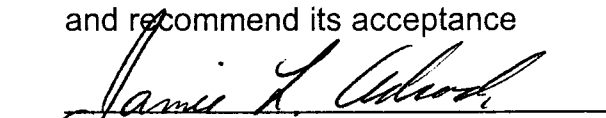
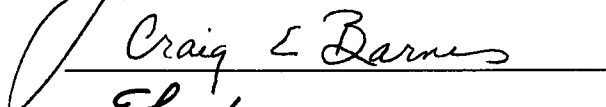


To the Graduate Council:

I am submitting herewith a dissertation written by Sven Eklund entitled "Tungsten Fluorides: Synthesis and Characterization, and Electrochemical Investigations in the FLINAK Molten Salt Eutectic." I have examined a copy of this dissertation for form and content and recommend that it be accepted in the partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.


James Q. Chambers, Major Professor

We have read this dissertation
and recommend its acceptance



Accepted for the Council:


Associate Vice Chancellor and
Dean of The Graduate School

**TUNGSTEN FLUORIDES: SYNTHESIS AND CHARACTERIZATION, AND
ELECTROCHEMICAL INVESTIGATIONS IN THE FLINAK MOLTEN SALT
EUTECTIC**

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Sven Erik Eklund

December, 1999

DEDICATION

The author dedicates this work to his
wife, Wakako, whose patient and loving
sacrifice made this work possible.

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Finally, I would like to thank God, who through His divine providence has enabled me to achieve this goal.

ABSTRACT

An improved method over a previous technique has been developed to determine the ppm oxide concentration of fluoride salts. The oxide is released as oxygen gas by the reaction of the test salt with potassium bromotetrafluoride at 450° C. The molecular oxygen released is then passed through a zirconia oxygen pump which selectively removes the oxygen. The current response is recorded as a chronoamperogram, from which the ppm oxide content of the salt can be obtained. Oxygen recovery from an yttrium oxide standard was better than 99%. The precision of analysis of FLINAK was better than 13% for samples containing 110 to 170 ppm oxide. The LOD was 12 µg of oxygen, and the analytical range was 120 ppm to >20% for a 0.1 g sample.

Mixtures of 1) WF_6 and KF and 2) WF_6 , W and MF (where M = Na, K, Rb or Cs) at temperatures near or above the melting point of the alkali salt produced K_2WF_8 and KWF_7 in the first case, and all four MWF_6 products in the second case, where MF was the limiting reactant. Stoichiometric amounts of MWF_6 and the corresponding MF salt produced two new compounds, K_2WF_7 and Rb_2WF_7 , and the compounds Na_3WF_8 , K_3WF_8 and Rb_3WF_8 . Longer reaction times, with excess W and MF, produced a mixture of K_3WF_8 and K_3WF_6 , from which crystals of the new compound K_3WF_6 were isolated. Raman spectra were acquired for all of the compounds, and crystal structures were obtained for K_2WF_7 and K_3WF_6 .

The chemical reduction of WF_6 in FLINAK containing tungsten metal produced equilibrium mixtures of W(V) and W(III) in the melt, rather than the WF_4

species suggested by previous work. The optimum plating baths reported in the previous studies was in the range where WF_6^{3-} and WF_8^{3-} were found to be in approximately equal proportions.

The electrochemistry of tungsten was adversely affected by residual HF in the melt, but could be removed by an extended sparge or by maintaining a vacuum over the melt. The W(V) discharge in FLINAK suggested both quasi-reversible and irreversible behavior and was dependent upon the bath temperature and the scan rate. This behavior was similar to the tantalum electrochemistry in FLINAK.

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CHAPTER I

INTRODUCTION

The last several decades have shown an increased interest in the electrochemistry and metallurgy of the refractory metals (groups IVA-VIA). Applications of these metals, ranging from aerospace technology to electrical and electronic devices, have spurred research efforts to produce the pure metals from electrolytic routes involving molten salts. These molten salts offer many unique properties, such as their high decomposition voltages and good ionic conductivities, which make them ideal solvents for electrochemical processes.

Of these molten salts, the alkali halides have been used extensively with studies involving the refractory metals. Deposits of refractory metals have been obtained from the alkali metal chlorides and fluorides, but coherent deposits have been obtained only from the latter at temperatures approaching 800°C. Deposits from the alkali chlorides were found to be powdery and dendritic.

A. Review of the Literature

1. Electrodeposition in FLINAK and other fluoride media.

Mellors and Senderoff (1) first patented a method to deposit all of the group IVA-VIA refractory metals, except titanium, from the eutectic alkali fluoride salt mixture LiF-NaF-KF (46.5, 11.5, and 42.0 mol% respectively, m.p. 454°C),

also known as FLINAK (although wide variations in the eutectic proportions were allowed for their process). Dense, coherent deposits of the metals were obtained on various substrates by this method including the electroforming of objects onto substrates which could subsequently be removed by dissolution in acid. The fluoride salts were chosen over other halogen salts in order to avoid the formation of cluster species, especially those associated with the chlorides, which were found to be detrimental to the electrodeposition process. Molten fluoride salts have played an important role in many other applications as well, including the electrowinning of aluminum from cryolite melts (2) and as homogeneous fluid fuels in molten salt nuclear reactors (3).

2. Deposition of tungsten from FLINAK.

Tungsten was first deposited by Mellors and Senderoff from a molten fluoride medium by preparing an *in situ* bath in which WF_6 gas was introduced into the molten FLINAK using a graphite bubbler (4). The WF_6 then reacted with tungsten metal in the bath to produce a lower valent species thought to possess a +4 valence. Deposits of tungsten from this bath and a similar bath containing 4.2 wt% W with a mean valence of +4.51 under various conditions were found to be dense and coherent. The authors proposed that an irreversible process was necessary to obtain coherent deposits. At temperatures of 600°C and below they found the process to be irreversible, but at temperatures higher than 600°C they reported that the bath experienced rapidly changing conditions from which meaningful data could not be extracted.

Broc (5) found the optimum plating conditions for the LiF-NaF eutectic were in a bath containing 5 to 12 wt% for an assumed WF_4 (formed by addition of WF_6 gas as above) with a mean tungsten oxidation state +4 to +4.5, an anodic current density 0.3 to 2 A/dm², and a cathodic current density 1 to 5 A/dm².

Baraboshkin and coworkers (6) reported optimum tungsten plating conditions in the FLINAK eutectic as 1 to 5 wt% tungsten ions in the temperature range 780 to 800°C and cathodic current densities of 0.04 to 0.08 A/cm². The deposits were all coherent and had the theoretical density of tungsten. The crystal structure and formation mechanism of the deposit have been studied (7).

In all of the above studies, the electroactive species was assumed to be dissolved WF_4 in the melt, ostensibly from the +4 and +4.5 mean valences found by potentiometric methods. The identity of the electroactive species as WF_4 , however, is unlikely since WF_4 has been found to decompose to WF_6 gas and W metal above 200 to 300°C (8). Also WF_4 would be expected to be a non-polar molecule and would not be expected to have an appreciable solubility in molten salts. Assuming a +4 oxidation state for the tungsten, species such as WF_6^{2-} would rather be expected to form in an excess fluoride environment. The +4.5 oxidation state found indicates either 'mixed' tungsten oxidation states or a tungsten cluster species. Cluster species are not common in molten fluorides though, so the mixed oxidation states would be a more likely explanation.

Further chemical and electrochemical investigations of the species present in the above melts could help in understanding the reduction mechanism of tungsten in FLINAK. Furthermore, spectroscopic characterization of the

tungsten species could yield structural information, which could identify the species present in the melt or a solidified boule of FLINAK. This may also be accomplished by synthesizing the tungsten compounds which produce this/these species in FLINAK, greatly simplifying the species characterization.

3. Raman spectroscopy.

A detailed description of the theory of Raman spectroscopy is beyond the scope of this work, so this technique will only be discussed briefly in the context of its use for the characterization of the tungsten fluorides (and similar compounds) encountered in this study.

When a molecule is irradiated with electromagnetic radiation with energy $h\nu c$, where h is Planck's constant, ν the frequency of light and c the speed of light, the energy will either be transmitted, absorbed or scattered (9). In the case of scattering, the molecule can experience electronic polarization when the incident radiation is in the visible or ultraviolet region. When no change in wavelength of the scattered photons is seen this is described as Rayleigh scattering. When an increase or decrease in energy of the scattered photons is seen, relative to the incident radiation, this is known as the Raman effect. The energy change in this case will be equal to $h\nu_i$ (where ν_i represents a vibrational frequency) and is known as the Raman shift. This shift is measured in cm^{-1} . The Raman effect is very weak in comparison to the Rayleigh scattering, being 10^{-3} to 10^{-4} less intense. However, with the development of lasers, which can provide intense monochromatic light, and CCD (charge-coupled device) detectors,

Raman spectroscopy has become a very powerful tool in the identification and structural characterization of molecules.

