Li_3N and graphite in a lithium melt. Inside the DRILAB, Li_3N 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_3N . In a similar reaction, Li_3N chunks were used instead of the Li_3N 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_3N 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_3N and graphite, indicating that there was no interaction between the two in the Na melt.

4.2.6. Interaction of Li_3N and LiN_3

This reaction was to explore the possibility of synthesizing Li_2N_2 . Lithium azide, LiN_3 , was synthesized through a metathesis reaction between Li_2SO_4 and NaN_3 . X-ray powder photography showed¹³ the recrystallized product to be very pure LiN_3 with a trace amount of NaN_3 . Inside the DRILAB, Li_3N 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_3N . 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_3N and LiN_3 .

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 ($a = 4.32 \text{ \AA}$ and $c = 3.71 \text{ \AA}$) and the second stage to be of $C_{12}Li$ ($a = 4.29 \text{ \AA}$ and $c = 7.04 \text{ \AA}$) as previously reported¹⁴. According to Hérold¹⁴, the reflection (100) at $6.40 \text{ \AA}$ of the ordered $C_{18}Li$ type can be seen in addition to the reflection (110) at $3.70 \text{ \AA}$ (the reflection (100) of the $C_{12}Li$ type is also at $3.70 \text{ \AA}$). In our study, the line at $6.40 \text{ \AA}$ was not observed.

The optimum reaction temperature for preparing the first stage C_6Li is about $315 \text{ }^\circ\text{C}$, at which the final product contains only a trace amount of the second stage $C_{12}Li$. Fischer¹⁵ 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 Fischer⁹, 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 $275 \text{ }^\circ\text{C}$, only the second stage $C_{12}Li$ and unreacted graphite were present in the reaction product. In the temperature range of $275 \text{ }^\circ\text{C} - 315 \text{ }^\circ\text{C}$, 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 $315 \text{ }^\circ\text{C}$. At $315 \text{ }^\circ\text{C}$, 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 $C_{12}Li$ formed the majority of the product, and the first stage was no longer present. Instead, Lithium acetylide, Li_2C_2 , 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 C_6Li , becomes positive above 315 °C at ordinary pressures.

At 315 °C, since $\Delta G^\circ \approx 0$, $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$, evidently at higher temperatures $-T\Delta S^\circ$ overwhelms ΔH° . 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 Wisnyi^{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 -

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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 Li_2C_2^a (CuK α Ni Filter)

I/I_0	$1/d^2 \times 10^4$		hkl
	<i>obsd.</i>	<i>calcd.</i>	
s	766	766	011
vs	1086	1086	110
w	1180	1177	101
m	1356	1352	020
w	1715	1712	002
s	2531	2528	121
m	2995	2994	200
w	3063	3064	022
m	3482	3469	031
mb	3774	3760	211
		3790	130
vw	4197	4191	013
vw	4353	4346	220
m	4610	4602	103
vw	4709	4707	202
w	5424	5407	040
vw	6054	6058	222
vw	6474	6464	231
vw	7046	7075	310

vw	7168	7185	213
vw	7931	7936	114
vw	8207	8202	024
vw	8412	8401	240
vw	8552	8517	321
vw	9202	9196	150
vw	10002 α_1	10008	143
vw	10025 α_2	10008	143
vw	10635	10640	134
vw	11206	11196	224

^aOrthorhombic unit cell with $a = 3.665 \text{ \AA}$, $b = 5.440 \text{ \AA}$, $c = 4.833 \text{ \AA}$, space group Immm.

4.3.2. Attempted synthesis of $C_x^+Li_2N^-$

It was reasoned that nitriding the Li intercalant layers in the Li-graphite intercalation compounds might produce Li_2N^- layers which would be then already in between the graphite layers. The 1st stage C_6Li was reacted with 10 atm N_2 at a rate of $12 \text{ }^\circ\text{C/min}$ to $300 \text{ }^\circ\text{C}$. Unfortunately, only Li_3N and the 2nd stage $C_{12}Li$ were produced:

A similar nitriding of a mixture of the 1st stage C_6Li and 2nd stage $C_{12}Li$ also only yielded Li_3N and $C_{12}Li$. No new phase was obtained from the nitriding of Li GIC's. It is possible that Li_3N is thermodynamically more stable at $300 \text{ }^\circ\text{C}$ ($\Delta G_f Li_3N = -20 \text{ kcal/mol}$)²¹ than a compound like $C_x^+Li_2N^-$ because of a very favorable lattice energy for Li_3N . The nitriding of C_6Li to yield Li_3N and $C_{12}Li$ shows that the latter 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 C_x⁺Li₂N⁻.

The synthesis of C_x⁺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 cyanamide, Li₂NCN.

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.

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

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 cyanimide reaction, therefore provides a very efficient way to fix dinitrogen. Reaction 4 is also much simpler and straightforward in making Li_2NCN than the other known methods.

As Li_3N has reasonably good solubility²³, in molten Li, a Li melt was used as a solvent for the reaction between Li_3N 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_3N 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_2N_2 , in which there would be a divalent dinitrogenyl anion, has been explored by interacting Li_3N with LiN_3 in hope that the reaction would proceed as follows:

Heating a mixture of Li_3N with LiN_3 slowly to 300 °C only produced Li_3N , as LiN_3 is not stable at moderately high temperature and decomposed into Li_3N 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_3N 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.

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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 Rüdorf and Schultze in 1954¹, the chemistry and physics of metal-ammonia-graphite ternary systems have been extensively explored^{2,3,4,5,6,7}. 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^{8,9,10}. 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*¹¹ 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*¹² 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)_{2.1}².

In the absorption study by Akuzawa *et al*¹², a significant uptake of gaseous ammonia by first stage alkali metal-graphite intercalation compounds, C_8M ($M = K, Rb, Cs$), was observed. For the K-graphite, the uptake of ammonia is somewhere between 1.0 and 1.33 in molar ratio of NH_3/K . But they reported that the X-ray diffraction patterns of their $C_8M(NH_3)_x$ 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, M_2N^- , and graphite carbon layers are interlaced, we examined the interaction of C_8K with gaseous NH_3 at ambient temperature. A new first stage ternary K- NH_3 -graphite intercalation compound was discovered. Some structural information on $C_8K(NH_3)_x$ was obtained. The interaction of K-graphites with gaseous NH_3 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 C_8K .

The brassy golden C_8K samples were prepared by the two-bulb technique described by Hérol¹³. 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 C_8K as all the reflections can be indexed for C_8K . C_8K 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 C_8K 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" procedure⁷ 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 $C_8K(NH_3)_x$ 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, KNH_2 , were present. The X-ray powder data are given in Table 5.1. In the X-ray diffraction photographs of $C_8K(NH_3)_x$ obtained from ammoniation at pressures below 200 torr, reflections of unreacted C_8K were found to be present.

Table 5.1. X-ray Powder Diffraction Data for $C_8K(NH_3)_x^a$ prepared at NH_3 pressure of 250 torr (CuK α Ni Filter)

I/I_0	$1/d^2 \times 10^4$		hkl
	obsd	calcd	
w.sh	114		
s	238	239	001
vw.sh	464		
w	574		
vw	806		
vs	959	955	002
ms.sh	1039		
ms.sh	1085		
vw	1314		
vw	1710		
vw	1781		
		2149	003
m	2177	2179	100
vw	2299		
m	2413	2418	101

vww	2632		
vw	3133	3134	102
vw	3825	3820	004
vww	4320	4328	103
vww	6001	6000	104
m	6536	6537	110
mw	6766	6776	111
vw	7494	7492	112
vww	8711	8716	200
vww	10335	10356	114
vw	15270 α_1	15253	210
vww	15284 α_2	15253	210

ash = sharp. The X-ray diffraction data is partially indexed for the carbon sub-lattice, hexagonal cell with $a_0 = 2.47 \text{ \AA}$, $c_0 = 6.47 \text{ \AA}$.

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*¹⁴. 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:

$$\Delta V = K(area)^2 t \sigma$$

where ΔV 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 σ , 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_i , (which is also the identity period, I_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 A|A|A.... 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 C₈K (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 C₈K indicates that the electron population in the antibonding π^* band (conduction band) of the carbon layer in C₈K(NH₃)_x is lower than that in the case of C₈K. This decrease of the electron population in the π^* 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 compound⁴ C₈K 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 (*hk*0) reflections of the carbon sublattice. It is possible that these lines are associated with the K-NH₃ 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 biperiodic⁴. Many such biperiodic graphite intercalation compounds have already been discovered⁴. 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 C₈K(NH₃)_x obtained from ammoniation at pressures below 200 torr still contained unreacted C₈K. The absorption isotherms for C₈K-NH₃ reported by Akuzawa *et al*¹² show that the absorption does not reach saturation at lower NH₃ pressures (see Figure 5.1). X-ray diffraction result from this study confirms 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_i , 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). Rüdorf reported an interlayer spacing of 6.56 Å for the first stage C_{12.5}K(NH₃)_{2.1}^{2,3}. Using similar preparation methods, Solin and his coworkers found $d_i = 6.516$ Å for the GIC prepared from C₈K + NH₃(l), and $d_i = 6.586$ Å from HOPG + K-NH₃(l)⁷. They also reported that the first stage C₂₄K(NH₃)_{4.3} has $d_i = 6.633$ Å⁷. From our study, the GIC obtained from C₈K + NH₃(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_i , 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_i , for different K-NH₃-Graphites

K-NH ₃ -Graphite	d_i (Å)	Reference
C _{12.5} K(NH ₃) _{2.1}	6.56	Rüdorf <i>et al</i> ^{2,3}
from C ₈ K + NH ₃ (l)	6.516	Solin <i>et al</i> ⁷
from HOPG + K-NH ₃ (l)	6.586	Solin <i>et al</i> ⁷
C ₂₄ K(NH ₃) _{4.3}	6.633	Solin <i>et al</i> ⁷
C ₈ K(NH ₃) _{1.1}	6.47	This work

5.3.2. Composition

The results of the absorption study by Akuzawa *et al*¹² indicate that the amount of NH₃ absorbed by C₈K at ambient temperature under the ammonia pressure of 400 torr is somewhere between 1.0 and 1.33 in molar ratio of NH₃/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 Å³. The effective volume of the K⁺ cation is ~19 Å³. This leaves approximately 47.5 Å³ for x NH₃ molecules. The effective molecular volume of NH₃ is between ~46 Å³ (estimated from the density of ammonia liquid at 293 K) and ~34 Å³ (from the density of solid ammonia at 88 K). It is reasonable to use the effective molecular volume of NH₃ derived from the similar first stage GIC C₂₄K(NH₃)_{4.3} which is ~44 Å³. Using Setton's model¹⁵, 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*¹². Therefore, this new first stage K-NH₃-graphite ternary intercalation compound probably has approximately the composition of C₈K(NH₃)_{1.1}.

5.3.3. The electrical conductivity

In the electrical conductivity measurement, the σ_{ab} of HOPG used in the synthesis of C₈K was found to be approximately $1.6 \times 10^4 \Omega^{-1} \text{cm}^{-1}$; and the σ_{ab} of C₈K was approximately $8.8 \times 10^4 \Omega^{-1} \text{cm}^{-1}$, which agrees well with the values reported by Murray and Ubbelohde¹⁶. The basal plane conductivity of C₈K(NH₃)_{1.1} after vapor-phase ammoniation was measured to be approximately $5.5 \times 10^4 \Omega^{-1} \text{cm}^{-1}$. Although the σ_{ab} of C₈K(NH₃)_{1.1} is more than 3 times that of graphite, there is a decrease in conductivity compared to C₈K. Disregarding the possible contribution from the K-NH₃ layer and correcting for

the expansion of the cross section compared to C_8K , the σ_{ab}^{corr} is then $6.7 \times 10^4 \Omega^{-1} \text{cm}^{-1}$, still lower than that of C_8K .

This decrease in conductivity compared to C_8K appears to correlate with the smaller expansion of the a parameter in $C_8K(NH_3)_{1.1}$. The smaller expansion of the a parameter is attributed to the decrease of electron population in the π^* 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 π^* 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 $C_8K(NH_3)_{1.1}$ compared to C_8K .

It will be very interesting to compare the conductivity of $C_8K(NH_3)_{1.1}$ with those of the other $K-NH_3$ -graphite intercalation compounds, especially that of $C_{24}K(NH_3)_{4.3}$. The NH_3/K layer in $C_{24}K(NH_3)_{4.3}$ 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 $C_{24}K(NH_3)_{4.3}$ 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, $C_8K(NH_3)_{1.1}$, was prepared by reacting C_8K 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 C_8K . This is attributed to the intercalated NH_3 solvating electrons from the conduction band. $\text{C}_8\text{K}(\text{NH}_3)_{1.1}$ 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 C_8K in NH_3 using a microbalance, in combination with *In Situ X-ray* diffraction study, will be essential to determine the composition more accurately.

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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: $a = 2.464 \text{ \AA}$, $c = 6.708 \text{ \AA}$; h-BN: $a = 2.504 \text{ \AA}$, $c = 6.660 \text{ \AA}$) 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 π 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 π 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 π 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 π 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 gap³ 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^{4,5,6,7,8,9,10} 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, $(\text{BN})_3\text{SO}_3\text{F}$, first prepared in this laboratory^{11,12,13}. As the oxidative intercalation of BN creates holes in the valence band, $(\text{BN})_3\text{SO}_3\text{F}$ is expected to become a conductor with greatly enhanced electrical conductivity. The conductivity studies by Biagioni and Mayorga in these laboratories showed that $(\text{BN})_3\text{SO}_3\text{F}$ is indeed conductive although the work by Hooley¹⁴ failed to confirm this. Therefore, this study was to provide a reliable set of data to support the hole conductor supposition for $(\text{BN})_3\text{SO}_3\text{F}$. The stability of $(\text{BN})_3\text{SO}_3\text{F}$ 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 nitride¹⁵ (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 method¹⁶. HSO_3F (Allied Chemical Co., Morristown, N.J.) was distilled and stored in a Pyrex vessel with a break-seal, prior to use.

Peroxydisulfuryl difluoride, $\text{S}_2\text{O}_6\text{F}_2$, was prepared via the interaction of XeF_2 and HSO_3F (reaction 1) and the subsequent decomposition of $\text{Xe}(\text{SO}_3\text{F})_2$ (reaction 2) according to the literature method¹⁷. $\text{S}_2\text{O}_6\text{F}_2$ was stored over KF to ensure $\text{S}_2\text{O}_6\text{F}_2$ was free of HF in a Pyrex glass vessel with a greaseless J. Young glass-Teflon valve.

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 $\text{S}_2\text{O}_6\text{F}_2$ over BN such that the BN sample was completely immersed in the liquid $\text{S}_2\text{O}_6\text{F}_2$. For powder samples, the reaction was usually complete in half an hour and a deep blue product was obtained. Excess $\text{S}_2\text{O}_6\text{F}_2$ 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 Mayorga¹².

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 SO_3F 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 ¼" 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 ¼" 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 K_2NiF_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 ¼" 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 H_2O could be generated via the interaction of 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, $(\text{BN})_3\text{SO}_3\text{F}$ 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.

$$\rho = \frac{V}{i} \cdot \frac{\pi}{\ln 2} \cdot t \quad (1)$$

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 $(\text{BN})_3\text{SO}_3\text{F}$

The composition for the powder samples proved to be close to $(\text{BN})_3\text{SO}_3\text{F}$. This implies that the SO_3F species must be closely packed between the BN sheets¹¹. Dry $(\text{BN})_3\text{SO}_3\text{F}$ 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 $(\text{BN})_3\text{SO}_3\text{F}$, it decomposed quickly and the blue solid became white and $\text{S}_2\text{O}_6\text{F}_2$ was detected in the gas phase product. A small amount of $\text{S}_2\text{O}_6\text{F}_2$ was added to $(\text{BN})_3\text{SO}_3\text{F}$ prior to the addition of AHF to ensure that there was always enough $\text{S}_2\text{O}_6\text{F}_2$ present and the decomposition was not a consequence of $\text{S}_2\text{O}_6\text{F}_2$ diffusing into the AHF solution from the $(\text{BN})_3\text{SO}_3\text{F}$. When $(\text{BN})_3\text{SO}_3\text{F}$ was exposed to HF vapor and later a small amount of moisture, quite unexpectedly the deep blue $(\text{BN})_3\text{SO}_3\text{F}$ 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 $(\text{BN})_3^+\text{SO}_3\text{F}^-$ salt with HF must be a consequence of addition of H-F to the BN framework as a consequence of initial F^- attack at the positive B sites. It is claimed¹⁸ that BN alone will interact with HF to eventually form $\text{NH}_4^+\text{BF}_4^-$. 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 $(\text{BN})_3\text{SO}_3\text{F}$

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 $(\text{BN})_3\text{SO}_3\text{F}$ was determined to be $\sim 1.5 \text{ Scm}^{-1}$. This value is rather low compared to the graphite intercalation compounds, or even to the highly crystalline pure HOPG which has a conductivity of $\sim 2.0 \times 10^4 \text{ Scm}^{-1}$. 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 $(\text{BN})_3\text{SO}_3\text{F}$ down to $\sim 100 \text{ K}$ 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 $\text{C}_{8.3}\text{SO}_3\text{F}$ is approximately $1.1 \times 10^5 \text{ Scm}^{-1}$, representing a 5-fold increase over that of HOPG. The charge carrier concentration in $\text{C}_{8.3}\text{SO}_3\text{F}$ should be comparable to that in $(\text{BN})_3\text{SO}_3\text{F}$ if there is complete electron transfer to form SO_3F^- as the sole guest species. Therefore, the low conductivity of $(\text{BN})_3\text{SO}_3\text{F}$ is unlikely to arise simply from difference in charge carrier concentration.

The specific conductivity, σ , is not only related to the concentration of free charge carriers, n , but also to the mobility, μ , of the charge carriers:

$$\sigma = ne\mu_e + pe\mu_p \quad (2)$$

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, τ :

$$\mu = e\tau/m^* \quad (3)$$

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 chain¹ with an interatomic spacing of a , and an interaction between neighboring atoms of β (β negative for bonding), the band width is $4|\beta|$ and the mobility of an electron near the bottom of the band is:

$$m^* = -\hbar^2 / (2\beta a^2) \quad (4)$$

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).

$$m^* = |\hbar^2 / (d^2E / dk^2)| \quad (5)$$

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 π 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 potentials²⁰, $I.P.(B) = 8.298 \text{ eV}$ and $I.P.(N) = 14.534 \text{ eV}$. Therefore, BN has some

ionic character and the π 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 $(\text{BN})_3\text{SO}_3\text{F}$ is a consequence of this low mobility of hole charge carriers in the $(\text{BN})_3\text{SO}_3\text{F}$ salt.

6.4. Conclusion

Boron nitride fluorosulfate $(\text{BN})_3\text{SO}_3\text{F}$ has been found to be quite stable in a dry environment. $(\text{BN})_3\text{SO}_3\text{F}$ 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 $(\text{BN})_3\text{SO}_3\text{F}$ has been clearly shown to be conductive, with the specific conductivity being approximately 1.5 Scm^{-1} . The much lower conductivity of $(\text{BN})_3\text{SO}_3\text{F}$, 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 $(\text{BN})_3\text{SO}_3\text{F}$. 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 $(\text{BN})_3\text{SO}_3\text{F}$ experimentally from the Hall effect.

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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 π bands of graphite.

Figure 6.3. Two nonbonding crystal orbital combinations at the point P.

Figure 6.5. Temperature dependence of the conductivity of $(\text{BN})_3\text{SO}_3\text{F}$

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_2 was passed through a metal coil cooled down to $-78^\circ C$ to remove any moisture. NF_3 was prepared by direct fluorination of N_2F_4 (Airco, Riverton, NJ) at room temperature. BrF_5 was prepared by direct fluorination of Br_2 first at room temperature and then heated to $300^\circ C$ with 10 atm F_2 . IF_5 was treated with F_2 at low temperature before use.

7.2.2. Reaction in the gas phase

7.2.2.1. Interaction of Xe, F_2 and AsF_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^{-7} torr. A thick clear plastic sleeve was put onto the reactor as a shield for protection against shattering or explosion. Xe, AsF_5 , and F_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_2 and AsF_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^{-7} torr. Xe, AsF_5 , and F_2 were condensed into the reactor and the vapor pressures of Xe, AsF_5 , and F_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 7.1⁴. 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 $\sim 30^\circ$ 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 XeFAsF₆. 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 XeF_2 but some mixed tungsten oxyfluorides (see Figure 7.2).

7.2.4. With HF as a solvent

7.2.4.1. Interaction of Xe, F_2 and AsF_5 in the dark

The reactor was made of a $\frac{1}{2}$ " 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 $\sim 30^\circ$ 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 AsF_5 , 0.90 mmole F_2 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 XeFAsF_6 . The weight of the product was 0.1144 g, giving a reaction yield of $\sim 60\%$.

7.2.4.2. Interaction of Xe, F_2 in the dark

The volume of the FEP reactor was approximately 42 ml. A mixture of F_2 (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 XeF_2 (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 O_2AsF_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 AsF_5 as a solvent

7.2.5.1. Interaction of Xe, F_2 and 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 AsF_5 , 1.42 mmole Xe, and 2.13 mmole F_2 were condensed into the Pyrex reactor. The liquid AsF_5 was approximately 1 ml in the reactor. The reaction temperature was maintained at $-60^\circ C$ 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 AsF_5 . Liquid AsF_5 and other unreacted volatiles were removed. And the solid was further evacuated at $-30^\circ C$. The weight of the product was 0.377 g. Raman spectroscopy and X-ray powder photography showed this solid was $XeFAsF_6$. The yield of this reaction was 78%.

In a separate experiment, AsF_5 (2.6 mmole), Xe (2.6 mmole), and F_2 (3.0 mmole) were condensed into the reactor. The volume of the liquid AsF_5 was about 0.35 ml. The reaction was agitated by sloshing the liquid 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 AsF_5 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 O_2 , F_2 and 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 ~13 ml. About 0.35 ml AsF_5 , 2.69 mmole O_2 (~5 atm partial pressure in the reactor), and 1.46 F_2 (~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 AsF_5 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 NF_3 , F_2 and 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 ~24 ml. About 0.35 ml liq. AsF_5 , 2.85 mmole O_2 and 2.85 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 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. AsF_5 . 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 O_2 , F_2 and AsF_5 in liq. BrF_5 in the dark

The volume of the $\frac{1}{2}$ " FEP reactor was approximately 44 ml. About 1 ml BrF_5 , 0.89 mmole AsF_5 , 0.89 mmole O_2 and 0.81 mmole F_2 were condensed into the reactor. Liq. BrF_5 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 BrF_3 present in BrF_5 , which would react with AsF_5 to yield⁵ BrF_2AsF_6 .

7.2.5.7. Interaction of BrF_5 , AsF_5 , and F_2 in the dark

The volume of the $\frac{1}{2}$ " FEP reactor was approximately 48 ml. About 1 ml AsF_5 , 0.89 mmole BrF_5 and 2 mmole F_2 were condensed into the reactor. The reaction was run at $\sim -60^\circ\text{C}$. A large amount of pinkish solid formed in the liq. AsF_5 at this temperature. This pinkish solid was probably an adduct of BrF_5 and AsF_5 . The reaction was agitated vigorously to stir up the solid so that it would have a better chance to react with F_2 . 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. AsF_5 had been. This was probably from the impurity BrF_3 present in BrF_5 , which would react with AsF_5 to yield⁵ BrF_2AsF_6 .

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⁻ + 1/2F₂(g) + A(g) → AF⁻(g)} in Table 7.1. For instance, the enthalpy change ΔH° (e⁻ + 1/2F₂(g) + AsF₅(g) → AsF₆⁻(g)) ≈ -171 kcal/mole, whereas ΔH° (e⁻ + 1/2F₂(g) → F⁻(g)) is only -60 kcal/mole.

Table 7.1. Standard Enthalpy ΔH° (kcal/mol) for the fluoride affinity of Lewis acids and for F₂/Lewis acid oxidation half-reaction.

HF(g) + F ⁻ (g) → HF ₂ ⁻ (g)	-37±2	Ref. ⁶
BF ₃ (g) + F ⁻ (g) → BF ₄ ⁻ (g)	-92±6	Ref. ⁷
PF ₅ (g) + F ⁻ (g) → PF ₆ ⁻ (g)	-101±8	Ref. 7
AsF ₅ (g) + F ⁻ (g) → AsF ₆ ⁻ (g)	-111±4	Ref. 7
F(g) + e ⁻ → F ⁻ (g)	-79	
HF(g) + F(g) + e ⁻ → HF ₂ ⁻ (g)	-116±2	
BF ₃ (g) + F(g) + e ⁻ → BF ₄ ⁻ (g)	-171±6	
PF ₅ (g) + F(g) + e ⁻ → PF ₆ ⁻ (g)	-180±8	
AsF ₅ (g) + F(g) + e ⁻ → AsF ₆ ⁻ (g)	-190±4	
1/2F ₂ (g) + e ⁻ → F ⁻ (g)	-60	
HF(g) + 1/2F ₂ (g) + e ⁻ → HF ₂ ⁻ (g)	-97±2	
BF ₃ (g) + 1/2F ₂ (g) + e ⁻ → BF ₄ ⁻ (g)	-152±6	
PF ₅ (g) + 1/2F ₂ (g) + e ⁻ → PF ₆ ⁻ (g)	-161±8	
AsF ₅ (g) + 1/2F ₂ (g) + e ⁻ → AsF ₆ ⁻ (g)	-171±4	

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:

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.

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.

When irradiated with sunlight, the gaseous mixture of $\text{O}_2/\text{F}_2/\text{AsF}_5$ rapidly generates⁸ the dioxygenyl salt O_2AsF_6 . Xe and O_2 have indistinguishable ionization potentials ($\text{IP} = 12.13 \text{ eV}$)², yet $\text{O}_2^+\text{AsF}_6^-$ 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 $\text{O}_2^+\text{AsF}_6^-$. 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_2AsF_6 (see Chapter 8 and reference⁹).

The reaction of Xe and F_2 in AHF in the dark at $\sim 20^\circ\text{C}$ 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).

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 $\text{BrF}_6^+\text{AsF}_6^-$ was produced. A small quantity of IF_6AsF_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_6AsF_6 was formed from the interaction of IF_7 and AsF_5 . The yield of IF_6AsF_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_6AsF_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 solid¹⁰. The molecular volume of XeFAsF_6 is $156.2 \text{ \AA}^3$ from the crystallographic data¹¹. 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, ΔH_V , of AsF_5 . ΔH_V can be evaluated by Trouton's law. The boiling point of AsF_5 is -53.2°C . Therefore, ΔH_V of AsF_5 is approximately 4.5 kcal/mole. We have

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

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

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

$$T\Delta S \approx -16 \text{ kcal mole}^{-1} \text{ at } 208 \text{ K } (-65^\circ\text{C})$$

We have the free energy change $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$:

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

Therefore, the reaction of Xe, F₂ and liq. AsF₅ is highly favored thermodynamically.

By analogy to the above analysis for the Xe case, the energetics of O₂AsF₆ reaction can also be evaluated (Figure 7.5).

Figure 7.5. Enthalpy change for the acid-assisted oxidation of O₂

Corrected with the ΔH_v of liquid AsF₅, the enthalpy change for the reaction of O₂/liq. AsF₅/F₂ at -65°C is:

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

S° 41 56 24 58

$$\Delta S^\circ \approx -63 \text{ e.u.} \qquad T\Delta S \approx -13 \text{ kcal mole}^{-1} \text{ at } 208 \text{ K } (-65^\circ\text{C})$$

$$\Delta G^\circ \approx -4.5 \text{ kcal mole}^{-1}$$

Again, although the free energy change is smaller than that for the oxidation of Xe, the oxidation of O₂ is highly favorable thermodynamically. It should be noted, however, that this favorability is less sure than in the XeFAsF₆ 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) AsF₅ or HF, suggests that a concerted interaction of the xenon donor (D) with F₂ 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 (σ^*) of the F₂, the π^* HOMO of the F₂, and the sigma LUMO of the acid. Donation of the Xe electron pair to the σ^* of the F₂ is more probable if the Lewis acid is already associated with the F₂ molecule (i.e. F₂:→A) via the F₂ HOMO (π^*) and the AsF₅ LUMO, the three reactants smoothly moving to products, as the (Xe-F)⁺ bond is made and the F-F bond is broken heterolytically:

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.

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

The bonding of Xe^+ with F atom, for which¹² $-\Delta H^\circ \{ \text{Xe}(\text{g})^+ + \text{F}(\text{g}) \rightarrow (\text{Xe-F})^+ \} \geq 47 \text{ kcal/mole (2.03 eV)}$, contrasts with that of O_2^+ , for which $-\Delta H^\circ \{ \text{O}_2^+(\text{g}) + \text{F}(\text{g}) \rightarrow (\text{O}_2\text{F})(\text{g})^+ \}$ 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 bonding¹³ in any $(\text{O}_2\text{F})^+$ species. The ion pair energy for $(\text{DF})^+$ with $(\text{AF})^-$ should be nearly the same in the two cases. All other enthalpy and entropy changes are either the same or comparable. Thus the $(\text{D-F})^+$ 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 XeF_2 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 IrF_6 rapidly oxidizes Xe to $XeFIr_2F_{11}$ in AHF while there is no interaction between them with the absence of AHF solvent.