Infrared (IR) and Raman spectroscopy are usually seen as complementary, since they both reveal vibrational frequencies, although the selection rules are quite different. For a molecule with a center of symmetry, the selection rules are mutually exclusive. To illustrate this, consider a molecule with a central atom that is coordinated with six equivalent ligands (octahedral, O_h , symmetry). The vibrations that are nonsymmetrical with respect to the center, exhibiting a change in the dipole moment, are infrared active, while the vibrations that are symmetrical, exhibiting a change in polarizability, are Raman active. This can be seen in Figure 1.1 where the symmetrical and nonsymmetrical vibrations of an octahedrally coordinated molecule are illustrated. The ν_1 and ν_2 vibrations show symmetric stretching along the axis, giving rise to a change in the polarizability but no change in dipole moment. These vibrations are Raman active and IR inactive. The ν_5 vibration shows a symmetric bending mode, which is also Raman active and IR inactive. The ν_3 and ν_4 vibrations are asymmetric with respect to the center of symmetry, causing a change in the dipole moment of the molecule, but no change in the polarizability, and so both are infrared active but Raman inactive. The ν_6 vibration is inactive in both, and so is usually estimated from an analysis of the combination and overtone bands.

In the Raman spectra of octahedral molecules, the ν_1 stretching frequency is generally much more intense than the ν_2 stretching frequency, and is generally more intense than the ν_5 bending frequency. Some general trends of the ν_1

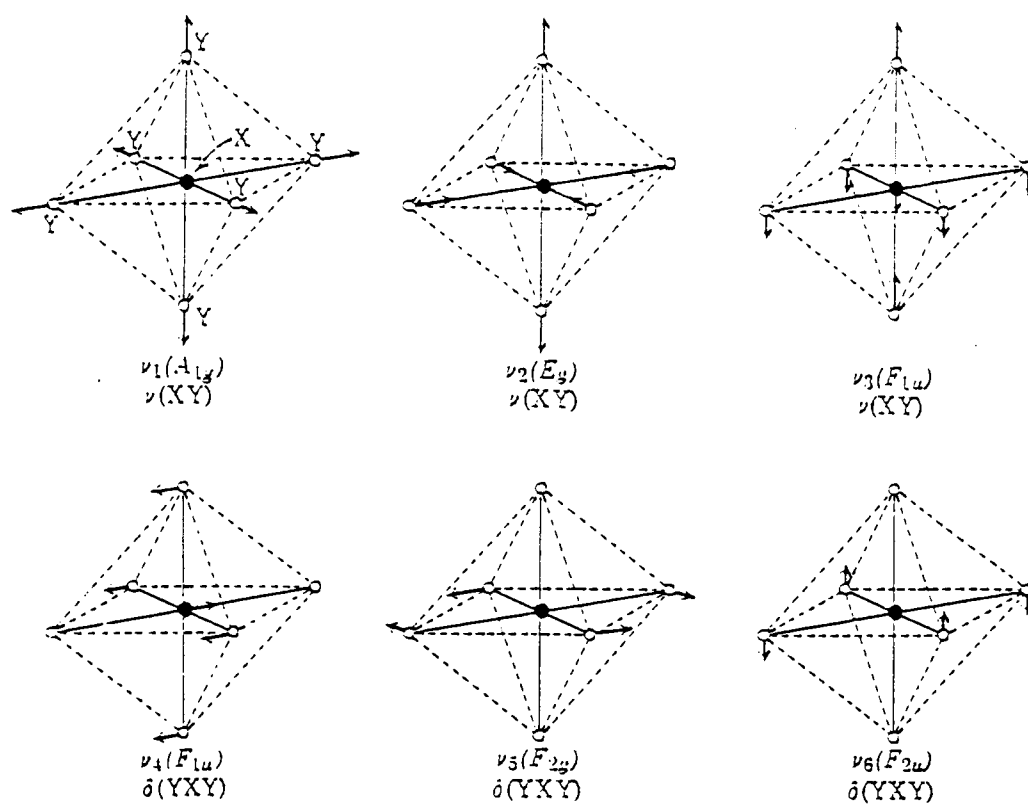


Figure 1.1. Normal modes of vibration of octahedral XY_6 molecules. Vibrations ν_1 , ν_2 and ν_5 are Raman active. Source: Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons: New York, NY, 1986.

stretching frequencies of octahedral molecules are: 1) the stretching frequencies decrease as the mass of the central atom increases in the same family, for example:

	$[\text{TaF}_6]^-$		$[\text{NbF}_6]^-$		$[\text{VF}_6]^-$
$\nu_1 (\text{cm}^{-1})$	692	>	683	>	676

2) the stretching frequencies increase across a period the higher the oxidation state of the central atom, such as:

	$[\text{HfF}_6]^{2-}$		$[\text{TaF}_6]^-$		WF_6		$[\text{ReF}_6]^+$
$\nu_1 (\text{cm}^{-1})$	572	<	692	<	770	<	797

and 3) the stretching frequencies increase the higher the oxidation state of a molecule with the same central atom, for example:

	WCl_6		$[\text{WCl}_6]^-$		$[\text{WCl}_6]^{2-}$
$\nu_1 (\text{cm}^{-1})$	437	>	382	>	341

The bending frequencies do not exhibit the same clear-cut trends.

Some of the main advantages (11) of Raman spectroscopy over infrared spectroscopy are: 1) the samples can be contained in glass, simplifying the analysis of air sensitive compounds, 2) the samples can be dissolved in water, 3) the use of lasers allows analysis of micro-samples, including surfaces, films, powders, etc., and 4) one Raman spectrometer can cover the entire vibrational frequency range. Some of the disadvantages include the higher cost of Raman instruments, no extensive libraries of Raman spectra, weaker overtone bands,

and the difficulty of Raman intensity comparisons from different instruments. Raman spectroscopy is also not as useful as infrared spectroscopy for quantitative analysis due to the weak Raman signal.

Homoleptic transition metal fluorides make ideal candidates for analysis by Raman spectroscopy due to their usually high structural symmetry. The bands from a Raman spectrum in this case can be used as fingerprints to match unknowns with known compounds, or unknown compounds can be related to known compounds with similar structure. The number of bands, their location and intensity can also be used to give specific structural information (10). As seen in Figure 1.1, an O_h coordinated molecule has six normal modes of vibration, three of which are Raman active: the $\nu_1(A_{1g})$, $\nu_2(E_g)$, and $\nu_5(F_{2g})$ modes. Seven and eight coordinated species are very rare and so have not been studied extensively. Seven-coordinate species have been known to be pentagonal-bipyramidal (D_{5h}), which has three Raman active vibrations. Eight-coordinate species can take on the form of a cube (O_h), an Archimedean antiprism (D_{4d}), a dodecahedron (D_{2d}), or a face-centered trigonal prism (C_{2v}). Normal coordinate analyses for a cubic (12) and an Archimedean antiprism (13) molecule have been reported.

A detailed spectroscopic study of tungsten fluoride species present in molten FLINAK would be very difficult experimentally due to the highly corrosive nature of the fluoride salts. No compatible window material is available, except for diamond, which can be used to interface with a spectroscopic probe. Even then, the diamond cannot be used above $\sim 600^\circ\text{C}$ in open air. A windowless cell

has been developed by Gilbert and coworkers (14) to observe complex ions in molten fluoride media. This technique suffers from the rapid reaction of the salt and analyte vapors with the quartz glass used to enclose the cell, thus adding oxide to the sample.

Rather than on molten fluorides, Raman spectroscopy can be performed on solidified fluoride salts to elucidate the species present. However, species in the solid may give quite different Raman spectra than species in the molten state (10). The symmetry of a molecule is generally higher in a solid than in a liquid. This change in symmetry may split the degenerate vibrations and activate infrared- (or Raman-) inactive vibrations in the solid. The spectra may also exhibit lattice modes due to translational or rotational molecular motions in the crystal lattice. In addition, the coordination number of a molecular species may be lower in the molten state at higher temperatures, although solid K_2TaF_7 was found by Raman spectroscopy to retain the TaF_7^{2-} coordination in molten FLINAK (15).

4. Oxide in fluoride salts.

An important consideration in many molten fluoride studies is the oxide content of the fluoride salt, which, depending on the concentration and other conditions, can cause desirable (such as better electroplates) or undesirable (such as precipitation of the electroactive species) effects. The oxide is present as O^{2-} or as part of a polyatomic ion, such as the sulphate or carbonate ion. The only reported (1) effect of oxide on the electrodeposition process of tungsten to

the metal indicated that oxide was detrimental to the deposition process. No detailed studies have been reported.

a. Effect on the deposition process. The effect of oxide concentration on the reduction of tantalum metal from a bath initially containing TaF_7^{2-} ions has been studied by Polyakova and coworkers (16). They found that the TaF_7^{2-} complex formed TaOF_5^{2-} and $\text{TaO}_2\text{F}_x^{(x-1)-}$ complexes at oxide/tantalum species ratios of 1:1 and 2:1 respectively. In the temperature range 625 to 815°C, the TaF_7^{2-} complex discharged irreversibly at scan rates >0.5 V/s and quasi-reversibly at scan rates <0.5 V/s. The TaOF_5^{2-} complexes discharged irreversibly at all the scan rates and temperatures studied. Both complexes produced coherent deposits of tantalum metal and showed that significant amounts of oxide could be tolerated in the electrodeposition process.