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 $(\text{XeF})^+$ 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.

$$\therefore \text{IP}(\text{XeF}) \leq 9.95 \text{ eV}$$

Figure 7.7. A thermal cycle for estimating $\text{IP}(\text{XeF})$

Radioactive ^{18}F ($t_{1/2} = 109.7 \text{ min.}$) 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}F exchange by Adams and

Schrobilgen¹⁶ on the activation of F₂ 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 ¹⁸F exchange is observed in the systems of HF/F₂, HF/AsF₅/F₂ and AsF₅/F₂ under similar reaction conditions. In the reaction system Xe/F₂/liq. AsF₅, ¹⁸F-labeled AsF₅ was used:

At the end of the reaction, the product XeFAsF₆ was found to contain some ¹⁸F activity but no transfer of ¹⁸F activity to F₂ was observed. If the reaction involved a radical mechanism and homolytic cleavage of F₂, it would be expected to result in some ¹⁸F/¹⁹F scrambling and consequently the transfer of ¹⁸F activity to F₂.

From our proposed mechanism, It is expected that there should be no ¹⁸F activity contained in the (FXe)⁺ cation in the product (FXe)⁺([¹⁸F]-AsF₆⁻) obtained in reaction 11. Therefore, it will be very interesting to carry out the following two experiments in the future ¹⁸F exchange study.

In reaction 12, XeFAsF₆ readily loses AsF₅ to give Xe₂F₃AsF₆ in a dynamic vacuum. Theoretically, the original ¹⁸F activity in XeFAsF₆ will be divided into a distribution of 7/12 in Xe₂F₃AsF₆ and 5/12 in AsF₅ if all the original ¹⁸F activity is only contained in AsF₆⁻ and is randomized¹⁷. 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 $\text{F}_2/\text{Lewis acid}$ 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 $\text{F}_2/\text{Lewis acid}$ 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 $\text{Cl}_2\text{F}^+\text{AsF}_6^{-18,19}$ 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.

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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 O_2^+ and Ag^{2+} Cations

8.1. Introduction

In 1962, the first O_2^+ compound, O_2PtF_6 , was described by Bartlett and Lohmann¹. In one of the syntheses of O_2PtF_6 , molecular O_2 was oxidized directly by PtF_6 at room temperature. This led to another ground-breaking discovery as Bartlett reasoned that, if O_2 could be oxidized by PtF_6 , so should Xe as they have indistinguishable ionization potentials², and thus prepared the first compound of an inert gas element.

O_2^+ cation is a powerful one-electron oxidizer as indicated by the high electron affinity of gaseous 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 O_2 , which is ordinarily lost from the reaction mixture as the gas. It was shown by Stein in 1973 that O_2SbF_6 in solid form can fix radon and also oxidize gaseous Xe to $XeFSb_2F_{11}$ ³. Richardson, Tanzella and Bartlett⁴ also used O_2^+ to oxidize hexafluorobenzene and other perfluoroaromatics. In this study, the utility of O_2^+ compounds, especially O_2AsF_6 , as a convenient one-electron oxidizer in the preparation of high oxidation state Ag compounds has been systematically studied. The use of O_2^+ salts in the syntheses of a new class of pseudo-trifluoride Ag compounds, $(AgF_2)_3MF_6$ ($M = As, Au, Pt$), will be discussed in detail in Chapter 10. In all this work the discovery that the O_2^+ salts dissolve in AHF to yield stable solutions has been of central importance.

It has been shown that solvated Ag^{2+} cation in AHF is a powerful oxidizer, capable of oxidizing Xe (Ref. ⁵), C_6F_6 and C_3F_6 (Ref. ⁶). Recently, the

remarkable oxidizing power of Ag^{2+} was further demonstrated⁶ by William Casteel in the oxidation of O_2 to O_2AsF_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_2AsF_6 was prepared according to literature method⁷. KIrF_6 was prepared⁶ 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_2AsF_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_2AsF_6 from O_2 , AsF_5 and F_2 . After scraping out most of the reaction product, there was still some white O_2AsF_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 BrF_5

In the DRILAB, 0.0823 g O_2AsF_6 (0.373 mmole) was loaded into an FEP reactor. About 2 ml liq. BrF_5 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, BrF_5 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 O₂AsF₆ (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 O₂AsF₆ and NaF in approximately equal amounts. The O₂AsF₆ solution at ~25°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 NaAsF₆.

8.2.3.2. reaction with IrF₆⁻ in AHF

In the DRILAB, O₂AsF₆ (0.0788 g, 0.3567 mmole) and KIrF₆ (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 O₂AsF₆ and KIrF₆. KIrF₆ dissolved partially in the AHF. The O₂AsF₆ solution was poured into the KIrF₆ 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 KIrF₆ solid disappeared and a white solid crystallized from the solution. The whole solution became yellow. HF and the volatile yellow species (IrF₆) were condensed into the side arm and kept at 0°C. SF₄ 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 photography⁸ showed that the white solid in the side arm was SF₃IrF₆ and the white solid in the first tube was KAsF₆. The weight of KAsF₆, 0.0874 g, exceeded the calculated yield, 0.0803 g, probably because of the interaction of the Teflon container with the molecular IrF₆.

8.2.3.3. reaction with AgF in AHF

AHF was further dried over O_2AsF_6 in a separate FEP reactor after having been dried over K_2NiF_6 . AgF (0.0632 g, 0.4981 mmole) and O_2AsF_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 O_2AsF_6 . The O_2AsF_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 O_2AsF_6 solution was added. Later, the interface where the O_2AsF_6 solution and the AgF solution met became blue. Gradually, as more O_2AsF_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 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 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 O_2AsF_6 solution instead. AgF (0.0692 g, 0.5454 mmole) and O_2AsF_6 (0.1223 g, 0.5536 mmole) were used in this reaction. When the AgF solution was first poured into

the O_2AsF_6 solution, the colorless O_2AsF_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_2AsF_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 ~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 $(\text{AgF}_2)_3\text{AsF}_6$ 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_2AsF_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_2NiF_6 , was further dried over O_2AsF_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_2AsF_6 . Most of the AgAsF_6 did not dissolve in the HF solution. The O_2AsF_6 solution was poured slowly, in several batches, into the AgAsF_6 solution. As soon as the O_2AsF_6 solution was poured in, the AgAsF_6 solution turned blue with simultaneous vigorous evolution of oxygen. As more O_2AsF_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_2AsF_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_2AsF_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_2AsF_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_2AsF_6 solid separately. The dissolution of KF and AgF in AHF gave a milky suspension. The O_2AsF_6 solution was poured slowly into the KF + AgF solution, which was being vigorously stirred. At the interface where the O_2AsF_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^- anion⁹ together with the AsF_6^- anion¹⁰ (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_2AsF_6 was loaded into the main tube of the reactor. This time, the $\text{KF} + \text{AgF}$ solution was poured into the O_2AsF_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 precipitate¹¹ 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 convert¹¹ AgF_3 to Ag_3F_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_3F_8 . From the weight of the reddish brown Ag_3F_8 obtained, the yield of KAgF_4 from the interaction of $\text{AgF} + 2\text{O}_2\text{AsF}_6$ in excess KF was calculated to be nearly 23%.

8.2.3.6. reaction with AgF_2 in basic AHF

Inside the DRILAB, AgF_2 (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 $\frac{1}{2}$ " FEP reactor. O_2AsF_6 (0.1227 g, 0.5554 mmole) was loaded into the reactor's side arm. AHF , treated with K_2NiF_6 , was further dried over O_2AsF_6 in another FEP reactor. About 2 ml AHF in total was condensed on to the $\text{KF} + \text{AgF}_2$ mixture and the O_2AsF_6 separately. With the $\text{KF} + \text{AgF}_2$ solution being stirred very vigorously, the O_2AsF_6 solution was gradually added. A very fast reaction took place with oxygen evolution and the $\text{KF} + \text{AgF}_2$ solution quickly turned yellow. After all the O_2AsF_6 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 KAgF_4 and KAsF_6 with a strong pattern of KAgF_4 , and the reddish brown solid was still AgF_2 . The weight of the unreacted AgF_2 was 0.0422 g (0.2893 mmole). Based on the amount of AgF_2 that was consumed, the yield of KAgF_4 was estimated to be ~42%.

8.2.3.7. reaction of O_2AsF_6 with AgF_2 in neutral AHF

The reaction is described in detail in Chapter 10. Reacting three parts of AgF_2 with one part of O_2AsF_6 (O_2AsF_6 slightly in excess) produces $(\text{AgF}_2)_3\text{AsF}_6$.

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_2AsF_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_2AsF_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_2AsF_6 solution was poured slowly into the blue AgFAsF_6 solution. There was no noticeable reaction. After all the O_2AsF_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_2AsF_6 . 0.0151 g black solid was retrieved from this experiment. The black solid was later characterized to be $(\text{AgF}_2)_3\text{AsF}_6$ (see Chapter 10).

8.2.3.9. interaction with $(\text{AgF}_2)_3\text{AsF}_6$ in AHF

This is essentially the same reaction described in the section above. In this case, the black $(\text{AgF}_2)_3\text{AsF}_6$ 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_2AsF_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 ½" 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 ~½ 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 $\sim -60^\circ\text{C}$, 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_2AsF_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

(~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 AgFAsF₆. AgFAsF₆ was quantitatively recovered.

8.2.4.2. Reaction of AgFAsF₆ 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*¹², 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 :

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 :

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:

8.3.2. The oxidation chemistry of O_2AsF_6

O_2AsF_6 reacts with alkali metal fluoride through a displacement reaction and generates the gaseous basic fluoride, O_2F radical, which dissociates into O_2 and F_2 :

This displacement of the base, O_2F , occurs whenever a strong fluorobase is present. AgF and any alkali fluoride must interact in this way.

O_2AsF_6 is found to oxidize IrF_6^- quantitatively, liberating IrF_6 :

The electron affinity of IrF_6 has been estimated at ≤ 160 kcal/mol (6.9 eV)¹³.

Also, no dioxygenyl salt has been observed⁸ from the interaction of IrF_6 and several atmosphere of O_2 at room temperature. O_2PtF_6 is found to be quite soluble in AHF and can be recrystallized quantitatively from AHF. This indicates that O_2^+ is incapable of oxidizing PtF_6^- in AHF solution at least at $\sim 20^\circ\text{C}$. The electron affinity of PtF_6 has been estimated at 182 kcal/mol (7.9 eV), approximately 1 eV higher¹³ than IrF_6 .

O_2AsF_6 interacts with AgF in AHF to produce AgFAsF_6 at 70 - 75% yield:

AgF_2 is produced as the major byproduct in this reaction. The reaction proceeds differently, depending on whether the O_2AsF_6 solution is poured into the AgF

solution or vice versa. When the O_2AsF_6 solution was poured into the AgF solution, AgF_2 was generated first and the blue solution characteristic of solvated Ag^{2+} appeared later. When the AgF solution was poured into the O_2AsF_6 solution instead, that solution became blue immediately and AgF_2 began to precipitate only as the concentration of Ag(II) increased and O_2^+ decreased.

Since O_2AsF_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 radical¹⁴ O_2F cannot occur) the ionization of the salt is likely to be complete:

When a strong base such as AgF is present, however, O_2F is displaced and this can act effectively as a fluorine atom source. The oxidation of Ag(I) to Ag(II) can be brought about in that way:

as well as by interaction with O_2^+ :

But either way, the high F(HF)_n^- concentration, existing in the AgF -rich solution, ensures precipitation of Ag(II) as AgF_2 :

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:

In neutral AHF, O₂AsF₆ oxidizes AgF₂ rapidly to generate a novel material (AgF₂)₃AsF₆, in which the average silver oxidation state is 2 $\frac{1}{3}$.

Reaction 6 proceeds quantitatively. Detailed discussion is given in Chapter 10.

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:

The yield of KAgF_4 from the interaction of O_2AsF_6 with $\text{AgF} + \text{KF}$ 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_2AsF_6 with $\text{AgF} + \text{KF}$ is quite satisfactory, being as high as 42%. Since some AgF_4^- is probably solvolyzed by HF to generate AgF_3 and $\text{F}(\text{HF})_n^-$. 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 prepared⁹ 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 times¹⁵. The yield of reaction 13 and 14 is probably also diminished by the loss of O_2^+ in combining with F^- to generate O_2F 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_2F . The oxidation reaction may proceed from AgF_2 as follows:

There is no detectable interaction between solvated Ag^{2+} cation and O_2AsF_6 in acidic HF. Neither is there interaction between $(\text{AgF}_2)_3\text{AsF}_6$ and O_2AsF_6 .

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

It has been demonstrated that cationic $\text{Ag}(\text{II})$ is capable of oxidizing Xe at ordinary pressure and temperature⁵. The initial attempt to oxidize O_2 with cationic $\text{Ag}(\text{II})$ 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 discovered⁶ that the cationic $\text{Ag}(\text{II})$ is able to oxidize O_2 at temperatures below -60°C when the AHF solution is highly acidic in AsF_5 :

In this study, the possible catalytic property of $\text{Ag}(\text{II})$ 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, $\text{Ag}(\text{II})$ was found to be completely reduced to $\text{Ag}(\text{I})$ 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_2AsF_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 $\sim 0^\circ\text{C}$. 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.

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^{16, 17}. The interaction¹⁸ of Cl_2 and IrF_6 , although providing some evidence of $\text{Cl}_2^+\text{IrF}_6^-$ as the intermediate product, quickly degrades via Cl_3^+ salts to the pentafluoride of iridium, Ir_5F_{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 $\text{Ag}(\text{AsF}_6)_2$, 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 not¹⁹ $\text{ClF}_2^+\text{AsF}_6^-$. By analogy to Br_2^+ and I_2^+ , the Cl_2^+ is expected¹⁷ 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 description²⁰ of $\text{Cl}_3^+\text{AsF}_6^-$, which is known to dissociate into Cl_2 , ClF , and AsF_5 at ordinary temperatures (reaction 20).

The vibrational frequency of Cl_2^+ in the gas phase²¹ 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 potential²² 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 $\text{Ag}^{2+}(\text{solv})$ is a powerful oxidizer both in water²³ and in HF. But the electron affinity of $\text{Ag}^{2+}(\text{solv})$ must be very much lower than the 2nd ionization potential of the gas because of the high solvation energy.

The lower limit of $\text{IP}(\text{Ag}^+(\text{solv}) \rightarrow \text{Ag}^{2+}(\text{solv}))$ can be evaluated from the Born-Haber cycle given in Figure 8.2 where E_{solv} , and U_L stand for the solvation energy and the lattice energy, respectively.

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

$$\Delta H_2 = -U_L(AgAsF_6) - U_L(O_2AsF_6) + E_{solv}(O_2^+(g)) + E_{solv}(Ag^+(g))$$

$$\begin{aligned} \Delta H = & IP(O_2(g) \rightarrow O_2^+(g)) - IP(Ag^+(solv) \rightarrow Ag^{2+}(solv)) + E_{solv}(Ag^+(g)) \\ & - U_L(AgAsF_6) - U_L(O_2AsF_6) \end{aligned}$$

Figure 8.2. Born-Haber Cycle for the oxidation of O_2 by 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 - 60°C but is reversed above that temperature, ΔH must be negative for ΔG to be negative below -60°C, but the value of ΔH must also be small. The lattice energy can be estimated¹³ within ~5 kcal/mole for each of $AgAsF_6$ and O_2AsF_6 .

Therefore, from the calculated $U_L(O_2AsF_6)$ (131 kcal/mol) and $U_L(AgAsF_6)$ (140 kcal/mol)²⁴, and the ionization potential of gaseous O_2 (280 kcal/mol), we have

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

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

This indicates that the oxidation of O_2 by solvated $Ag(II)$ in highly acidic HF at low temperatures is lattice energy driven as the high $IP(O_2(g) \rightarrow O_2^+(g))$ is offset by the lattice energy released from the formation of solid $AgAsF_6$ and O_2AsF_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 $\text{IP}(\text{Ag}^+(\text{solv}) \rightarrow \text{Ag}^{2+}(\text{solv}))$.

The upper limit of $\text{IP}(\text{Ag}^+(\text{solv}) \rightarrow \text{Ag}^{2+}(\text{solv}))$ can be evaluated from the oxidation of $\text{Ag}^+(\text{solv})$ to $\text{Ag}^{2+}(\text{solv})$ by $\text{O}_2^+(\text{solv})$ at room temperature. When the AgF solution is poured into the O_2AsF_6 solution, the solution rapidly becomes blue, indicating that the oxidation of $\text{Ag}^+(\text{solv})$ to $\text{Ag}^{2+}(\text{solv})$ by $\text{O}_2^+(\text{solv})$ is very favorable at room temperature:

$$\begin{aligned} \Delta H &= -\text{IP}(\text{O}_2(\text{g}) \rightarrow \text{O}_2^+(\text{g})) + E_{\text{solv}}(\text{O}_2^+(\text{g})) + \text{IP}(\text{Ag}^+(\text{solv}) \rightarrow \text{Ag}^{2+}(\text{solv})) \\ &= -\text{IP}(\text{O}_2(\text{g}) \rightarrow \text{O}_2^+(\text{solv})) + \text{IP}(\text{Ag}^+(\text{solv}) \rightarrow \text{Ag}^{2+}(\text{solv})) \end{aligned}$$

As a consequence of its higher charge, the standard entropy, S° , for $\text{Ag}^{2+}(\text{solv})$ must be smaller than that for $\text{Ag}^+(\text{solv})$, 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.

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

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

$\text{Ag}^{2+}(\text{solv})$ has been found to be capable of oxidizing $\text{IrF}_6^-(\text{solv})$ in acidic HF at room temperature²⁵, 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 $\text{IrF}_6^-(\text{solv})$ to $\text{IrF}_6(\text{solv})$ by $\text{O}_2^+(\text{solv})$ 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, $\text{IP}(\text{Ag}^+(\text{solv}) \rightarrow \text{Ag}^{2+}(\text{solv}))$ is probably comparable to $\text{IP}(\text{O}_2(\text{g}) \rightarrow \text{O}_2^+(\text{solv}))$ with $[\text{IP}(\text{O}_2(\text{g}) \rightarrow \text{O}_2^+(\text{solv})) + 14]$ 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

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

The electron affinity of PtF_6 (7.9 eV) is 1 eV higher¹³ 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:

$$\begin{aligned} \Delta H &= -\text{IP}(\text{O}_2(\text{g}) \rightarrow \text{O}_2^+(\text{g})) + E_{\text{solv}}(\text{O}_2^+(\text{g})) + \text{EA}(\text{IrF}_6) + E_{\text{solv}}(\text{IrF}_6^-) - E_{\text{solv}}(\text{IrF}_6) \\ &= -\text{IP}(\text{O}_2(\text{g}) \rightarrow \text{O}_2^+(\text{solv})) + \text{EA}(\text{IrF}_6) + E_{\text{solv}}(\text{IrF}_6^-) - E_{\text{solv}}(\text{IrF}_6) \end{aligned}$$

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 $S^\circ(\text{O}_2(\text{g}))$ (49 e.u.). At room temperature (295 K), the $T\Delta S$ term is then smaller than 14 kcal/mol.

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

$$\begin{aligned} \therefore IP(O_2(g) \rightarrow O_2^+(solv)) &> EA(IrF_6) + E_{solv}(IrF_6^-) - E_{solv}(IrF_6) - 14 \\ &> 146 + E_{solv}(IrF_6^-) - E_{solv}(IrF_6) \quad (\text{kcal/mol}) \end{aligned}$$

The upper limit for $IP(O_2(g) \rightarrow O_2^+(solv))$ can then be reasonably set at $[169 + E_{solv}(IrF_6^-) - E_{solv}(IrF_6)]$ kcal/mol.

8.4. Conclusions

It has been demonstrated that O_2^+ cation in AHF is a very powerful one-electron oxidizer, capable of oxidizing IrF_6^- to IrF_6 , and Ag^+ to cationic Ag^{2+} . It can even oxidize $Ag(I)$ and $Ag(II)$ to $Ag(III)$ in anionic AgF_4^- under basic conditions, or oxidize $Ag(II)$ to $(AgF_2)_3MF_6$.

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

$$E_{solv}(Ag^+(g)) + 9 < IP(Ag^+(solv) \rightarrow Ag^{2+}(solv)) < IP(O_2(g) \rightarrow O_2^+(solv)) + 14$$

Once the solvation energies of Ag^+ and O_2^+ in AHF are assessed, the oxidizing power of solvated Ag^{2+} can be more quantitatively placed. An interaction of Ag^{2+} and Cl_2 in AHF may proceed via a Cl_2^+ salt but it is unstable at ordinary temperatures.

8.5. References

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Figure 8.1. Raman spectrum of a mixture of KAgF₄ and KAsF₆

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^{1,2,3,4,5}. AgFAsF_6 and AgFBF_4 were synthesized by either reacting AgF_2 with the corresponding Lewis acid AsF_5 and BF_3 or by fluorinating AgAsF_6 and AgBF_4 ^{1,2,3}. AgFlrF_6 was also prepared by fluorinating AgIrF_6 ⁵. AgFAuF_6 and AgFAuF_4 were prepared through metathesis reactions with AgFAsF_6 ⁴. In these compounds the AgF^+ cation exists as a one-dimensional chain $(\text{AgF})_n^{n+}$. Single crystal structure analysis has shown that AgFAsF_6 and AgFlrF_6 are very alike structurally^{1,5}. $(\text{AgF})_n^{n+}$ in AgFAsF_6 and AgFlrF_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 $(\text{AgF})_n^{n+}$ chains in AgFBF_4 are linear³, 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 $\text{W}_2\text{O}_2\text{F}_9^-$ anion and the other has a complex anion formed by WOF_5^- with BF_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_5^- with BF_3 is also of same significance.

The relative stabilities of the AgF^+ salts and the failure to prepare AgFWOF_5 will be discussed in the context of the Lewis acid character of the $(\text{AgF})_n^{n+}$ cation.

9.2. Experimental

9.2.1. Materials

The preparation of WOF_4 was as previously described^{6, 7}. The sublimation product was checked by Raman spectroscopy and X-ray powder photography and was found to be free of detectable contaminants. WF_6 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 SiO_2 .

9.2.2. Preparation of AgWOF_5

Inside the DRILAB, WOF_4 (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 WOF_4 in approximately equal amounts. Both solids dissolved in AHF upon warming to room temperature to give colorless solutions. To avoid the formation of $\text{AgW}_2\text{O}_2\text{F}_9$ during the reaction, the WOF_4 solution was decanted into the AgF solution in the main tube of the reactor. White solid AgWOF_5 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 AgWOF_5 to $\text{AgW}_2\text{O}_2\text{F}_9$, the white solid was washed. The AHF was removed under dynamic vacuum and the AgWOF_5 was vacuum-dried for several hours. Raman

spectroscopy⁸ confirmed that it was mainly AgWOF_5 , containing only a small amount of $\text{AgW}_2\text{O}_2\text{F}_9$ (see Figure 9.1).

9.2.3. Preparation of $\text{KW}_2\text{O}_2\text{F}_9$

The reaction was originally designed to prepare KWO_2F_5 . Inside the DRILAB, KF (0.0720g, 1.239 mmole) and WOF_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 on to the KF and WOF_4 . The KF solution was decanted into the WOF_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 $\text{KW}_2\text{O}_2\text{F}_9$ ⁹ (see Figure 9.2).

9.2.4. Synthesis and crystal structure of $\text{AgW}_2\text{O}_2\text{F}_9$

9.2.4.1. Preparation of $\text{AgW}_2\text{O}_2\text{F}_9$

Inside the DRILAB, AgF (0.0715g, 0.5628 mmole) and WOF_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_4 . The AgF solution was decanted into the WOF_4 solution in the main tube of the reactor. White solid $\text{AgW}_2\text{O}_2\text{F}_9$ 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 $\text{AgW}_2\text{O}_2\text{F}_9$ was vacuum-dried for several hours.

9.2.4.2. Crystal growth

The following synthesis was originally intended to grow crystals of AgWOF_5 . A small amount of AgWOF_5 (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 AgWOF_5 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 $\sim 3^\circ\text{C}$ 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 $\text{AgW}_2\text{O}_2\text{F}_9$

AIM

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Silver Spring, Maryland 20910
301/587-8202

Centimeter

Inches

MANUFACTURED TO AIIM STANDARDS
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3 of 3

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 $P2_1/c$ 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 $\text{AgW}_2\text{O}_2\text{F}_9$.

Formula, mol wt	$\text{AgW}_2\text{O}_2\text{F}_9$, 678.57 a.u.
temperature	295 K
a_0	10.402 Å
b_0	12.307 Å
c_0	13.639 Å
β	90.2°
V	1746.0 Å ³
Z	8
Space group	$P2_1/c$ (No. 14)

$d_{\text{calc.}}$	$3.109 \text{ g} \cdot \text{cm}^{-3}$
Crystal size	$0.25 \cdot 0.18 \cdot 0.17 \text{ mm}$; colorless
Wavelength (Mo $K\alpha$)	$0.71069 \text{ \AA}$
Diffractometer	Enraf-Nonious CAD4, graphite monochromator
Scan range	$\pm h, k, l$
Scan angle	$0.60 + 0.35 \cdot \tan\theta$
Data collected	3369
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	$1/\sigma^2$
Extinction correction	$F_{\text{corr}} = F_{\text{obs}} \cdot (1 + g \cdot I)$, $g = 6.3 \times 10^{-8}$
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 $0^\circ C$ 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_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_2 were removed under a dynamic vacuum and a white solid was retrieved. X-ray powder photography confirmed the white solid to be WOF_4 .

9.4. Synthesis of "AgFWOF₅BF₃"

9.4.1. Reaction of AgWOF₅, BF₃, and F₂ in AHF

Inside the DRILAB, AgWOF₅ (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 AgWOF₅. The reactor was pressurized to about 1100 torr with BF₃. With vigorous agitation, nearly all the white AgWOF₅ dissolved in the HF in the presence of BF₃, 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_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_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^{-3} torr. The blue color of the product appeared to be lighter than that of AgFBF₄. The X-ray powder pattern of the blue product showed a new phase with a marked resemblance to that of AgFBF₄ (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 K α , Ni filter) for the blue phase, orthorhombic cell with $a = 6.77 \text{ \AA}$, $b = 6.60 \text{ \AA}$, $c = 11.78 \text{ \AA}$, $V = 526.1 \text{ \AA}^3$, possible space group Imm2.

I/I_0	$1/d^2 \times 10^4$		hkl
	<i>obs.</i>	<i>calc.</i>	
mw	295	288	002
		291	101
vs	449	448	110
m	739	736	112
vvs	877	874	200
		878	013
ms	923	918	020
wn	1158	1154	004
		1162	202
m	1764	1752	213
		1785	123
ms	1789	1791	220
m	2199	2195	310
m	2285	2283	130
s	2605	2595	006
		2615	303
mw	2714	2714	033
ms	3044	3043	116
w	3470	3469	206
msn	3515	3513	026
wb	3582	3587	233
vw?	3686	3671	040
vw?	3766	3751	107
		3783	402
wb	4035	4031	330

s	4383	4387	226
w	4538	4538	143
		4544	240
ms	4792	4791	316
ms	4877	4879	136
w	5687	5690	510
		5692	145
vw	5940	5954	150
m.sh	6053	6058	109
		6069	019
vwd	6244	6242	152
wvd	6609	6626	336
wvb	6945	6943	219
vw	7127	7107	154
vwd	7909	7905	039
wd	8290	8285	048
		8285	516
vwd	8536	8547	062
wvb	8758	8741	613
vwd	9127	9126	163
		9133	260

9.4.2. Reaction of AgBF_4 , WOF_4 , and F_2 in AHF

Inside the DRILAB, WOF_4 (0.0606 g, 0.220 mmole) and AgBF_4 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 WOF_4 and AgBF_4 in approximately equal amounts. The clear solution of WOF_4 was decanted into the AgBF_4 solution and AHF was condensed back into the main tube to rinse off any residual WOF_4 in the main tube. A small amount of BF_3 (~0.1 mmole) was admitted into the reactor. Enough F_2 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 supernatant 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 " $\text{AgFWOF}_5\text{BF}_3$ " 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 supernatant 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 supernatant 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 " $\text{AgFWOF}_5\text{BF}_3$ "

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 F_2 into the solution. About 25 torr BF_3 (about 0.0721 mmole) and 100 torr F_2 (0.2883 mmole) were introduced into the reactor. The bottom part of the solution where the white $AgBF_4$ solid was kept at $0^\circ C$ with an ice bath to reduce the solubility of $AgBF_4$ in AHF. Blue crystals slowly formed on the reactor wall between the AHF surface and the solid $AgBF_4$. The reaction was left undisturbed until it appeared that all of the $AgBF_4$ 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 $AgWOF_5$ was used as the starting material with BF_3 and F_2 to grow crystals of " $AgFWOF_5BF_3$ ", in the first few hours all the solid $AgWOF_5$ 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 crystal⁵, 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 $\text{AgFW}_2\text{O}_2\text{F}_9$

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 K α , Ni filter) for the lavender AgFW₂O₂F₉

I/I_0	$1/d^2 \times 10^4$ obs.	I/I_0	$1/d^2 \times 10^4$, obs.
vw	231	vw	2598
vw	445	vw	2641
vw	468	mw	2742
vw	517	ms	2800
vw	566	vw	2853
s	593	mw	3017
vs	701	vw	3153
vw	758	vw	3338
vw	860	vw	3373
msd	907	vw	3418
vwd	1018	vw	3541
vw?	1124	w	3664
vw?	1224	vw	3778
vw?	1355	w	3941
vwd?	1515	w	3988
vw?	1602	w	4101
ms	1703	vw	4278
ms	1728	ms	4388
ms	1771	ms	4442
vw?	1891	vwd	5531
vw	1970	wd	5891
vw	2086	vwd	6127
vw	2245	wvb	6342
mw	2327	vwd	6702
s	2351	vw	7117
vw	2398	vw	7267
ms	2460		

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, AgWOF₅ (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:

The low solubility of AgW₂O₂F₉ and the high solubility of AgF combine to complete 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 (F_b). The tungsten atoms are in distorted octahedral environments with the bond distances falling into three categories: (a) tungsten to nonbridging fluorines (F_{nb}), 1.831 - 1.880 Å, (b) tungsten to bridging fluorines (F_b), 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 F_{nb} -W- F_b 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- F_b 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 $AgW_2O_2F_9$ and that of WOF_4 . In the crystal structure of WOF_4 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. WOF_4 is tetrameric in the structure with four corner-sharing distorted octahedra bridged through fluorine. The W- F_b -W bridging angle being 173°. The bond lengths are comparable to those in $W_2O_2F_9^-$ 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:

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(SbF₆)₂¹² whereas the corresponding Ag(AsF₆)₂ salt has never been prepared. Evidently Ag²⁺ captures F⁻ to generate the polymeric (Ag-F)_nⁿ⁺ 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 produces⁵ 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:

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 $\text{W}_2\text{O}_2\text{F}_9^-$ and the complex anion $(\text{WOF}_5\text{BF}_3)^-$ 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:

Although the AgWOF_5 solid is only sparingly soluble in HF, it dissolves on addition of BF_3 . Subsequent fluorination quickly produces the blue material which has a paler blue than AgF_2BF_4 .