Similar results for niobium were found by Matthiesen and coworkers (17, 18) for the deposition of niobium metal from FLINAK containing the NbF_7^{2-} complex. In this case the authors found that the amount of niobium oxide complexes formed upon addition of oxide to the melt was temperature dependent. At 700°C they found that partially nonmetallic surface layers were obtained at oxide/Nb(V) ratios equal to or greater than one. The reduction of Nb(V) in FLINAK was proposed to follow the mechanism $\text{Nb(V)} \Rightarrow \text{Nb(IV)} \Rightarrow \text{Nb(0)}$, from which coherent deposits were obtained.

b. Determination of oxide in fluoride salts. A reliable method for determining the oxide content of bulk fluoride salts at the ppm level was developed at Oak Ridge National Laboratory (ORNL) by Goldberg, Meyer, and

White (19). In their process, the oxygen produced by the reaction of fluoride salts with potassium bromotetrafluoride (KBrF_4) in a nickel cell maintained at 450°C for two hours was measured manometrically. A mercury-filled Toepler pump was used to remove the product gases from the reaction cell and deliver them to the measurement apparatus. A major interference in these determinations was nitrogen gas released from the reaction due to traces of absorbed nitrogen and nitride salts. The O_2/N_2 ratio had to be found by mass spectrometry or gas chromatography following the manometric measurement, or as shown by Dupraw and O'Neill (20), the oxygen could be removed by passing the O_2/N_2 mixture through a copper furnace followed by a manometric determination of the remaining nitrogen. The detection limit of this system was shown to be as low as a few hundred ppm.

Other oxide determination techniques for fluoride salts have been developed with a wide variety of applications. The alumina content of cryolite was determined by carbothermic reduction using a LECO instrument (21). The alumina in a sample was reduced with carbon at high temperature and the quantity of CO produced measured. The standard deviation of free alumina analysis was found to be 0.11%. However, the LECO instrument does not perform well with many cations found in fluoride salts such as lithium and potassium. White (22) reported that oxide added to a molten fluoride salt was directly proportional to the anodic peak current on a linear sweep voltammogram, and recently Polyakova, Polyakov and Bjerrum (23) reported that the peak

anodic current in the LiF-NaF-KF eutectic ("FLINAK") at a glassy carbon electrode follows the equation

$$j_{550} = 309.1c_{O^{2-}} \quad [1.1]$$

where j_{550} is the current density at 550 °C and $c_{O^{2-}}$ is the oxide concentration from added Na₂O. Residual oxide was reported as low as 1.7×10^{-2} mol % (66 ppm). This technique is useful for in-situ oxide determinations but requires the salt to be in the molten state.

Ito and coworkers (24) used a Pt(O₂)/stabilized zirconia electrode immersed in the LiF-KF eutectic and measured the residual oxide concentration of the salt as a function of potential down to a reported 4.0×10^{-4} mole fraction (about 150 ppm) range. This technique is useful for in-situ oxide measurements as well, but requires larger samples in the molten state. Bjerrum and coworkers (15) showed that oxide concentrations as low as 0.2 mol % (about 800 ppm) could be determined from the tantalum fluoride and tantalum oxide vibrational (Raman and/or IR) peak ratios of the solid that results from the reaction of tantalum fluoride (added as K₂TaF₇) with FLINAK .

B. Proposal of Research

An improved method for the determination of oxide at the ppm level in bulk fluoride salts is described. This method will then be used to establish the

initial oxide content of the FLINAK purified by an HF sparge.

The synthesis and isolation of tungsten compounds formed from the combination of WF_6 and MF (where M = Na, K) and by reduction of WF_6 and W metal in MF (where M = Na, K, Rb and Cs) will be described. These compounds are characterized by various techniques including Raman spectroscopy and X-ray diffraction (crystal and powder).

The chemical formation and reduction of the above compounds in FLINAK are studied by combining WF_6 and W metal in various proportions in the eutectic salt and examining the products. The electrochemical reduction of the above compounds are also studied by using them as addition compounds to FLINAK. The effect of oxide on the electrochemical reduction of these compounds is also investigated.

CHAPTER II

DETERMINATION OF OXIDE IN FLUORIDE SALTS

A. Introduction

An improved oxygen determination technique using the ORNL-developed procedure (19) is described which employs the KBrF_4 reaction scheme, but which replaces the manometric measurement with an yttria-stabilized-zirconia (YSZ) oxygen pump. In this technique the molecular oxygen produced in the reaction cell is swept through a stabilized zirconia electrochemical cell and 'pumped' out with an applied potential across the zirconia membrane. The quantity 'pumped' is recorded as a chronoamperogram from which the total coulombs of charge can be obtained and converted to ppm oxide. This technique eliminates the nitrogen background interference of the ORNL technique, the use of a mercury pump, the necessity for a temperature calibration, and also offers a possible lower detection limit.

YSZ oxygen pumps or electrodes have been employed widely for various technologies including the automotive industry where it is used to control the air-to-fuel ratio in automobiles (25), and in glove boxes to determine the ppm O_2 present in the inert atmosphere. A YSZ tube used in these experiments measures the partial pressure of oxygen gas on the inside of the tube compared to a reference oxygen gas partial pressure (usually atmospheric) on the outside

of the tube by creating a potential difference across the inside and outside of the YSZ tube. The potential difference is measured by making electrical contact to porous platinum coatings which have been applied to the inside and outside tube surfaces. If the reference gas oxygen partial pressure (P_2) is known, then the unknown partial oxygen pressure (P_1) can be calculated from the Nernst relation (25):

$$EMF = (RT/4F) \ln (P_1/P_2) \quad [2.1]$$

where R is the gas constant, T the temperature in Kelvin, and F the Faraday constant. Normally one would measure potential, but according to this equation the tube can also act as an oxygen 'pump' if a DC voltage (V) is instead applied across the two platinum coatings. The YSZ tube can then selectively 'pump' oxygen either into or out of the tube depending on the sign and magnitude of the applied potential. When a DC potential is applied across the tube, oxygen gas is reduced at the negative pole (cathode):



The YSZ tube then acts as a solid ionic conductor and oxide is oxidized to oxygen gas at the positive pole (anode):



The current, I , has been shown (25) to be proportional to the applied potential according to the equation

$$I = (V + EMF) / R_i \quad [2.4]$$

where R_i is the cell impedance. The current is also a function of the temperature (Equation 2.1) of the YSZ tube, but the tube temperature is kept constant to

prevent this parameter from affecting the current response. The YSZ tube surface area and platinum coating quality also limit the maximum current by affecting R_i .

B. Experimental

1. Chemicals.

a. Preparation of KBrF_4 . Potassium fluoride (Fluka, >99%) and bromine trifluoride (Ozark-Mahoning) were used without further purification. The KF was dried under vacuum at 300°C overnight in a pyrex tube to remove excess moisture prior to use. Approximately 10 grams of the dried KF was then added to the metal reaction cell described below under a positive helium gas pressure. The reaction cell was then cooled below the BrF_3 freezing point and evacuated with the BrF_3 addition cap attached. Approximately 12 ml of BrF_3 (excess) was then let into the reaction cell. The reaction vessel cap was then replaced under positive helium pressure and the reaction cell heated to 450°C for 5 hours. The reaction cell was then cooled to 120 - 130°C and the excess BrF_3 distilled into a cold trap under vacuum. A white solid, KBrF_4 , remained in the reaction cell.

b. Preparation of Test Salts. Low oxide FLINAK was prepared from the individual salts potassium fluoride (Fluka, >99%), sodium fluoride (Fluka, >99%), and lithium fluoride (Fluka, >99%) after drying under vacuum at 300°C overnight. KF, NaF, and LiF were then combined in a controlled atmosphere glove box in 42.0, 11.5, and 46.5 mol % proportions respectively in a graphite crucible to form

the eutectic salt FLINAK (mp ~ 454°C). The crucible was sealed in a vacuum tight stainless steel cell and the mixture was heated to 550°C to fuse the salts. A small seed of FLINAK was added to initiate the melting of the eutectic since the individual salts all melt above 845°C. A graphite tube was then inserted into the FLINAK through which gaseous HF (Matheson, 99.99%) was bubbled overnight to achieve the 100 to 200 ppm oxide range FLINAK, and for 3 to 4 days to achieve <12 ppm oxide FLINAK. Upon completion of the reaction, excess HF that was dissolved in the melt was removed by a helium or helium/H₂ sparge before cooling. The FLINAK was then opened in an inert atmosphere glove box and stored in a glass container for future use. Yttrium oxide (A. D. Mackay, 99.9%) was used without further purification except for drying at 300°C overnight under vacuum before storing in an inert atmosphere glove box.