Raman data are consistent with the presence of both BF_4^- and WOF_5^- anions⁸ (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^+ salts³ (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 WOF_5^- and BF_3 form a complex anion like $(\text{WOF}_5\text{BF}_3)^-$ with a fluorobridged structure $[\text{OF}_4\text{W-F-BF}_3]^-$ which could be consistent with the Raman spectra. The bridging role of F in the $(\text{WOF}_4)_4$ tetramer indicates that a fluorine ligand is more likely to bridge to BF_3 than is the oxygen ligand of WOF_5^- . A good quality structural study should settle this matter definitively.

The X-ray powder pattern has been indexed with an orthorhombic unit cell, $a = 6.77 \text{ \AA}$, $b = 6.60 \text{ \AA}$, and $c = 11.78 \text{ \AA}$. The unit cell volume is $526.1 \text{ \AA}^3$. The average of the a and b parameters is $6.68 \text{ \AA}$, very close to the a value ($6.69 \text{ \AA}$) of the tetragonal AgFBF_4 . And the c parameter is approximately three times that of AgFBF_4 ($4.00 \text{ \AA}$). Consequently, the line positions of many of the corresponding $(hk0)$, $(hk3)$, and $(hk6)$ reflections of " $\text{AgFWOF}_5\text{BF}_3$ " and AgFBF_4 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 $\text{Imm}2$. 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 AgF_2 , BF_3 , and WOF_4 upon washing with AHF is akin to the similar solvolysis of AgFBF_4 :

Thus the combined WOF_5^- , BF_3 (probably as the fluorobridged anion $[\text{OF}_4\text{W-F-BF}_3]^-$) is able to stabilize AgF^+ , which WOF_5^- alone is not, but the complex anion is evidently extensively solvolyzed by AHF.

9.6.4. $\text{AgFW}_2\text{O}_2\text{F}_9$

$\text{AgFW}_2\text{O}_2\text{F}_9$ has been produced via the following reactions in HF solutions:

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 $\text{AgW}_2\text{O}_2\text{F}_9$ thus needs some WOF_4 present. With vigorous agitation, the reaction proceeded quickly. Fluorination of $\text{AgW}_2\text{O}_2\text{F}_9$ 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:

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 AgBF_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 ⁵. In the fluorination of $\text{AgW}_2\text{O}_2\text{F}_9$, addition of a small amount of BF_3 helped to produce the lavender $\text{AgFW}_2\text{O}_2\text{F}_9$ although some " $\text{AgFWOF}_5\text{BF}_3$ " was also generated during the reaction.

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 " $\text{AgFWOF}_5\text{BF}_3$ " via the interaction with BF_3 :

It is possible that $\text{AgFW}_2\text{O}_2\text{F}_9$ can also be prepared from the metathesis reaction between AgFAsF_6 and $\text{KW}_2\text{O}_2\text{F}_9$:

At the same time as this work was carried out, Dr. Hagiwara and his coworkers in Kyoto University¹³ also synthesized $\text{AgFW}_2\text{O}_2\text{F}_9$. They prepared it from the stoichiometric interaction of AgF_2 and WOF_4 . The reaction was found to be very sluggish and was attributed to the low solubility of AgF_2 in AHF. Attempts by Hagiwara *et al* to prepare AgFWOF_5 , $\text{Ag}(\text{WOF}_5)(\text{W}_2\text{O}_2\text{F}_9)$, or $\text{Ag}(\text{W}_2\text{O}_2\text{F}_9)_2$ from the interaction of AgF_2 and WOF_4 were unsuccessful, the only new phase detected being $\text{AgFW}_2\text{O}_2\text{F}_9$.

The magnetic data for $\text{AgFW}_2\text{O}_2\text{F}_9$ 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^+ salts³. Therefore the lavender material can be reasonably formulated as $\text{AgFW}_2\text{O}_2\text{F}_9$, and not the structural isomer $\text{Ag}(\text{WOF}_5)_2$. The latter would be a simple one-electron paramagnet obedient to the Curie-Weiss law as observed^{3, 14} for $\text{Ag}(\text{AuF}_4)_2$ and $\text{Ag}(\text{AgF}_4)_2$. It was also shown by Hagiwara *et al* from Raman and IR vibrational data that the lavender material contains the dimeric anion $\text{W}_2\text{O}_2\text{F}_9^-$ and not WOF_5^- .

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 $\text{AgFW}_2\text{O}_2\text{F}_9$ contains the $(\text{Ag-F})_n^{n+}$ one-dimensional cation and the anion $\text{W}_2\text{O}_2\text{F}_9^-$ but a crystal structure of $\text{AgFW}_2\text{O}_2\text{F}_9$ 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 $\text{W}_2\text{O}_2\text{F}_9^-$ 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 $\text{AgW}_2\text{O}_2\text{F}_9$ has been solved and the anion $\text{W}_2\text{O}_2\text{F}_9^-$ shown to a fluorine bridged species with the $\text{W}=\text{O}$ bonds trans to the bridging F ligand.

Evidently $(\text{AgF})_n^{n+}$ chain polymer can be stabilized by $[\text{OF}_4\text{W-F-WF}_4\text{O}]^-$ and $[\text{OF}_4\text{W-F-BF}_3]^-$ but not by $[\text{OWF}_5]^-$, thus WOF_4 in this context is an inferior fluoroacid to BF_3 since BF_4^- stabilizes the $(\text{AgF})_n^{n+}$ cation. Thus BF_4^- , $\text{W}_2\text{O}_2\text{F}_9^-$, WO_5BF_3^- are comparable, and weaker fluorobase than WOF_5^- .

9.8. References

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Table 9.2. Positional parameters and their estimated standard deviations for $\text{AgW}_2\text{O}_2\text{F}_9$.

Atom	x	y	z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)	Beqv
W1	0.10220(8)	0.19365(8)	0.41282(1)	2.39(4)	1.68(4)	2.28(3)	-0.25(4)	-0.46(3)	0.02(3)	2.12(2)
W2	0.41612(8)	0.05683(7)	0.68722(1)	1.67(3)	2.22(4)	1.77(3)	-0.86(3)	0.23(3)	0.11(3)	1.89(2)
W3	0.76727(8)	0.20778(8)	0.66497(1)	1.93(3)	2.06(4)	2.18(3)	-0.34(3)	0.12(3)	0.48(3)	2.06(2)
W4	0.26221(8)	0.03664(7)	0.05085(1)	1.80(3)	1.75(4)	1.57(3)	0.09(3)	0.04(3)	0.18(3)	1.71(2)
Ag1	0.4766(2)	-0.2470(2)	0.5763(1)	4.04(8)	2.21(7)	2.63(6)	0.47(8)	0.13(6)	-0.20(6)	2.96(4)
Ag2	0.9394(2)	-0.0041(2)	0.2163(1)	1.95(7)	3.62(9)	3.23(7)	-0.22(7)	0.01(6)	-0.83(7)	2.93(4)
F1	0.273(1)	0.162(1)	0.3980(8)	2.3(5)	4.9(8)	4.2(6)	0.3(6)	0.2(5)	-0.2(6)	3.8(3)
F2	0.950(1)	0.238(1)	0.9420(9)	3.2(6)	6.8(9)	5.1(6)	0.7(7)	0.6(5)	-1.2(7)	5.0(4)
F3	0.122(1)	0.201(1)	0.8154(7)	4.3(6)	3.4(6)	2.5(5)	-1.4(6)	0.3(4)	-0.2(5)	3.4(3)
F4	0.100(1)	0.121(1)	0.5310(8)	5.3(7)	4.4(7)	2.9(5)	-1.0(6)	-1.0(5)	2.1(5)	4.2(3)
F5	0.182(1)	0.182(1)	0.0019(8)	6.2(7)	2.5(6)	3.3(5)	1.3(6)	-0.9(5)	-0.0(5)	4.0(3)
F6	0.908(1)	0.993(1)	0.9233(8)	1.3(5)	5.6(8)	4.4(6)	-1.0(6)	-1.0(4)	1.1(6)	3.8(3)
F7	0.227(1)	-0.004(1)	0.9205(8)	3.6(6)	3.5(7)	2.9(5)	0.6(6)	-1.0(5)	-0.8(5)	3.3(3)
F8	0.268(1)	0.113(1)	0.1660(8)	5.8(7)	2.5(6)	3.1(5)	0.9(6)	-0.9(5)	-0.2(5)	3.8(3)
F9	0.410(1)	0.106(1)	0.0069(9)	2.8(6)	4.2(7)	5.4(6)	-1.0(6)	-0.6(5)	1.7(6)	4.1(3)
F11	0.410(1)	0.155(1)	0.5843(7)	4.6(6)	2.4(6)	2.4(5)	-0.9(5)	0.0(5)	0.6(5)	3.1(3)
F12	0.541(1)	0.049(1)	0.4026(8)	3.0(6)	2.6(6)	4.7(6)	1.0(5)	0.3(5)	-0.3(5)	3.4(3)
F13	0.526(1)	0.033(1)	0.2160(8)	2.6(6)	6.0(8)	4.5(6)	-0.4(6)	-0.5(5)	3.3(6)	4.3(3)
F14	0.418(1)	0.174(1)	0.7744(8)	3.3(6)	4.7(8)	4.3(6)	0.2(6)	0.5(5)	-1.8(6)	4.1(3)
F15	0.613(1)	0.096(1)	0.6795(8)	2.2(5)	2.5(6)	3.9(5)	-0.6(5)	0.3(4)	1.0(5)	2.8(3)
F16	0.850(1)	0.109(1)	0.7469(8)	3.2(6)	2.4(6)	4.3(5)	0.9(5)	0.1(5)	1.4(5)	3.3(3)
F17	0.686(1)	0.231(1)	0.2736(8)	3.7(5)	3.7(7)	3.0(5)	-0.3(6)	0.9(4)	-0.2(5)	3.5(3)
F18	0.806(1)	0.119(1)	0.5609(9)	5.3(7)	2.8(7)	5.0(6)	-0.7(6)	1.7(5)	-0.6(6)	4.3(3)
F19	0.649(1)	0.221(1)	0.0864(8)	3.7(6)	5.1(8)	3.7(5)	0.3(6)	-1.2(5)	-2.9(5)	4.1(3)
O1	0.043(1)	0.098(1)	0.343(1)	5.6(9)	4.4(9)	3.8(7)	-1.5(8)	-2.6(6)	0.4(7)	4.6(4)
O2	0.260(1)	0.027(1)	0.6951(9)	2.7(7)	5.1(9)	2.5(6)	0.6(7)	-0.5(5)	0.2(7)	3.4(4)
O3	0.886(1)	0.203(1)	0.157(1)	3.3(7)	2.2(7)	5.1(7)	0.5(7)	-0.2(6)	-0.9(7)	3.5(3)
O4	0.672(1)	0.080(1)	0.9148(8)	2.2(6)	1.9(6)	1.8(5)	-0.4(5)	-0.5(5)	0.5(5)	2.0(3)

Table 9.3 (a) Intramolecular distances in $\text{AgW}_2\text{O}_2\text{F}_9$.

ATOM 1	ATOM 2	DISTANCE
W1	F1	1.831(11)
W1	F2	1.839(13)
W1	F3	1.867(12)
W1	F4	1.845(12)
W1	F5	2.124(12)
W1	O1	1.636(16)
W2	F11	1.851(11)
W2	F12	1.843(12)
W2	F13	1.824(13)
W2	F14	1.873(13)
W2	F15	2.110(10)
W2	O2	1.672(13)
W3	F15	2.122(11)
W3	F16	1.858(12)
W3	F17	1.870(11)
W3	F18	1.836(13)
W3	F19	1.850(12)
W3	O3	1.664(14)
W4	F5	2.080(13)
W4	F6	1.843(10)
W4	F7	1.880(11)
W4	F8	1.832(12)
W4	F9	1.858(12)
W4	O4	1.657(13)
AG1	F1	2.829(11)
AG1	F9	2.445(13)
AG1	F11	2.740(11)
AG1	F12	2.463(13)
AG1	F14	2.503(12)
AG1	F17	2.666(11)
AG1	F19	2.600(11)
AG1	O4	2.635(13)
AG2	F3	2.544(13)
AG2	F6	2.486(11)
AG2	F7	2.545(11)
AG2	F16	2.592(11)
AG2	O1	2.387(16)
AG2	O2	2.419(13)
AG2	O3	2.725(15)

Table 9.3 (b) Intramolecular bond angles in AgW₂O₂F₉.

ATOM 1	ATOM 2	ATOM 3	ANGLE	ATOM 1	ATOM 2	ATOM 3	ANGLE	ATOM 1	ATOM 2	ATOM 3	ANGLE
F1	W1	F2	163.5(6)	F5	W4	O4	177.7(5)	F6	Ag2	O3	81.3(4)
F1	W1	F3	87.0(5)	F6	W4	F7	86.9(5)	F7	Ag2	F16	137.3(4)
F1	W1	F4	90.5(5)	F6	W4	F8	88.0(5)	F7	Ag2	O1	144.5(5)
F1	W1	F5	80.0(5)	F6	W4	F9	161.5(6)	F7	Ag2	O2	77.0(4)
F1	W1	O1	98.2(7)	F6	W4	O4	99.0(6)	F7	Ag2	O3	67.0(4)
F2	W1	F3	86.1(6)	F7	W4	F8	162.3(5)	F16	Ag2	O1	75.1(5)
F2	W1	F4	91.1(6)	F7	W4	F9	88.5(5)	F16	Ag2	O2	124.7(4)
F2	W1	F5	83.2(6)	F7	W4	O4	96.6(6)	F16	Ag2	O3	133.9(4)
F2	W1	O1	97.0(7)	F8	W4	F9	91.0(6)	O1	Ag2	O3	95.0(5)
F3	W1	F4	163.9(5)	F8	W4	O4	101.0(6)	O1	Ag2	O3	79.3(5)
F3	W1	F5	82.1(5)	F9	W4	O4	98.5(6)	O2	Ag2	O3	94.0(5)
F3	W1	O1	97.1(7)	F1	Ag1	F9	83.5(4)	W1	F1	Ag1	143.2(7)
F4	W1	F5	81.0(5)	F1	Ag1	F11	63.0(3)	W1	F3	Ag2	138.9(5)
F4	W1	O1	99.0(7)	F1	Ag1	F12	71.7(4)	W1	F5	W4	163.6(6)
F5	W1	O1	178.7(4)	F1	Ag1	F14	69.0(4)	W4	F6	Ag2	140.7(6)
F11	W2	F12	87.9(5)	F1	Ag1	F17	117.6(3)	W4	F7	Ag2	144.2(6)
F11	W2	F13	162.6(5)	F1	Ag1	F19	128.4(3)	W4	F9	Ag1	152.0(7)
F11	W2	F14	88.0(5)	F1	Ag1	O4	146.6(4)	W2	F11	Ag1	149.6(6)
F11	W2	F15	81.2(5)	F9	Ag1	F11	74.1(4)	W2	F12	Ag1	142.6(6)
F11	W2	O2	99.2(6)	F9	Ag1	F12	145.5(4)	W2	F14	Ag1	144.9(6)
F12	W2	F13	88.4(6)	F9	Ag1	F14	83.1(4)	W2	F15	W3	152.3(6)
F12	W2	F14	164.7(5)	F9	Ag1	F17	136.1(4)	W3	F16	Ag2	146.3(6)
F12	W2	F15	83.5(5)	F9	Ag1	F19	74.5(4)	W3	F17	Ag1	150.1(7)
F12	W2	O2	97.3(6)	F9	Ag1	O4	73.0(4)	W3	F19	Ag1	139.0(7)
F13	W2	F14	90.3(6)	F11	Ag1	F12	73.4(4)	W1	O1	Ag2	165.7(10)
F13	W2	F15	81.6(5)	F11	Ag1	F14	128.4(4)	W2	O2	Ag2	153.2(7)
F13	W2	O2	98.1(6)	F11	Ag1	F17	149.2(4)	W3	O3	Ag2	138.5(7)
F14	W2	F15	81.3(5)	F11	Ag1	F19	66.2(4)	W4	O4	Ag1	158.1(6)
F14	W2	O2	97.9(6)	F11	Ag1	O4	128.0(3)				
F15	W2	O2	179.1(6)	F12	Ag1	F14	108.6(4)				
F15	W3	F16	82.4(5)	F12	Ag1	F17	77.8(4)				
F15	W3	F17	81.2(5)	F12	Ag1	F19	102.3(4)				
F15	W3	F18	81.4(5)	F12	Ag1	O4	138.7(4)				
F15	W3	F19	82.0(5)	F14	Ag1	F17	71.5(4)				
F15	W3	O3	178.2(6)	F14	Ag1	F19	148.5(4)				
F16	W3	F17	89.9(5)	F14	Ag1	O4	84.7(4)				
F16	W3	F18	88.6(5)	F17	Ag1	F19	110.4(3)				
F16	W3	F19	164.4(5)	F17	Ag1	O4	69.6(4)				
F16	W3	O3	97.4(6)	F19	Ag1	O4	67.9(4)				
F17	W3	F18	162.6(6)	F3	Ag2	F6	94.0(4)				
F17	W3	F19	88.0(5)	F3	Ag2	F7	75.1(4)				
F17	W3	O3	97.1(6)	F3	Ag2	F16	76.6(4)				
F18	W3	F19	88.0(5)	F3	Ag2	O1	137.4(5)				
F18	W3	O2	100.4(6)	F3	Ag2	O2	76.1(5)				
F19	W3	O3	98.2(6)	F3	Ag2	O3	142.1(6)				
F5	W4	F6	81.1(5)	F6	Ag2	F7	82.4(3)				
F5	W4	F7	81.3(5)	F6	Ag2	F16	68.7(4)				
F5	W4	F8	81.1(5)	F6	Ag2	O1	103.6(5)				
F5	W4	F9	80.5(5)	F6	Ag2	O2	159.9(4)

Figure 9.1. Raman spectrum of AgWOF₅, region 1 and 2

Figure 9.2. Raman spectrum of $\text{KW}_2\text{O}_2\text{F}_9$, region 1 and 2

Figure 9.3 (a) Tungsten (W1 and W4) coordination environment in $\text{AgW}_2\text{O}_2\text{F}_9$

Figure 9.3 (b) Tungsten (W2 and W3) coordination environment in $\text{AgW}_2\text{O}_2\text{F}_9$

Figure 9.4 (a) Silver (Ag1) coordination environment in $\text{AgW}_2\text{O}_2\text{F}_9$

Figure 9.4 (b) Silver (Ag2) coordination environment in $\text{AgW}_2\text{O}_2\text{F}_9$

Figure 9.5. Raman spectrum of AgFWOF₅BF₃, region 1 and 2

Figure 9.6. Magnetic susceptibility data for $\text{AgFWOF}_5\text{BF}_3$

Figure 9.7. Magnetic susceptibility data for AgFW₂O₂F₉

Chapter 10

Pseudo-trifluoride $(\text{AgF}_2)_3\text{MF}_6$: 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*¹ 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_6 (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 phase².

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 Bartlett³ that AgFAsF_6 in interaction with successive aliquots of AsF_5 -free AHF yielded a mixture of the black solid and AgAsF_6 (colorless) in a disproportionation associated with solvolysis by AHF (reaction 1). The black solid was shown, chemically, to contain Ag(III) as it yielded bright red AgF_3 when titrated with AsF_5 (reaction 2). The black solid was also obtained by fluorinating AgFAsF_6 (reaction 3) and from interaction of AgF_2 with AgFAsF_6 (reaction 4) in reactions apparently related to (1).

In this study, an efficient systematic approach using 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 $(\text{AgF}_2)_3\text{MF}_6$ ($\text{M} = \text{As}, \text{Au}, \text{Sb}, \text{Pt}$). The structures of $(\text{AgF}_2)_3\text{MF}_6$ salts will be discussed.

10.2. Experimental

10.2.1. Materials

O_2AsF_6 , O_2PtF_6 , O_2AuF_6 , and $\text{O}_2\text{Sb}_2\text{F}_{11}$ were prepared by literature methods^{4,5,6}. CuF_2 (Aldrich, Milwaukee, WI) was used as received. AgBF_4 was prepared⁷ by fluorinating AgBF_4 in the presence of BF_3 . The reactants were checked by X-ray powder photography and each powder pattern was entirely attributable to each reagent. AgF_2 was produced by fluorinating AgF in AHF solution.

10.2.2. Synthesis of $(\text{AgF}_2)_3\text{AsF}_6$

10.2.2.1. From the disproportionation of AgFAsF_6

Pure $(\text{AgF}_2)_3\text{AsF}_6$ was obtained initially, in this work, from the disproportionation of AgFAsF_6 (0.1353 g, 0.4284 mmole) in AHF (~1.5 ml) in the presence of O_2AsF_6 . The experimental detail has been described in Chapter 8. Any Ag(I) formed by disproportionation in the solvolysis to produce $(\text{AgF}_2)_3\text{AsF}_6$ is oxidized by O_2AsF_6 to Ag^{2+} in the solution. O_2AsF_6 and AgFAsF_6 (as the acid solubilized $\text{Ag}(\text{AsF}_6)_2$) were easily washed away by decantation to leave high purity $(\text{AgF}_2)_3\text{AsF}_6$ (0.0151 g, 0.02410 mmole). $(\text{AgF}_2)_3\text{AsF}_6$ was obtained from AgFAsF_6 . The extent of the disproportionation under the stated condition therefore amounts to approximately 22.5% ($0.0241 \times 4 / 0.4284$).

10.2.2.2. Interaction of O_2AsF_6 with AgF_2 in AHF

Inside the DRILAB, AgF_2 (0.0693 g, 0.4751 mmole) and O_2AsF_6 (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 O_2AsF_6 in a separate FEP reactor. AHF (~1.5 ml) was condensed on to approximately equimolar amounts of AgF_2 and O_2AsF_6 in separate arms of the reactor. The O_2AsF_6 solution was poured slowly into the AgF_2 suspension in

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 $(\text{AgF}_2)_3\text{AsF}_6$ 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 $(\text{CuF}_2)_3\text{AsF}_6$

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 CuF_2 solid dissolved in the solution. Upon adding another equivalent of AsF_5 , all the CuF_2 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 O_2AsF_6 and a second, predominant pattern. The latter was identical to that of the white solid obtained by George Lucier and identified by him as CuFAsF_6 . The theoretical yield of CuFAsF_6 was 0.1765 g. Therefore, the total weight of CuFAsF_6 and O_2AsF_6 in the side arm should have been 0.2146 g (0.0067 g O_2AsF_6 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 O_2AsF_6 by reductive interaction with the container.

10.2.4. Synthesis of $(\text{AgF}_2)_3\text{PtF}_6$

10.2.4.1. Interaction of O_2PtF_6 with AgF in AHF

This reaction was initially designed to synthesize AgFPtF_6 . In the DRILAB, AgF (0.0348 g, 0.2743 mmole) and O_2PtF_6 (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 O_2PtF_6 in approximately equal amounts. The O_2PtF_6 solution had an intense yellow color and about half of the O_2PtF_6 remained as solid in contact with the solution. The AgF solution was poured slowly into the O_2PtF_6 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 O_2PtF_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 PtF_5 generated during the reaction. The reaction was not complete as there was some O_2PtF_6 left even though there was a slight deficiency of O_2PtF_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 O_2PtF_6 with AgF_2 in AHF

This reaction was carried out by George Lucier in these laboratories. O_2PtF_6 and 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 O_2PtF_6 with AgFBF_4 in AHF

Inside the DRILAB, AgFBF_4 (0.0583 g, 0.2728 mmole) and O_2PtF_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 AgFBF_4 and O_2PtF_6 . AgFBF_4 did not seem to dissolve in HF. The O_2PtF_6 dissolved to some extent to give a yellow solution. The O_2PtF_6 solution, with the solid O_2PtF_6 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 O_2PtF_6 solution was added. After all the O_2PtF_6 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 AgFBF_4 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 O_2PtF_6 . X-ray powder photographs of the nearly black solid were sharp and indicative of good microcrystallinity. Its pattern closely resembled that of $(\text{AgF}_2)_3\text{AsF}_6$. 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 $(\text{AgF}_2)_3\text{PtF}_6$.

10.2.5. Synthesis of $(\text{AgF}_2)_3\text{AuF}_6$

10.2.5.1. Interaction of O_2AuF_6 with AgF_2 in neutral AHF

Inside the DRILAB, O_2AuF_6 (0.0943 g, 0.2750 mmole) was loaded into the main tube of a prepassivated $\frac{1}{2}$ " T-shaped Teflon-FEP reactor and AgF_2 (0.1143 g, 0.7836 mmole) into the side arm. AHF (~2 ml) was condensed on to O_2AuF_6 . The O_2AuF_6 dissolved to some extent to give a yellow solution. In the beginning, the AgF_2 solid was tapped into the O_2AuF_6 solution slowly. But the

reaction appeared to be very sluggish, oxygen evolution being very slow. Therefore, the AgF_2 was added into the O_2AuF_6 solution all at once. HF was condensed into the side arm to rinse down any residual AgF_2 . 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 AgF_2 , with a weak pattern very like that of $(\text{AgF}_2)_3\text{AsF}_6$ and therefore probably that of $(\text{AgF}_2)_3\text{AuF}_6$. The orange yellow solid in the side arm was shown by X-ray powder photography to be O_2AuF_6 . The weight of the dark brown solid was 0.1686 g and that of the unreacted O_2AuF_6 was 0.0336 g (0.0980 mmole). From the difference in the weight of O_2AuF_6 before and after the reaction, the weight of the reaction product $(\text{AgF}_2)_3\text{AuF}_6$ was calculated to be 0.1325 g. The total weight of $(\text{AgF}_2)_3\text{AuF}_6$ and the unreacted AgF_2 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 O_2AuF_6 with AgF_2 in acidic AHF

Inside the DRILAB, O_2AuF_6 (0.1458 g, 0.4251 mmole) was loaded into the main tube of a prepassivated $\frac{1}{2}$ " T-shaped Teflon-FEP reactor and AgF_2 (0.1432 g, 0.9817 mmole) into the side arm. AHF (~2 ml) was condensed on to the O_2AuF_6 . The O_2AuF_6 dissolved to some extent to give a yellow solution. BF_3 (~0.14 mmole) was admitted into the reactor to render the HF solution acidic and convert the AgF_2 to AgFBF_4 . The AgF_2 solid was tapped into the O_2AuF_6 solution slowly. There was gas evolution as the AgF_2 solid fell into the O_2AuF_6

solution and black material started to precipitate. Some of the HF was condensed over to the side arm to rinse down AgF_2 into the O_2AuF_6 solution. As the cold BF_3 -saturated HF was poured back into the O_2AuF_6 solution, the color of the O_2AuF_6 solution turned blue probably from dissolution of the AgF_2 . 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 $(\text{AgF}_2)_3\text{AuF}_6$. The other lines in the pattern were attributable to AgFAuF_6 . The weight of the solid was 0.2447 g, close to the theoretical yield of 0.2449 g. The weight of the unreacted O_2AuF_6 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 $(\text{AgF}_2)_3\text{SbF}_6$

Inside the DRILAB, AgFBF_4 (0.1634 g, 0.7647 mmole) and a mixture of O_2SbF_6 and $\text{O}_2\text{Sb}_2\text{F}_{11}$ (0.1619 g), which is mainly $\text{O}_2\text{Sb}_2\text{F}_{11}$, 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 AgFBF_4 and $\text{O}_2\text{SbF}_6/\text{O}_2\text{Sb}_2\text{F}_{11}$. The $\text{O}_2\text{SbF}_6/\text{O}_2\text{Sb}_2\text{F}_{11}$ dissolved completely to give a colorless solution. The $\text{O}_2\text{SbF}_6/\text{O}_2\text{Sb}_2\text{F}_{11}$ 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

$\text{O}_2\text{SbF}_6/\text{O}_2\text{Sb}_2\text{F}_{11}$ solution was added. After all the $\text{O}_2\text{SbF}_6/\text{O}_2\text{Sb}_2\text{F}_{11}$ 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 $(\text{AgF}_2)_3\text{AsF}_6$. The weight of the recovered black-brown solid was 0.0633 g (0.1306 mmole).

10.2.7. The structural arrangement in $(\text{AgF}_2)_3\text{MF}_6$

10.2.7.1. Structure determination of $(\text{AgF}_2)_3\text{AsF}_6$

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

The close resemblance of the X-ray powder photograph of $(\text{AgF}_2)_3\text{AsF}_6$ to that of a trifluoride, typified by the rhombohedral⁸ RuF_3 suggested that $(\text{AgF}_2)_3\text{AsF}_6$ was a pseudo-trifluoride, $\text{Ag}_3\text{MF}_{12}$, 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 $a = 5.61 \text{ \AA}$, $b = c = 5.69 \text{ \AA}$, $\alpha = 55.28^\circ$, $\beta = \gamma = 55.28^\circ$, and $V = 114.0 \text{ \AA}^3$. For comparison, the cell parameters for bimolecular rhombohedral RuF_3 are $a = 5.41 \text{ \AA}$ 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 β closest to 90° was selected: $a = 5.61 \text{ \AA}$, $b = 5.25 \text{ \AA}$, $c = 7.80 \text{ \AA}$, $\beta = 96.49^\circ$, $V = 228.0 \text{ \AA}^3$, 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 $K\alpha$ 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: $a = 5.6045$, $b = 5.2567$, $c = 7.8061 \text{ \AA}$, $\beta = 96.594^\circ$, $V = 228.5 \text{ \AA}^3$, $Z = 1$, space group P2/c.