2. Apparatus.

a. Reaction Cell. The reaction cell (Figure 2.1) was machined from 1" Inconel bar and was isolated from the rest of the system by two Hoke Inconel diaphragm valves. The valves were silver-soldered to ¼" Monel tubing which was in turn welded to the cell body. The cap was machined from brass to prevent galling of the threads. An insert machined from nickel fit between the cell and cap and reached down to the inlet/outlet holes of the welded tubing. This insert reduced the space in the reaction cell and promoted flow-through of the gases. A nickel divider was welded to the insert to promote better sweep of the product gases into the oxygen measurement stage. A Teflon gasket was

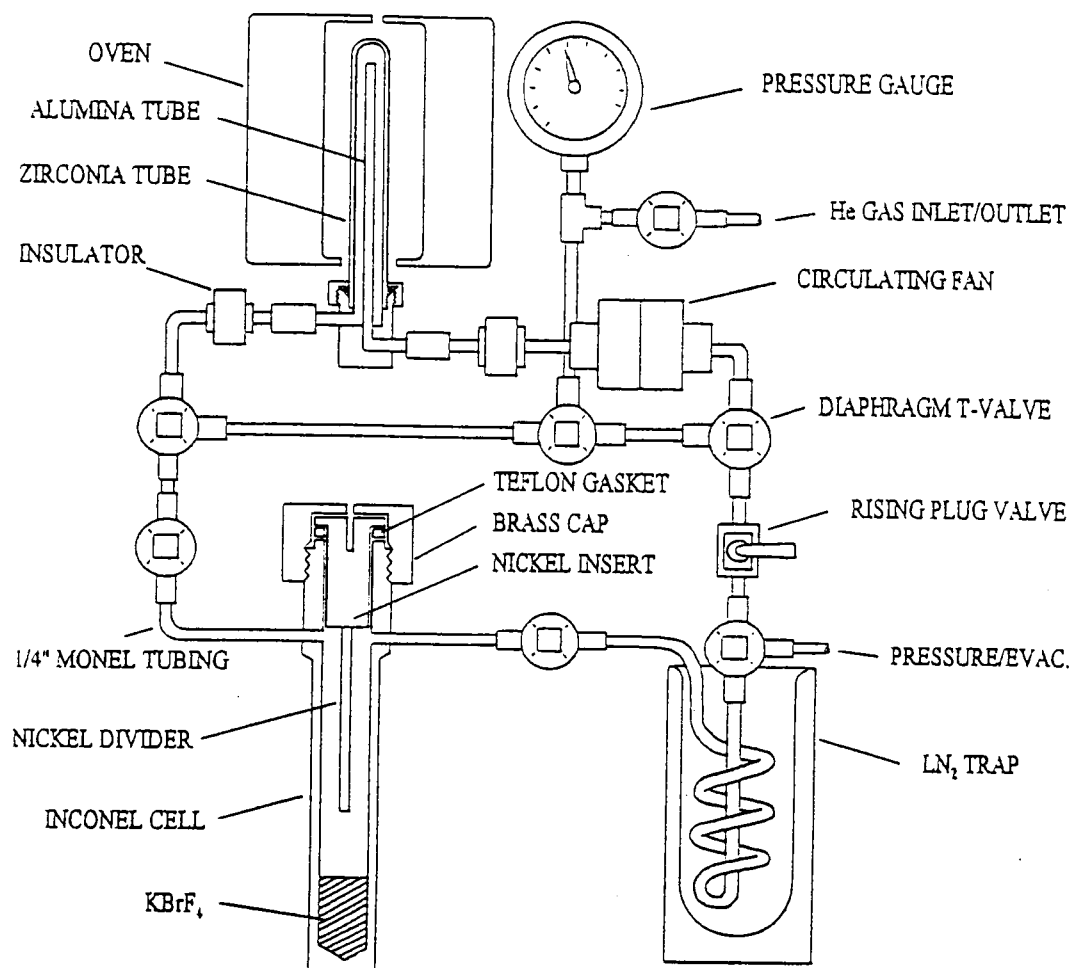


Figure 2.1. Oxide determination apparatus.

used to seal between the insert and cell. Two ¼" holes were drilled for the insertion of ¼" Chromel-Alumel thermocouples, one in the center of the cap to insure the Teflon gasket did not exceed 120 - 130°C, and the other off to one side in the cell bottom to measure the reaction temperature.

b. Circulating System. The circulating system was composed of ¼" Monel tubing connected with Swagelok unions. All valves were either straight or T-pattern Hoke Inconel diaphragm valves or Whitey rising-plug valves with Teflon seats and Monel stems. The T-pattern valves were used to eliminate eddy pockets from side arms while the rising plug valves prevented restricted gas flow.

A miniature fan (486 CPU cooler) was placed in line with the tubing to circulate the gases at a rate of approximately 100 ml/min. It was found that this provided the best flow for the gases in the system for oxygen pumping. Other gas circulating techniques were tested, but were found to either cause the gases to circulate too quickly through the system, thus cooling the zirconia tube and changing the temperature-dependent current response, or causing the gases to circulate too slowly and extending the pumping times beyond practicable limits. The circulating fan housing (Figure 2.2) was machined from aluminum and designed to promote even gas flow. Part of the circulating line was coiled and immersed in liquid nitrogen (LN₂) to trap the volatile bromo- and fluoro-compounds produced in the reaction cell. These compounds degraded the platinum coating and caused the background current to drift. Helium was used as the carrier gas so that it would not condense in the LN₂ trap and was

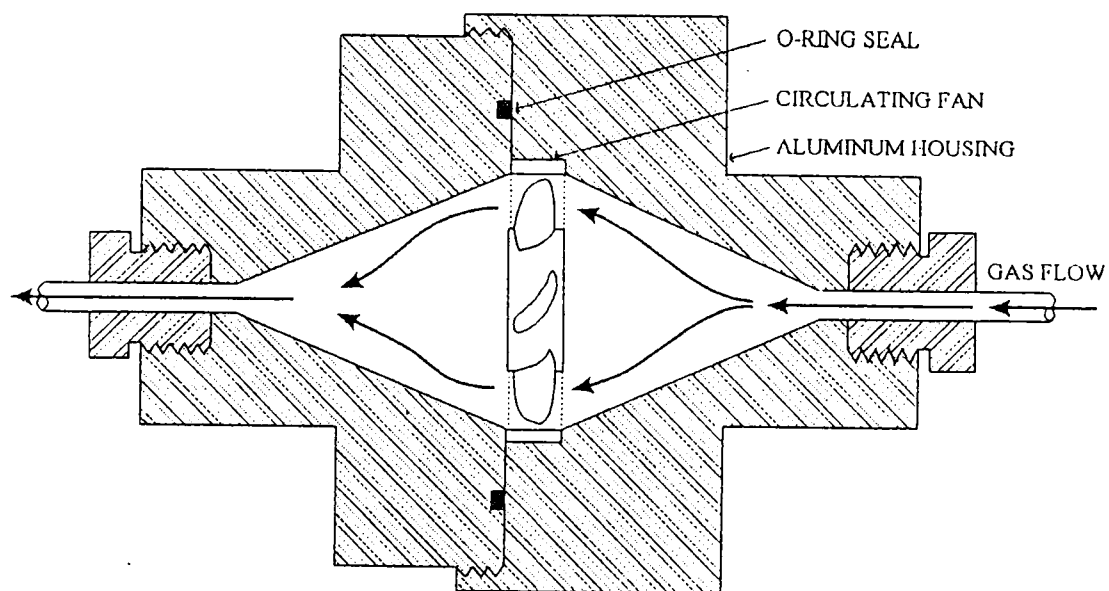


Figure 2.2. Circulating fan assembly.

maintained at a positive pressure of approximately 2 - 5 psi. The reaction cell and LN₂ trap were isolated from the main circulation loop in order that the initial background O₂ present in the system could be circulated through the YSZ tube and pumped out. This established an O₂ background baseline from which the coulombs of charge from the O₂ produced in the reaction cell could be separated.

c. Oxygen Pumping System. The oxygen pumping apparatus consisted of a platinum-coated YSZ tube placed in line with the circulating system. The YSZ tube was attached to an EG&G PAR 273 Potentiostat/Galvanostat which was used to apply a 0.25 V direct current (DC) potential across the inside and outside of the tube and record the current response as a function of time (chronoamperogram). The area under the resultant curve was integrated to obtain the total number of coulombs of charge passed. The potential leads were attached to the YSZ tube by a spring clip on the exterior and by a coiled platinum wire inside the tube. The software used to collect the data and calculate the area was the EG&G PAR Model 270/250 Research Electrochemistry Software version 4.23.

The YSZ tubes were either purchased complete with platinum coating from Thermox (Amatek), or uncoated tubes were purchased (Zircoa, stabilized with 8% yttria) and then coated with a platinum ink (Engelhard) in-house, which in turn was thermally decomposed at successively higher temperatures up to 800°C to produce the porous platinum coating. The entire *interior* of the YSZ tube was coated with platinum while one inch at the bottom of the *exterior* was

left uncoated in order to provide a nonconducting barrier where the tube could be sealed in the system and to electrically separate the interior and exterior electrodes. Examination of the platinum coatings by SEM (scanning electron microscopy) revealed a more uniform thickness with the coating on the in-house prepared tubes than with the purchased tubes.

The relative pumping quality of the tubes was tested by applying a predetermined potential across the tube which pumped oxygen *into* the system, while the system was under a vacuum, and observing the peak current. Using this test method, the purchased tubes generally reached a maximum current around 110 mA, while the in-house prepared tubes often surpassed three times that amount at 350 mA.

The reference in all cases was atmospheric oxygen. Attempts to flow a lower oxygen content reference gas over the exterior of the tube resulted in a drifting current response from what was interpreted as a cooling effect, i.e., the current response is temperature dependent. Since the heat conduction of zirconia is very poor, the YSZ tubes were sealed in the system near the base of the tube with a Cajon fitting using a rubber o-ring while the top portion of the tube was thermostated at 800 °C. No problems with o-ring melting were encountered. Alumina tubing was inserted inside the YSZ tube to sweep the gases over the inner surface. The YSZ tube assembly was isolated electrically from the rest of the system with either Teflon bushings or alumina tubing in place of a section of Monel tubing in order to reduce background noise on the chronoamperograms.

The oxygen pumping reproducibility of the YSZ tubes was tested by pumping the oxygen out of an oxygen/nitrogen mixture of known oxygen content. The results of four consecutive cycles of a) evacuation of the loop, b) test gas filling, then c) oxygen pumping are shown in Table 2.1. These results have a standard deviation of 1.14 mC. The expected charge as calculated from the diluted test gas was 878 mC (2.27×10^{-6} moles of $O_2 = 51.0 \mu\text{l}$ at STP), which indicated some error in the gas mixing process if the oxygen pumping process was assumed to be 100% efficient.