I/I_0	I_{calc}^*	$1/d^2 \times 10^4$		hkl
		obs	calc	
ms	530	671	665	002
s	1000	692	685	110
ms	364	1252	1243	$11\bar{2}$
m	178	1295	1290	200
ms	99	1459	1448	020
	175		1456	112
vww?	15	1646	1652	210
vw	27	1748	1743	$20\bar{2}$
vww	21	1784	1770	120
vwd	35	1882	1859	013
	36		1883	$12\bar{1}$
vw	37	1927	1925	211
m	141	2117	2113	022
w	76	2172	2168	202
vww		2247		imp?
mw	67	2669	2661	004
ms	135	2746	2738	220
m	145	3142	3133	$11\bar{4}$
m	130	3202	3190	$22\bar{2}$

m	137	3267	3265	310
mwvb	30	3573	3526	204̄
	70		3558	114
	78		3580	130
ms	65	3621	3611	312̄
	61		3616	222
mdd	73	4134	4108	024
	58		4138	132̄
w	62	4235	4250	312
mdd	87	4358	4351	132
	48		4377	204
mw	60	4976	4973	224̄
vw	25	5148	5162	400
mw	40	5300	5288	314̄
vw	19	5409	5402	402̄
m	14	5812	5790	040
	27		5824	224
wd	9	6008	5987	006
	21		6028	134̄
w	18	6160	6161	330
vw	8	6245	6253	402
wdd?	33	6358	6352	116̄
w	38	6449	6453	134
	30		6455	042
vw	28	6489	6507	332̄
unobs.	33		6565	314
vw	33	6604	6609	420
vww	14	6632	6639	206̄
vw	26	6845	6849	422̄
w	22	6971	6972	404̄
	22		6991	116
vw	26	7070	7081	240
vw	20	7116	7145	332
vww	0	7313	7309	043
vw	26	7435	7434	026

vw	27	7540	7533	24 $\overline{2}$
vw	27	7674	7700	422
wd	15	7954	7916	206
	28		7959	242
vw	18	8077	8087	22 $\overline{6}$
vww	23	8165	8183	33 $\overline{4}$
vww	14	8282	8316	31 $\overline{6}$
wd	16	8411	8419	42 $\overline{4}$
	19		8427	510
	17		8451	044
wvdl	16	9346	9316	24 $\overline{4}$
	13		9363	226
	16		9370	150
vw	13	9608	9625	512
wvb	11	9891	9872	40 $\overline{6}$
	16		9886	136
	18		9929	15 $\overline{2}$
vwwd	19	10018	10024	51 $\overline{4}$
wvb	20	10156	10121	424
	17		10141	152
	17		10167	244

10.2.7.1.2. Crystal growth of (AgF₂)₃AsF₆

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 F₂ during crystal growth. Typically, AgFAsF₆ (in excess by 15 - 20%) was loaded into the main arm of the FEP reactor, and the other starting materials such as AgF₂ or AgFBF₄ were loaded into the side arm. 1 to 2 ml AHF was condensed onto AgFAsF₆. 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. F_2 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 AgF_2 or $AgFBF_4$ 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 F_2 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 $(AgF_2)_3AsF_6$ 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 $LiAsF_6$ and KBF_4 were sometimes added to the HF to modify its solvent properties. A single crystal of $(AgF_2)_3AsF_6$ was eventually obtained from the reaction of $AgFBF_4$, $AgFAsF_6$, and F_2 with a small amount of KBF_4 present in the HF.

10.2.7.1.3. Crystal structure determination of $(AgF_2)_3AsF_6$

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 $I_{\min}/I_{\max}=0.82$ 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 correction⁹ was made to the data based on the combined differences of F_{obs} and F_{calc} following refinement of all atoms with isotropic thermal parameters ($\text{Corr}(\text{max})=1.32$, $T_{\min}=0.79$, 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 $h0l$, $l \neq 2n$. 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 ($R_I=4.3\%$ 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 R_{ALL} . 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 $\sum w(|F_o| - |F_c|)^2$, 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 $\sin\theta/\lambda$, $|F_o|$, 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 $e^-/\text{\AA}^3$, and the lowest excursion -1.06 $e^-/\text{\AA}^3$. There was no indication of secondary extinction in the high-intensity low-angle data.

Table 10.2. Crystal and Data parameters for disordered $(\text{AgF})_2(\text{AgF}_4)(\text{AsF}_6)$.

Formula, mol. wt.	$\text{Ag}_3 \text{As F}_{12}$, 626.5 amu
Temperature	25°C [a,b]
a	5.6045(6) $\text{\AA}$
b	5.2567(6) $\text{\AA}$
c	7.8061(8) $\text{\AA}$
β	96.594(9)°
Space Group	P2/c
Z	1
V	228.5(0) $\text{\AA}^3$
d(calc)	4.55 g cm^{-3}
μ (calc)	100.6 cm^{-1}
Size	0.05x0.05x0.07 mm
Radiation	Mo $K\alpha$ ($\lambda = 0.71073\text{\AA}$)
Monochromator	Highly-oriented graphite ($2\theta = 12.2$)
Detector	Crystal scintillation counter, with PHA.
Reflections measured	+/-H, + K, +/-L
2θ range	3 -> 60 deg
Scan Type	theta-2theta
Scan width	$\Delta\theta = 1.00 + 0.35 \tan\theta$
Scan speed	5.49 (θ , deg/min)
Background	Measured over $0.25^*(\Delta\theta)$ added to each end of the scan.
apertures	Vert. aperture = 4.0 mm Horiz. aperture = $2.3 + 1.0 \tan\theta$ mm
Data collected	1463
Independent	670

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 K α 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 Casteel² from the interaction of O₂AuF₆ and AgBF₄ 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, *I*_{calc}, 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 = As, Au, Sb, Pt).

	$(\text{AgF}_2)_3\text{AsF}_6$	$(\text{AgF}_2)_3\text{AuF}_6$	$(\text{AgF}_2)_3\text{PtF}_6^a$	$(\text{AgF}_2)_3\text{SbF}_6$
a (Å)	5.6045(6)	5.660	5.689	5.699
b (Å)	5.2567(6)	5.240	5.250	5.267
c (Å)	7.8061(8)	7.788	7.807	7.830
β (°)	96.594(9)	97.53	97.70	97.21
V (Å ³)	228.5(0)	229.0	231.1	233.2

^aThe indexing of $(\text{AgF}_2)_3\text{PtF}_6$ is not complete.

Table 10.4. X-ray powder data (Cu K α 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, β = 97.53°, Z = 1, V = 229.0 Å³, possible space group P2/c.

*The reflection intensities, *I*_{calc}, were calculated with only metal atoms in the structure.

<i>I</i> / <i>I</i> ₀	<i>I</i> _{calc} *	$1/d^2 \times 10^4$		<i>hkl</i>
		obs	calc	
m	51	675	671	002
vs	100	686	682	110
s	47	1233	1232	11 $\bar{2}$
w	22	1268	1270	200
s	19	1463	1457	020

	36		1474	112
vw	15	1703	1699	20 $\bar{2}$
vw	0.5	1884	1874	013
	0.5		1882	12 $\bar{1}$
m	21	2126	2128	022
vw	10	2186	2184	202
w	7	2684	2684	004
s	15	2720	2727	220
s	12	3123	3124	11 $\bar{4}$
s	11	3159	3156	22 $\bar{2}$
m	11	3224	3223	310
w	5	3471	3470	20 $\bar{4}$
w	10	3533	3531	31 $\bar{2}$
sb	9	3610	3595	130
	9		3608	114
	9		3640	222
mb	7	4138	4141	024
	7		4145	13 $\bar{2}$
wb	7	4270	4257	312
sb	7	4398	4387	132
	3		4439	204
mb	5	4927	4927	22 $\bar{4}$
vwb	3	5056	5082	400
wb	5	5190	5181	31 $\bar{4}$
wb	4	5873	5895	224
wb	4	6126	6136	330
wb	4	6330	6358	11 $\bar{6}$

Table 10.5. X-ray powder data (Cu K α radiation, Ni filter) for (AgF₂)₃SbF₆, monoclinic cell with $a = 5.699 \text{ \AA}$, $b = 5.267 \text{ \AA}$, $c = 7.830 \text{ \AA}$, $\beta = 97.21^\circ$, $Z = 1$, $V = 233.2 \text{ \AA}^3$, possible space group P2/c.

*The reflection intensities, *I*_{calc}, were calculated with only metal atoms in the structure.

$1/d^2 \times 10^4$

<i>I/I₀</i>	<i>Icalc</i> *	obs	calc	<i>hkl</i>
vs	510	670	663	002
	1000		673	110
s	462	1220	1221	11 $\bar{2}$
m	224	1250	1251	200
s	184	1452	1442	020
	364		1450	112
vw	147	1685	1685	20 $\bar{2}$
vw		1856		
s	211	2105	2104	022
w	103	2144	2142	202
m	74	2656	2650	004
s	143	2696	2693	220
sbd	114	3103	3095	11 $\bar{4}$
	112		3127	22 $\bar{2}$
s	110	3181	3176	310
vw	48	3442	3444	20 $\bar{4}$
w	93	3491	3495	31 $\bar{2}$
sbd	91	3563	3552	114
	91		3557	130
	89		3584	222
s	71	4091	4092	024
	71		4105	13 $\bar{2}$
m	69	4176	4181	312
sb	64	4332	4334	132
	32		4359	204
w	52	4880	4886	22 $\bar{4}$
vw	25	4973	5005	400
w		5107		
mw	20	5781	5768	040
	39		5801	224
vw	19	5946	5963	006
vw	34	6270	6293	11 $\bar{6}$

Table 10.6. X-ray powder data (Cu K α radiation, Ni filter) for (AgF₂)₃PtF₆, monoclinic cell with $a = 5.689 \text{ \AA}$, $b = 5.250 \text{ \AA}$, $c = 7.807 \text{ \AA}$, $\beta = 97.70^\circ$, $Z = 1$, $V = 231.1 \text{ \AA}^3$, possible space group P2/c.

*The reflection intensities, *I*_{calc}, were calculated with only metal atoms in the structure.

<i>I</i> / <i>I</i> ₀	<i>I</i> _{calc} *	$1/d^2 \times 10^4$		<i>hkl</i>
		obs	calc	
vw		574		
vw		603		
vs	508	668	668	002
	1000		677	110
w		707		
w		737		
vw		784		
vww		837		
vww		903		
vww		1031		
s	468	1220	1223	11 $\bar{2}$
s	225	1272	1258	200
vw		1371		
s	185	1452	1451	020
msd		1564		
msd	150	1680	1681	20 $\bar{2}$
vwd		1858		
vwd		1962		
ms	213	2119	2120	022
vw	103	2183	2172	202
ms		2267		
vw	74	2671	2673	004
ms	145	2714	2710	220
vwd		2792		
vw		2928		
ms	117	3099	3105	11 $\bar{4}$
ms	111	3181	3194	310

vwd		3255		
w	96	3503	3494	$31\bar{2}$
ms	92	3577	3580	130
	91		3596	114
vw		3805		
ms	72	4131	4125	024
	72		4125	$13\bar{2}$
vw	69	4235	4231	312
ms	65	4370	4371	132
vww		4669		
vww		4835		
vww	50	5118	5130	$31\bar{4}$

10.3. Results and Discussion

10.3.1. The structures of $(\text{AgF}_2)_3\text{MF}_6$ salts

The crystal structure of the AsF_6^- salt was solved on a perfectly disordered single crystal (Figure 10.1 - 10.6). The lattice parameters are: $a = 5.6045(6)$, $b = 5.2567(6)$, $c = 7.8061(8)\text{\AA}$, $\beta = 96.594(9)^\circ$, $V = 228.5\text{\AA}^3$, $Z = 1$, space group $P2/c$. The structure shows that the material is composed of zigzag $(\text{AgF})_n^{n+}$ chains enclosing anion arrays of alternating inclined planar and octahedral anions AgF_4^- and AsF_6^- running along the c axis (Figure 10.6). Therefore, the material should be formulated as $(\text{AgF}^+)_2\text{AgF}_4^-\text{AsF}_6^-$.

Each F ligand of AsF_6^- makes a long bridging contact, $\text{F}\cdots\text{Ag}$, 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 $(\text{Ag-F})_n^{n+}$ chains which run parallel to c . Each of the Ag(II) species also makes four long-bridge $\text{Ag}\cdots\text{F}$ 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 $\text{Ag}\cdots\text{F}$ 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 $153.9(11)^\circ$. 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 twoneighboring F4 positions is 1.01 Å). The coordination is nearly octahedral. But because of the inherently longer M-F distance¹⁰ in AgF_4^- of 1.89 Å compared with that¹¹ in AsF_6^- of 1.715 Å, the distances to F2 and F3 (1.80 Å) are longer than the distance to F4 (1.72 Å). The former is identical to the average of AgF_4^- 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 (2.61 Å) 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 $[\text{AgF}_4]^-$ anion, the fluorine-bridged Ag-F assembly can be viewed as a $(\text{AgF}_2)_3^+$ cage for the 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 AgFAsF_6 in HF solution, and has several structural relatives in which the AsF_6^- is substituted by other MF_6^- .

The other $(\text{AgF}_2)_3\text{MF}_6$ salts ($\text{M} = \text{Au}, \text{Sb}, \text{Pt}$) 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 AsF_6^- , AuF_6^- , PtF_6^- , and SbF_6^- .

	FUV ($\text{\AA}^3$)	ref.		FUV ($\text{\AA}^3$)	ref.
KAsF_6	116.49	12	CsAsF_6	138.4	13
KAuF_6	117.8	14	CsAuF_6	141.3	14
KPtF_6	118.7	15	CsPtF_6	143.4	16
KSbF_6	130.7	17	CsSbF_6	148.8	18

10.3.2. Reactions and chemistry

The AgF^+ cation appears to be unstable in neutral AHF. AgFAsF_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 $(\text{AgF}_2)_3\text{AsF}_6$. 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 $\text{Ag}^{2+}_{(\text{solv})}$. We can write the following equation to represent the equilibrium products:

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 $(\text{AgF}_2)_3\text{AsF}_6$, and the solvation of AsF_5 by HF.

In the experiment to study the interaction of AgFAsF_6 and O_2AsF_6 (Chapter 8), as the O_2AsF_6 solution was added to the AgFAsF_6 solution which already contained the disproportionation products from equilibrium 1, any Ag(I) formed by disproportionation would be oxidized by O_2AsF_6 back to Ag(II) as the acid solubilized $\text{Ag}(\text{AsF}_6)_2$ (see Chapter 8).