C. Procedure

1. System Preparation.

$KBrF_4$, prepared as noted above, was introduced into the cell, after which the system was heated to 470 °C for 5 hours while maintaining the cap at 120 - 130°C. This procedure effectively eliminated any oxides or oxygen containing compounds present in the reaction cell, especially from the Inconel cell walls. A background run was then performed using the same procedure as an oxide analysis run as detailed below, except without the addition of the sample. If the background was out of the range of the previous average backgrounds, then the reaction cell was heated to 470 °C again for 2 hours for another background run. This usually resulted in a background within the standard deviation reported in Table 2.2.

Table 2.1. Zirconia tube test cycles for oxygen gas pumping using $\sim 51.0 \mu\text{l}$ of oxygen diluted in nitrogen gas.

Cycle number	mC of Charge		Standard Deviation
	Expected	Obtained	
1	878	881.2	1.14 mC
2	878	882.3	
3	878	882.4	
4	878	883.8	

2. Oxide Analysis Procedure.

The samples were added by opening the reaction vessel cap under helium pressure and quickly adding the sample from a glass vial to minimize addition of moisture and oxygen. The entire reaction vessel was then heated to 120 - 130°C under vacuum until the pressure dropped to less than 2 micrometers of mercury, thus removing condensable gases . At this point the valve to the vacuum line was closed off. The temperature of the bottom of the cell was then increased to 450°C for two hours while maintaining the cap at 120°C to prevent condensation of BrF₃ (from the equilibrium decomposition of KBrF₄), so that it would recombine as the reactant. The reaction between KBrF₄ and a representative oxide (Y₂O₃) is believed to be



with traces of other products such as Br₂ and BrF.

Upon cooling to room temperature, the cell was opened to the circulating path where the product gases were swept through the system by the circulating fan. The gases passed through the LN₂ trap first where the volatile fluoride and bromide products were trapped, and then through the YSZ tube where the oxygen was pumped out and the quantity of charge passed recorded as a chronoamperogram. The millicoulombs (mC) of charge passed were converted to ppm oxide by Faraday's Law:

$$\frac{(mC) (0.08291)}{\text{Sample Wt.}} = \text{ppm oxide} \quad [2.6]$$

where the sample weight is in grams. This equation assumes 100% current efficiency for the oxygen pumping process. Blank runs were performed in the same manner including opening the reaction cell cap and simulating addition of a sample.

D. Results

1. Backgrounds.

The background reproducibility was between 50 and 60 μg of oxygen, similar to the 30 to 50 μg reported in the ORNL technique, and gave a limit of detection of 12 μg of oxygen (Table 2.2). The background oxygen was thought to arise from either incomplete removal of moisture or adsorbed oxygen prior to the background run, or to a slight leak through the Teflon gasket during the background run, since the reaction cell was under a vacuum.

2. Determinations.

The precision of analysis was tested (Table 2.2) using FLINAK samples from the overnight HF purification ranging from 100 to 225 mg. All samples were taken from the same batch, which had an oxide content near the detection limit of 12 μg . The analysis gave a coefficient of variation better than 13% and

Table 2.2. Oxide determinations for FLINAK, yttrium oxide, and the background.

Sample	Weight (g)	mC pumped*	$\mu\text{g O}_2$	ppm	Standard Deviation
Background [†]	---	598	49.6	---	4.0 μg
		597	49.5		
		651	54.0		
		712	59.0		
		695	57.6		
		703	58.3		
		642	53.2		
FLINAK	0.1363	277	23.0	168	18 ppm
	0.2033	316	26.2	129	
	0.2250	378	31.3	139	
	0.1574	283	23.5	149	
	0.1151	155	12.9	112	
	0.1264	230	19.1	151	
Y_2O_3 [‡]	0.0116	294×10^2	24.4×10^2	210×10^3	1×10^3 ppm
	0.0103	263×10^2	21.8×10^2	212×10^3	
	0.0104	266×10^2	22.1×10^2	211×10^3	
	0.0110	280×10^2	23.2×10^2	211×10^3	

*For FLINAK and Y_2O_3 the average background has been subtracted.

[†]The limit of detection is 12 μg of oxide.

[‡]The relative error for an expected 213×10^3 ppm was -0.8%.

indicated the FLINAK samples contained residual oxide in the 110 to 170 ppm range after the overnight HF purification. FLINAK samples obtained from the 3 to 4 day HF purification were added in the 1 g range and showed the oxide to be below the detection limit of 12 ppm. Sample sizes much larger than 1 g are not recommended for this system though, since this may require longer reaction times and would deplete the reactant more quickly. If a lower detection limit is required then a modified version of this system may be designed for that purpose. This may be accomplished by enlarging the reaction cell to accommodate the larger samples, and enlarging the electroactive surface area of the YSZ oxygen pump to decrease the pumping time. The accuracy was tested by analyzing samples of yttrium oxide which had been compressed into pellets. As can be seen in Table 2.2, more than 99% of the oxide was recovered from the this salt. With these data the analytical range for a 0.1 g sample would be 120 ppm to >20%.

3. Chronoamperograms.

A typical chronoamperogram generated by the oxygen pumping can be seen in Figure 2.3. The peaks were generally sharp with a noticeable amount of tailing. As long as the baseline was established before pumping out the oxygen produced in the reaction vessel, the baseline background could be eliminated from the peak by drawing a horizontal line across the base and calculating only the coulombs of charge above that line. The blank run coulombs could then be subtracted from the sample run coulombs to get the final charge.

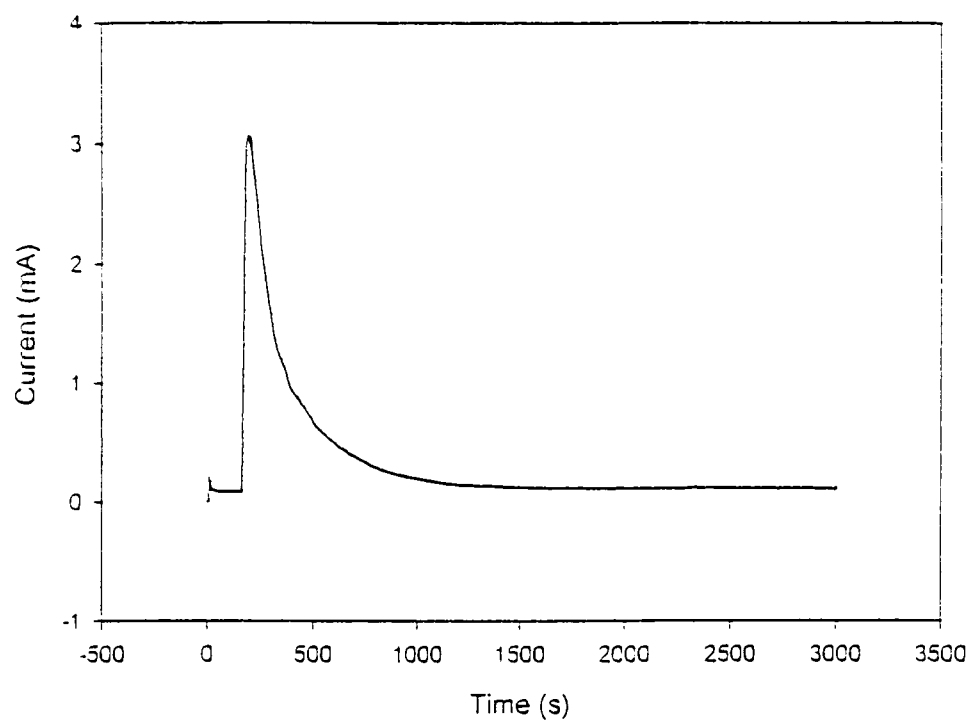


Figure 2.3. Typical O_2 pumping chronoamperogram.

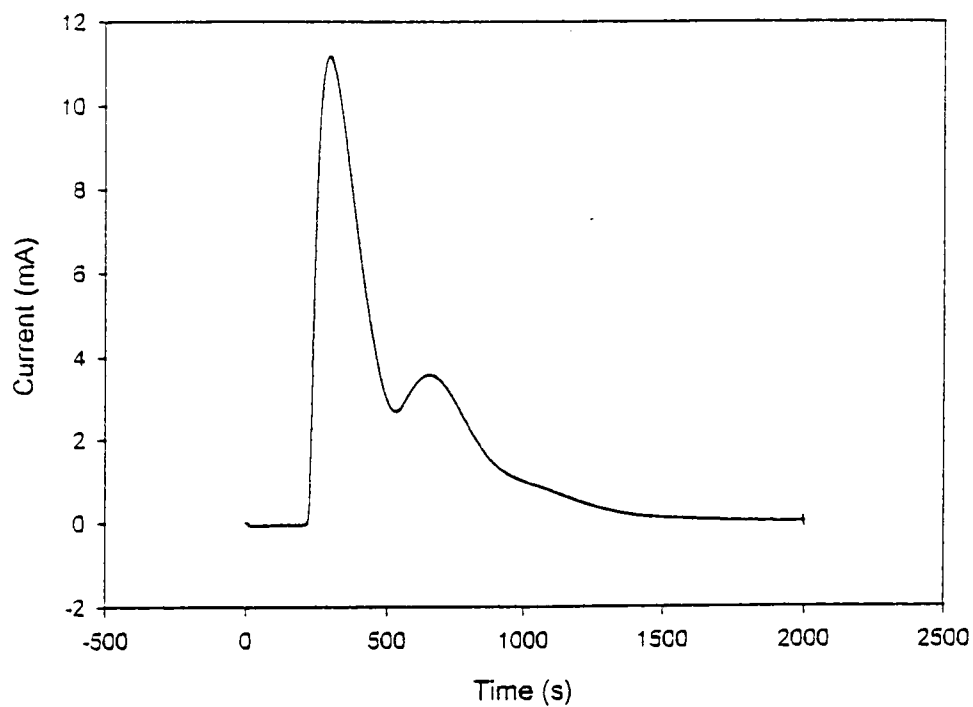


Figure 2.4. Overloaded O_2 pumping chronoamperogram.

The circulating system was designed to produce sharper chronoamperogram peaks by increasing the current and thus reducing the pumping time. This was achieved by minimizing the system volume to maximize the oxygen concentration. Often with larger quantities of oxygen in the system, the zirconia tube would be 'overloaded' on the first pumping pass and a second current maximum could be seen on the chronoamperogram (Figure 2.4). 'Overloading' was interpreted as being due to a plug flow of O_2 that was not completely pumped out on the first pass through the YSZ tube. Then on passing a second time, another peak appeared for the remainder of the plug. The time for this second peak was consistent with the pumping speed of the system. A third peak was slightly visible as well. This did not significantly affect the accuracy or precision of the determination since the oxygen continued to circulate and eventually was pumped out. The chronoamperogram did have increased tailing and thus increased pumping time.

Typical pumping times ranged from 1000 - 3000 seconds. Increased YSZ tube surface area, smaller internal circulating volumes, and faster circulating rates reduced this time significantly. Increasing the applied potential did not necessarily decrease the pumping time, and the system was found to work best with an applied potential of 0.25 V. Potentials greater than 0.3 V caused the background current to drift, and potentials greater than 1.0 V tended to decompose the zirconia.

4. Reaction Cell Seal.

The Teflon ring insert used to seal the reaction cell lasted for more than 40 sample determinations as opposed to six reported by the ORNL method. Since a batch of KBrF_4 in the quantity described above will provide 20 to 25 determinations, the Teflon insert was replaced when a new batch was prepared.

The source of the background variation was not known with certainty but was assumed to arise from either addition of moisture during the addition of the sample, or from minute leakage of the Teflon seal during the sample run, since the cell was under vacuum during the reaction period.

E. Conclusions

An oxide determination apparatus has been developed for use as a simple, inexpensive tool for routine, ppm oxide analysis of fluoride salts such as the fuel and flush salts from the Molten Salt Reactor Experiment (MSRE). This technique can be used for solid samples in the 10 to 250 mg range, depending on the oxide content, and can be assembled in most part from materials found in fluoride salt labs. The detection limit could be lowered significantly by reducing the standard deviation of the background. This may be accomplished by enclosing the reaction cell top, or the entire reaction cell, in an inert atmosphere, i.e., oxygen and moisture free. This would eliminate any addition of oxygen or moisture into the reaction cell during addition of the sample and possibly decrease the background variation.

Chapter III

SYNTHESIS AND CHARACTERIZATION OF TUNGSTEN FLUORIDE COMPOUNDS

A. Introduction

In order to more fully understand the reduction process of tungsten fluorides in FLINAK, the reduced tungsten species encountered during the reduction of tungsten hexafluoride (WF_6) with tungsten (W) metal in the melt from previously reported experiments (1, 4-6) need to be identified and characterized. Since the FLINAK eutectic contains multiple cations, it is difficult to isolate and characterize individual compounds. Therefore the individual model salts, potassium fluoride (KF) and sodium fluoride (NaF), were used to synthesize reduced compounds analogous to those reduced in FLINAK. The Raman bands of the synthesized compounds could then be used as fingerprints to identify species or compounds present in the FLINAK eutectic.

Since the reduced tungsten fluorides produced in FLINAK were formed at high temperatures (600 - 800°C), the synthesis of the individual compounds was also performed at high temperatures. This resulted in a new synthesis route for all of the known compounds produced at high temperature in this study, namely K_2WF_8 , KWF_7 , K_3WF_8 and MWF_6 (where M = Na, K, Rb and Cs), and also produced two new tungsten fluoride compounds: K_2WF_7 and K_3WF_6 . In addition,

a $[\text{Cu}(\text{WF}_6)_2(\text{CH}_3\text{CN})_3]_2$ dimer was produced at lower temperatures (100 - 175°C), but was not used as an addition compound. The dimer did provide Raman spectroscopic data on the WF_6^- vibrations and so has been included in the studies.

B. Experimental Details for the Synthesis and Characterization of the Tungsten Compounds

1. Chemicals used in the synthesis steps.

Potassium fluoride and sodium fluoride (Fluka, >99%) were first dried at 300°C overnight under vacuum, then were purified by slow recrystallization as follows: approximately 100 g of the individual salt was placed in a glassy carbon or graphite crucible and heated under a helium atmosphere to 20°C above the melting point of the salt, then slowly cooled at ~ 4°C per hour to 20°C below the melting point. The crucible containing the salt was then allowed to cool to room temperature over a 5-hour period and the contents opened in the glove box. After breaking apart the resultant lump of material, the outer clear portions (90% to 95% of the material) were manually separated from the impurities, which had concentrated toward the center of the solid. The clear portions were then stored in an inert atmosphere glove box for use in the synthesis of the tungsten compounds. However, this method did not remove hydroxides since the phase diagrams (26) of MF and MOH (where M = Na, K, Rb or Cs) reveal solid solutions with the alkali metal with nearly 10% hydroxide present. However,

infrared spectra of the salts did not reveal any observable hydroxide, which gives several absorption bands in the 3550 to 3700 cm^{-1} range (27), so the salts were used with this purification process alone.

Rubidium fluoride (Alfa/Aesar, 99.98%) and cesium fluoride (Alfa/Aesar, 99.9%) were used without further purification, except that they were dried in situ by evacuating the reaction cell for 5 hours while heating to 600 °C before the synthesis with tungsten hexafluoride (WF_6) gas was performed. WF_6 gas (Cerac, 99.9%) and tungsten metal powder (Aesar, 99.9%, 100 and 300 mesh) were used without further purification. K_2TaF_7 (Alfa/Aesar, 99.9%) was used without further purification, although only the portions that appeared the most clear or crystalline were used. The cloudier portions were shown to have some residual oxide (28). Benzene (Fisher, reagent grade) was purified by reflux with lithium metal wire overnight to remove moisture, then distilled into a dry glass vessel. Acetonitrile (Fisher, reagent grade) was purified by reflux with calcium hydride overnight to remove trace moisture, followed by distillation to a dry glass vessel. All purified chemicals were handled in an inert atmosphere glove box (Vacuum Atmospheres model HE 43-2) which was filled with purified nitrogen and operated at < 2 ppm H_2O .

2. Synthesis Apparatus.

The nickel/stainless steel reaction assembly is shown in Figure 3.1. The reaction cell was made from Inconel pipe to which was welded an Inconel plate to form the cell bottom. Stainless steel (SS) knife-edge flanges (Huntington)

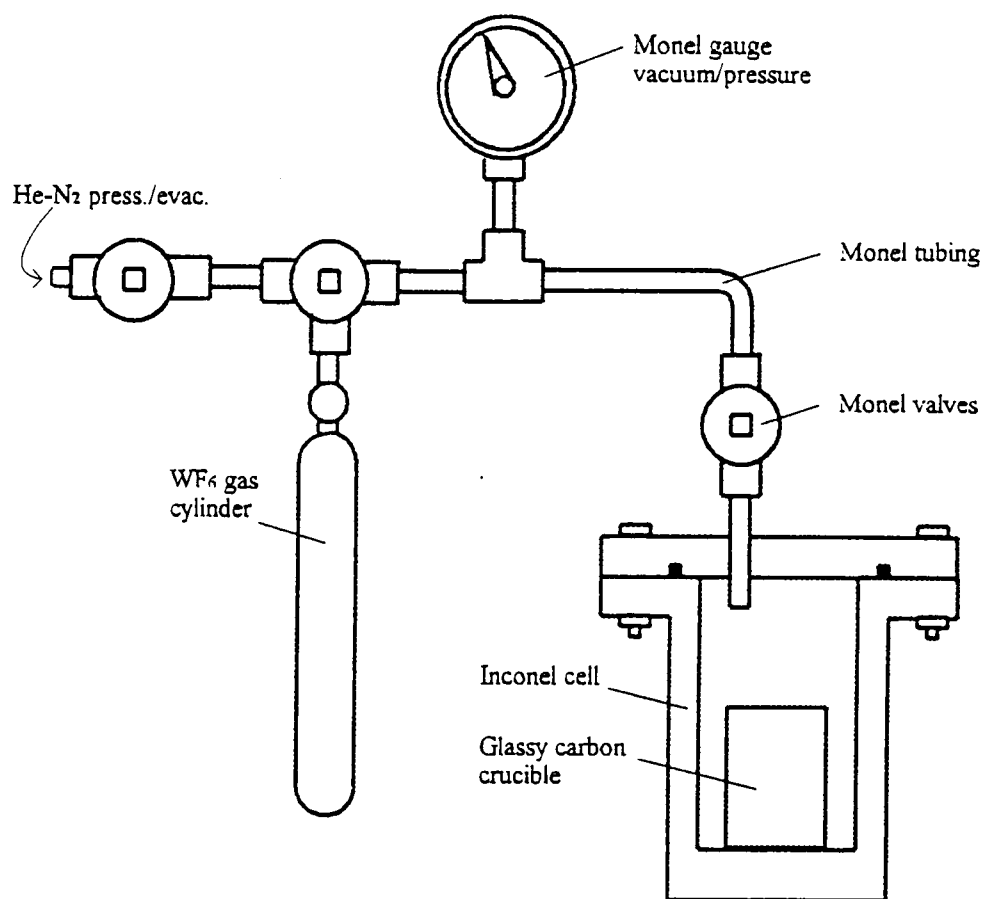


Figure 3.1. Reaction apparatus for tungsten compounds.