As the O_2AsF_6 and $\text{Ag}(\text{AsF}_6)_2$ can be easily washed away, $(\text{AgF}_2)_3\text{AsF}_6$ was obtained in high purity. This provided reliable X-ray powder data for a successful indexing.

The crystal growth of $(\text{AgF}_2)_3\text{AsF}_6$ 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 $(\text{AgF}_2)_3\text{AsF}_6$. Reactions 7 and 8 yielded jet black crystals of $(\text{AgF}_2)_3\text{AsF}_6$ 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.

A more efficient synthesis of $(\text{AgF}_2)_3\text{AsF}_6$ was achieved via the interaction of AgF_2 and O_2AsF_6 . In spite of the fact that the solubility of AgF_2 is very low in AHF, the reaction of AgF_2 and O_2AsF_6 in 3:1 ratio with O_2AsF_6 slightly in excess (reaction 10) is quantitative and very facile, the net reaction being:

The similar reaction between AgF_2 and O_2PtF_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 AgF_2 and other O_2MF_6 ($\text{M} = \text{Au}, \text{Sb}$) seems to be very slow. In the reaction of AgF_2 and O_2AuF_6 , acidifying AHF with BF_3 appears to promote the oxidation reaction, probably because of the greater solubility of the AgF_3BF_4 salt.

Reactions which were initially designed to synthesize AgFAuF_6 , and AgFPtF_6 , via the interaction between AgF and the corresponding O_2AuF_6 , and O_2PtF_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 AgF and O_2AsF_6 is cleaner and produced 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.

M = Au, Pt

A more generally satisfactory and efficient route to crystalline $(\text{AgF}_2)_3\text{MF}_6$ (M = As, Au, Pt, Ru, Sb) was discovered with AgFBF_4 in place of AgF_2 :

M = As, Au, Pt, Sb

This reaction scheme works very well probably because AgFBF_4 is slightly soluble in HF and the other products of the reaction are gaseous BF_3 and O_2 .

Pure, crystalline $(\text{AgF}_2)_3\text{SbF}_6$ was prepared (reaction 13) via the interaction of 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 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.

The variable temperature magnetic susceptibility measurements on $(\text{AgF}_2)_3\text{AsF}_6$, done by George Lucier¹⁹, 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 AgF^+ salts²⁰. Magnetic measurements also show that repeated washing of

(AgF₂)₃AsF₆ with AHF resulted in some solvolysis to produce some AgF₂ and an unidentified product that is strongly diamagnetic below 63 K.

Attempts to synthesize the Cu analog, (CuF₂)₃AsF₆, through the interaction of CuF₂ and O₂AsF₆ were unsuccessful. CuFAuF₄, as described by Müller²¹, contains linear (CuF)_nⁿ⁺ chains. And square planar CuF₄⁻ also exists in the compound CsCuF₄ prepared by Hoppe²². Therefore, it appears plausible that a trifluoride-like (CuF)₂CuF₄MF₆ analogous to (AgF)₂AgF₄MF₆ could also be prepared. It does seem likely that the CuF₄⁻ species is very much less favorable energetically relative to CuF₂ than AgF₄⁻ relative to AgF₂. This correlates with the very high third ionization energy of Cu, which is actually the highest among the coinage metals²³. Formation of Cu(III) fluorocomplexes requires more extreme reaction conditions²⁴.

10.4. Conclusion

A new class of pseudo-trifluoride silver compounds, (AgF₂)₃MF₆ (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 (AgF₂)₃MF₆, 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 (AgF₂)₃AsF₆ has been determined which showed that this material is a new (AgF)_nⁿ⁺ salt with a formulation best represented as (AgF⁺)₂AgF₄⁻AsF₆⁻. The X-ray powder diffraction data shows that the other (AgF₂)₃MF₆ salts are isostructural with (AgF₂)₃AsF₆. Efficient synthetic routes to (AgF₂)₃MF₆ of high purity and crystallinity have been established using O₂⁺ salts. It is also clear that similar materials such as (AgF₂)₃MF₆ (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 $(\text{AgF})_n^{n+}$ salts.

10.5. References

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Table 10.7. Positional Parameters and Their Estimated Standard Deviations for (AgF₂)₃AsF₆.

Atom	x	y	z	B(Å ²)
AG1	0.000	0.000	0.000	1.04(2)
AG2	0.500	0.500	0.000	1.43(2) **
AS	0.500	0.500	0.500	1.4 **
F1	0.000	0.086(3)	0.250	2.6(3)
F2	0.207(2)	0.367(2)	-0.064(2)	3.6(2)
F3	0.353(2)	-0.223(2)	0.075(2)	3.5(2)
F4	0.485(4)	0.326(4)	0.185(2)	2.8(4)* **

* 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.

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)	Beqv
AG1	1.10(4)	1.11(4)	0.93(3)	-0.0(2)	0.16(3)	-0.2(2)	1.04(2)
AG2	1.34(5)	1.34(4)	1.58(4)	-0.9(1)	0.13(4)	-0.8(2)	1.43(2)
AS	B(1,1)	B(2,2)	B(3,3)	-B(1,2)	B(1,3)	-B(2,3)	(constrained)
F1	2.7(5)	2.2(5)	3.0(5)	0	1.1(4)	0	2.6(3)
F2	3.0(5)	3.1(5)	4.3(5)	0.4(5)	-1.9(4)	-1.1(5)	3.6(2)
F3	3.9(5)	2.4(4)	4.3(4)	0.2(4)	1.0(4)	-2.2(4)	3.5(2)

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 (AgF₂)₃AsF₆.

Atom	Min.	Int'med.	Max.
AG1	0.098	0.117	0.128
AG2	0.053	0.138	0.180
AS	0.053	0.138	0.180
F1	0.160	0.166	0.212
F2	0.136	0.188	0.291
F3	0.103	0.222	0.270

Table 10.10. Intramolecular Distances for (AgF₂)₃AsF₆.

ATOM 1	ATOM 2	DISTANCE
AG1	F1	2.003(4)
AG1	F2	2.336(17)
AG1	F3	2.316(17)
AS/AG2	F2	1.802(15)
AS/AG2	F3	1.806(14)
AS	F4	1.719(24)
AG2	F4	2.61(3)
F2	F3	2.510(21)
F2	F3	2.59(3)
F2	F4	2.36(4)
F2	F4	2.62(3)
F3	F4	2.60(3)
F3	F4	2.38(3)
F1	F2	3.193(20)
F1	F2	2.957(21)
F1	F2	3.193(20)
F1	F2	2.957(21)
F1	F3	3.005(18)
F1	F3	3.119(19)
F1	F4	3.14(3)
F1	F4	3.09(3)
F2	F2	2.98(3)
F2	F3	3.22(3)
F2	F3	3.114(22)
F2	F4	3.26(3)
F2	F4	3.09(3)
F3	F3	3.16(4)
F3	F3	3.02(4)
F3	F4	3.08(3)
F3	F4	3.09(4)
F3	F4	3.26(3)

Table 10.11. Intramolecular Angles for (AgF₂)₃AsF₆.

ATOM 1	ATOM 2	ATOM 3	ANGLE
F1	AG1	F1	180.00(0)
F1	AG1	F2	94.4(6)
F1	AG1	F2	85.6(6)
F1	AG1	F3	87.8(5)
F1	AG1	F3	92.2(5)
F2	AG1	F2	180.00(0)
F2	AG1	F3	92.4(7)
F2	AG1	F3	87.6(7)
F3	AG1	F3	180.00(0)
F2	AG2	F2	180.00(0)
F2	AG2	F3	88.2(9)
F2	AG2	F3	91.8(9)
F2	AG2	F4	93.2(8)
F2	AG2	F4	86.8(8)
F3	AG2	F3	180.00(0)
F3	AG2	F4	86.7(9)
F3	AG2	F4	93.3(9)
F4	AG2	F4	180.0(26)
F2	AS	F2	180.00(0)
F2	AS	F3	88.2(9)
F2	AS	F3	91.8(9)
F2	AS	F4	93.2(8)
F2	AS	F4	86.8(8)
F3	AS	F3	180.00(0)
F3	AS	F4	86.7(9)
F3	AS	F4	93.3(9)
F4	AS	F4	180.00(0)
AG1	F1	AG1	153.9(11)
AG1	F2	AS/AG2	136.0(9)
AG1	F3	AS/AG2	137.2(9)
AS	F4	AG2	127.3(13)

Figure 10.1 - Monoclinic view of the unit cell of the $(\text{AgF})_2\text{AgF}_4\text{AsF}_6$ $\{(\text{AgF}_2)_3\text{AsF}_6\}$. View direction is roughly down *a*, with *b* horizontal on the page. The central metal atom has been assigned to As to emphasize the cage-like nature of the AsF_6^- 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 $(\text{AgF})_2\text{AgF}_4\text{AsF}_6$, including four long Ag-F contacts to show the approximate octahedral environment of Ag(II).

Figure 10.5. View of one $\text{AsF}_6^-/\text{AgF}_4^-$ chain in $(\text{AgF})_2\text{AgF}_4\text{AsF}_6$, showing the grossly distorted octahedral environment of Ag(III).

Figure 10.6 - View of three neighboring $\text{AsF}_6^-/\text{AgF}_4^-$ 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^{1,2,3,4,5,6,7}. It remains of interest to further develop and improve such mnemonic diagrams. Recently, three dimensional mnemonic diagrams were presented by Phillips⁶. Rodriguez and Brainhard⁷ worked on the improvement of mnemonic diagram which was originally developed by Callen². 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 μ_i 's ($i = 1, 2, \dots, r$). 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 $f = f(X_1, \dots, X_n)$ is a natural function of $X_1, \dots, X_n$, then

$$df = \sum_{i=1}^n Y_i dX_i, \quad \text{with} \quad Y_i = (\partial f / \partial X_i)_{X_j}$$

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

The macroscopic thermodynamics of equilibrium for simple systems can be described by the internal energy as a natural function of the extensive independent variables, $E = (S, V, N_1, \dots, N_r)$. 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 $E = E(S, V, N_1, \dots, N_r)$ 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 symmetry¹. It has also been noticed that the presence of certain superficial geometric symmetry could be utilized in determining the signs in the Maxwell relations². 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:

$$(\partial H / \partial S)_P = T \quad (3.1) \qquad (\partial H / \partial P)_S = V \quad (3.2)$$

$$(\partial G / \partial P)_T = V \quad (3.3) \qquad (\partial G / \partial T)_P = -S \quad (3.4)$$

$$(\partial F / \partial T)_V = -S \quad (3.5) \qquad (\partial F / \partial V)_T = -P \quad (3.6)$$

$$(\partial E / \partial V)_S = -P \quad (3.7) \qquad (\partial E / \partial S)_V = T \quad (3.8)$$

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 Li⁴. 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 "δ" is used for any small variation away from the equilibrium state, then we have the following expressions:

$(\delta S)_E, V \leq 0$	(4.1)	$(\delta S)_H, P \geq 0$	(4.2)
$(\delta P)_H, S \leq 0$	(4.3)	$(\delta P)_G, T \geq 0$	(4.4)
$(\delta T)_F, V \geq 0$	(4.5)	$(\delta T)_G, P \geq 0$	(4.6)
$(\delta V)_E, S \geq 0$	(4.7)	$(\delta V)_F, T \geq 0$	(4.8)
$(\delta H)_S, P \geq 0$	(4.9)	$(\delta G)_P, T \geq 0$	(4.10)
$(\delta E)_V, S \geq 0$	(4.11)	$(\delta F)_T, V \geq 0$	(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).

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:

$$(\partial P / \partial T)_V = (\partial S / \partial V)_T \quad (5.1) \quad (\partial T / \partial P)_S = (\partial V / \partial S)_P \quad (5.2)$$

$$(\partial P / \partial S)_V = -(\partial T / \partial V)_S \quad (5.3) \quad (\partial S / \partial P)_T = -(\partial V / \partial T)_P \quad (5.4)$$

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, $i = 1, 2, \dots, r$. $N_i \rightarrow \mu_i$ implies a mathematical operation involving only (N_i, μ_i) with all the other N_j 's held constant, or a particular mathematical operation involving all $(N_i$'s, μ_i 's) summed over the subscript i when it is suitable. Now S, T, P, V, N_i, μ_i are at the vertices of a regular octahedron. All the energy functions can, in addition to their original "natural" variables, have N_i '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, μ_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 μ_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 μ_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.

$$(\partial H / \partial N_i)_{S, P, N_j} = \mu_i \quad (6.1) \quad (\partial G / \partial N_i)_{P, T, N_j} = \mu_i \quad (6.2)$$

$$(\partial F / \partial N_i)_{T, V, N_j} = \mu_i \quad (6.3) \quad (\partial E / \partial N_i)_{V, S, N_j} = \mu_i \quad (6.4)$$

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

$$dH = TdS + VdP + \sum \mu_i dN_i \quad (7.1) \quad dG = VdP - SdT + \sum \mu_i dN_i \quad (7.2)$$

$$dF = -SdT - PdV + \sum \mu_i dN_i \quad (7.3) \quad dE = TdS - PdV + \sum \mu_i dN_i \quad (7.4)$$

3. Again the symmetry property can be utilized in deriving the Maxwell relations involving N_i and μ_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_i , are obtained (see Figure 4(a) and 4(b)).

$$(\partial \mu_i / \partial T)_{P, N_{i,j}} = - (\partial S / \partial N_i)_{T, P, N_j} = - s_i \quad (8.1)$$

$$(\partial \mu_i / \partial P)_{T, N_{i,j}} = (\partial V / \partial N_i)_{T, P, N_j} = v_i \quad (8.2)$$

Figure 4. a) The symmetries in the Maxwell relations involving S, T, N_i, μ_i . P on the arrow perpendicular to the (S, T, N_i, μ_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, μ_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, μ_i 's are intensive. For instance:

$$E(\lambda S, \lambda V, \lambda N_1, \dots, \lambda N_r) = \lambda E(S, V, N_1, \dots, N_r) \text{ for any } \lambda$$

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:

Figure 5. a) The corresponding three-dimensional diagram when the size of the thermodynamic system is increased to λ times as large. b) The zero function $0(P, T, \mu_i)$ 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 λ 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.

$$H = TS + \sum \mu_j N_j \quad (9.1)$$

$$G = \sum \mu_j N_j \quad (9.2)$$

$$F = -PV + \sum \mu_j N_j \quad (9.3)$$

$$E = TS - PV + \sum \mu_j N_j \quad (9.4)$$

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

$$O(P, T, \mu_j) = G - \sum \mu_j N_j \equiv 0 \quad (10)$$

which is a natural function of the intensive variables P, T, μ_j 's (see Figure 5). The differential form of this Zero function can be simply written from the rules:

$$dO(P, T, \mu_j) = VdP - SdT - \sum N_j d\mu_j \equiv 0 \quad (11)$$

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 [+ → -]". Therefore it is unnecessary to preassign some variables negative as most of the previous mnemonic diagram do^{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.

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