were used to cap the cell. Copper or nickel-plated copper gaskets were used to seal the cell at the knife edges for the higher temperature reactions. An in-house fabricated Teflon gasket was used to seal the cell for the reactions below 200°C. Hoke Inconel diaphragm valves in either the straight or tee patterns were used throughout the system except for the WF_6 cylinder valve which was supplied by the vendor. The vacuum/pressure gauge (Ashcroft, 30 in. Hg to 30 psi) was also Monel, which resisted corrosion by the WF_6 gas and its byproducts such as HF. An Inconel sheathed chromel-alumel thermocouple was placed on the external face of the bottom of the cell to measure the temperature. The interior cell temperature was assumed to be only 2 - 3°C lower than the exterior cell reading, since this temperature difference was found with similar cells in which a thermocouple was inserted directly into the melt.

The oven was made in-house to fit the reaction cell by wrapping Kanthal wire (1200°C maximum temperature) around alumina tubing, which was then insulated with quartz wool and inserted into a larger alumina or silica tube. The temperature of this oven was controlled by a large-current variac. Compressed air was blown across the top of the cell to keep the bolts from heating too high and seizing. Helium gas was used in all cases to pressurize the system, except when the reaction was performed without release of the pressure. In this case the cell contained nitrogen from the inert atmosphere glove box. All connections were made by either silver-soldering or using Monel Swagelock unions and connectors with Monel ferrules, except where Teflon tubing was used as mentioned in the synthesis procedures. The crucible used to contain the

reactants at the higher temperatures was in all cases made from glassy carbon (Sigridur G, obtained from EMC Industries). The reaction mixtures at lower temperatures were contained in the nickel/SS cell only, i.e., without the glassy carbon crucible, and were sealed with a Teflon or copper gasket.

3. Density Measurements.

The density of several of the tungsten compounds was measured by dropping solid crystalline samples into a graduated pipet filled with dry benzene. No significant dissolution of the compounds into the non-polar solvent was observed. The crystals were weighed on an analytical balance and the volume displacement measured to two or three decimal places (depending on the pipet used). All measurements were performed in the inert atmosphere glove box.

4. Melting Points.

Approximate melting points for three of the compounds were determined by placing the sample in a silica glass tube to which was wired a 1/8" chromel-alumel thermocouple for a general temperature reading. The tubing was then heated with an in-house built oven. Upon melting, the compounds rapidly attacked the glass, making boiling points impossible to determine by this method. The other melting points were estimated by observing the various products and unmelted reactants when the reaction mixture was cooled and opened in the glove box. When a reaction mixture was found to be partially melted at the attempted reaction temperature, a better estimate of the melting point could be

obtained. When condensation of a product was observed as a ring or deposit on the cell or crucible walls, the working temperature of that experiment was considered to be at least above the melting point. The *relative* freezing points of the various products could be estimated when multiple bands of the colored condensates could be seen at different levels on the walls or cell top.

5. X-ray Crystallography.

a. X-ray Diffractometer and Crystal Structure Determinations. The X-ray crystal structures were determined using a Siemens R3m/V diffractometer fitted with a Nicolet LT-2 low temperature device. The intensity data were measured with graphite-monochromated Mo K α radiation ($\lambda = 0.710713 \text{ \AA}$). While the crystal and counter were kept stationary, background counts were measured before and after each scan. Three standard reflection intensities were measured after every 97 reflections, and the intensity data were corrected for absorption and for polarization and Lorentz effects using an empirical absorption correction based upon ψ scans. The unit cell parameters, along with the orientation matrix, were determined from a least-squares fit of 30 reflections from an automatic peak search routine and from a rotation photograph. The SHELXTL 93 (versions 5.0 and 5.10) software packages were used to solve the crystal structures by direct methods.

b. Crystal Preparation. Crystals of the material of suitable size for mounting for X-ray analysis were spread out on a glass slide in the inert atmosphere glove box. The crystals were then covered with a few drops of

paratone oil (Exxon) and removed from the glove box for examination under a microscope. The paratone oil protected the samples from attack by moisture once outside the inert atmosphere. Suitable crystals were mounted on glass fibers and immediately placed under a stream of cold nitrogen to freeze the paratone oil during data collection, which prevented movement of the crystal and sealed out room air. The crystals frozen in paratone showed no signs of attack by moisture for many days. Room temperature samples were encased in epoxy and mounted on glass fibers for data collection. The crystals coated in this manner were also stable for many days.

6. Raman Spectroscopy.

a. Raman spectra. All Raman spectra were recorded with a Dilor XY CCD detector multichannel spectrometer using the 514 nm line of an Ar ion laser as an excitation source. Focusing on the sample was achieved through a Spex microscope fitted to the Dilor instrument with 10X, 80X, and 100X objectives. Most spectra were obtained using the 80X objective since this significantly reduced the glass background signal and provided the optimum signal response. Several spectra were obtained with the 10X objective, but elimination of the glass signal with this objective was more difficult. The laser power used was between 5 and 100 mW, depending on whether the sample decomposed at the higher powers or was significantly heated, causing broadening of the Raman bands. The incident beam was focused through the microscope objective, which was also used to collect the Raman scatter. The detection window was set from

118 to 1059 cm^{-1} for most spectra, since this was the general frequency range for the tungsten fluoride and tungsten oxide vibrations. The average interrogation size was an 83 μm diameter spot on the sample for the 10X objective and a 10 μm diameter spot for the 80X objective.

b. Sample tubes. The samples were sealed in specially designed glass tubes which were made by attaching a 10 - 15 mm length of 3 mm square pyrex tubing (Vitro Dynamics) to approximately 150 mm lengths of 7 mm round pyrex tubing. The square tubing was sealed off at the open end so the compounds could be loaded and sealed under a vacuum. Since a portion of the tubing was lost each time the tube was opened, the round tubing was made long enough to allow the Raman tubes to be opened and resealed multiple times. The sample tubes were placed horizontally on the Raman microscope stage, where the microscope was used to focus through the flat surface of the square pyrex glass and onto the surface of the sample, thus reducing or eliminating the glass signal.

When the sample was in the form of a powder, which was pressed against or clinging to the glass walls, or when the crystals were near the glass surface, a glass signal would be more prominent. Focusing at least a third of the distance down through the flat surface of the square glass tubing usually eliminated the glass signal. This was not always possible with powders except when the powder did not adhere as well to the glass walls, i.e., had less static attraction. Even then there was always some powder clinging to the glass walls. One way to overcome this problem was to fill the square tubing halfway with the powder; then under the microscope, some of the powder was allowed to fall towards the

upper half of the square tubing, but with the powder lying on one face of the glass only and leaving some space between the top surface of the powder and the glass walls. In this way the beam could be focused several millimeters through the glass before focusing onto the surface of the powder. The glass signal was generally eliminated by this method.

c. Background Raman signals. The glass background produced very broad bands at 800 cm^{-1} and 450 cm^{-1} . The band at 450 cm^{-1} was much more intense than the band at 800 cm^{-1} and provided the largest source of interference. The use of the *microscope* stage usually allowed the collection of the Raman signal outside the focus of the glass signal. On the *macro* stage, elimination of the glass signal was more difficult, although Raman spectra of liquid samples on this stage allowed for better focusing through the glass than for the solid samples, and hence a reduced glass signal. The main interfering band for the tungsten oxide stretch originated from the fluorescent room lights and light from the windows, which gave a broad signal in the 950 cm^{-1} region. Most or all of this interference was eliminated by darkening the room during data collection.

C. Synthesis and Characterization of the Individual Tungsten Compounds

The synthesis and characterization of various tungsten compounds is described in the following section. The reactions described are either *addition*

reactions, where MF (M = Na, K, Rb or Cs) is combined with either WF₆ gas or a previously synthesized compound, or *reduction* reactions where W metal is present in the above mixtures as a reductant to produce compounds containing W oxidation states between W(0) and W(VI). In the former case MF adds to the reactant compound in the following manner:



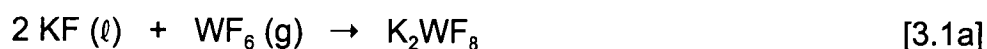
Initially, the two different cases of reaction mixtures described above containing KF succeeded in producing W(VI), W(V), and W(III) compounds, although the W(III) compound was produced pure in only one instance under conditions which were difficult to reproduce. No W(IV) compound was obtained. NaF, RbF and CsF were then used in place of KF in the reaction mixtures in an attempt to produce a W(IV) compound and more easily synthesize the W(III) compound. However, only W(V) compounds were obtained with these salts.

Each synthesis below is subdivided into the synthetic procedures, which also contains some physical descriptions, the Raman spectrum of the material, and the X-ray structure/powder pattern (when obtained or reported), followed by any discussion or additional information obtained.

1. Potassium octafluorotungstate (VI), K₂WF₈.

a. Synthetic procedures. Crystals of KF (5.0 g, 86 mmoles total) were placed in a glassy carbon crucible in an inert atmosphere glove box which was then loaded into the reaction cell. The reaction cell was then attached to the WF₆ gas addition system, located outside the glove box, and lowered into the in-

house built oven. After heating to 870°C and achieving a vacuum of less than 15 μm of Hg, the vacuum line was closed off and WF_6 gas was allowed to fill the cell. The reaction was very fast as indicated by the system vacuum gauge, which initially showed the WF_6 gas pressure in the system to drop to 0.0 in. Hg in 1 to 2 seconds (when the WF_6 supply was closed off at the beginning of the reaction). Approximately 10 minutes after the initial WF_6 addition, the system was cooled to 800°C to prevent excessive condensation of the product on the cell top during the remainder of the reaction. The reaction was much slower at this stage in the synthesis, with the pressure decreasing to 0.0 in. Hg over several minutes. The presumed reaction



was thought to be complete when the system WF_6 gas pressure ceased to decrease when the supply was closed off. This took about 1 hour for the initial 5.0 g of KF. When the product was weighed (12.3 g), a > 97% yield was obtained when K_2WF_8 was assumed to be the product. The material was observed to be a white powder which was caked at the bottom of the crucible. A faint pink color at times was interpreted as a very slight amount of oxide contamination since, upon exposure to moist room air, the compound quickly turned a dark purple, indicative of tungsten oxides. When the product was left in the system at the 870°C temperature for several more hours, after the indicated completion of the reaction, it would begin to condense on the cooler interior cell top. Crystals were not obtained by this method. Along with the weight gain, the

product was characterized by the Raman spectra, which matched the reported bands for K_2WF_8 as detailed below.

Although K_2WF_8 has been made previously (29) according to the reaction



the high temperature method of the present study is a possibly easier synthetic route which can produce any desired quantity of the product by direct combination of the reactants, with no secondary removal of byproducts. A related method of synthesis, which used the addition of MF_6 gases (where $M = U, W$ and Mo) to alkali metal fluorides (NaF, KF, RbF and CsF) at elevated temperatures ($100 - 250^\circ C$), produced complexes of the form $MF_6 \cdot 2NaF$ (30). However, these compounds represent complexes where the MF_6 is adsorbed onto the high surface area alkali metal fluoride, and have been shown to not contain discrete MF_6^{2-} ions.

b. Raman spectrum. The Raman spectrum of K_2WF_8 has been reported by Beuter et al. (31) with bands at 667, 417, and 385 cm^{-1} . These bands match fairly well with the bands of the spectrum of the high-temperature synthesized compound which showed bands at 667 (strong), 419 and 389 cm^{-1} . The spectrum is shown in Figure 3.2. Since the crystal structure for K_2WF_8 is not known, it is difficult to give band vibration assignments. Beuter (31) assumed a square antiprism from known structural data of eight coordinated compounds. The resultant D_{4d} symmetry of the square antiprism gives rise to 13 vibrations of which 7 are Raman active. Since the Raman spectra were obtained on the solid, some of the bands may be lost due to crystal effects. Beuter reported that only 2

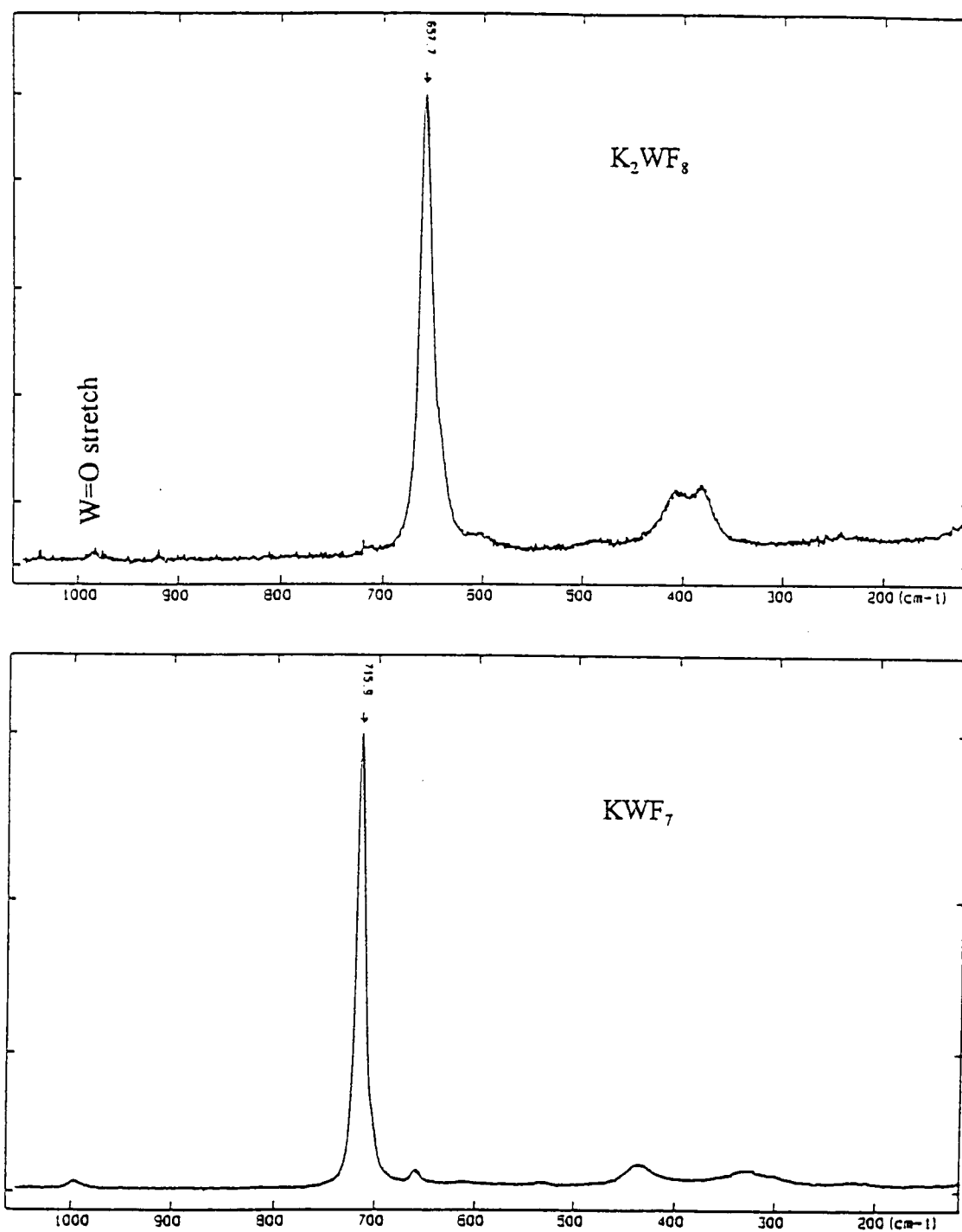


Figure 3.2. Raman spectra of solid samples of A) K₂WF₈ and B) KWF₇.

or 3 Raman bands usually appeared for the solid samples. The Raman bands of the Rb and Cs analogs to K_2WF_8 have also been reported by Beuter and coworkers as 657, 406 and 383 cm^{-1} , and 656, 406 and 385 cm^{-1} , respectively.

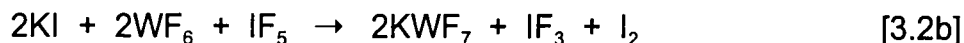
2. Potassium heptafluorotungstate (VI), KWF_7 .

a. Synthetic procedures. KF and WF_6 were combined according to reaction [1] except with the addition of one more step. Rather than close off the WF_6 gas before cooling the newly formed K_2WF_8 , the WF_6 gas overpressure was maintained over several days at 750°C . The following reaction is thought to occur:



A bright yellow powder condensed on the cooler interior cell top. No crystals were obtained from the condensate. The yield of this reaction for the assumed KWF_7 was approximated at >60% by weighing the bulk of the bright yellow layer. Some K_2WF_8 condensed on the cell top as well, as indicated by Raman spectroscopy. The two apparent products condensed as separable layers, the first condensate being identified as the K_2WF_8 compound.

The synthesis of KWF_7 has been reported by Hargreaves and Peacock (28,32) who combined KF and WF_6 in liquid IF_5 at room temperature in a thoroughly dried silica vessel. Beuter and coworkers (31) used a similar method, except they replaced the KF with KI in the following reaction with excess IF_5 :



They reported the KWF_7 product as nearly white, while the high-temperature synthesized material described above was a very bright yellow. This difference in color is most likely due to an impurity, such as an oxide, in the product obtained at high temperature in the present study, since a material with tungsten in its highest oxidation state is expected to be colorless.

b. Raman spectrum. The Raman spectrum of KWF_7 has been reported by Beuter and co-workers (31) to exhibit bands at 718, 665, 620, 550, 438 and 330 cm^{-1} . The Raman spectrum for the material synthesized at high-temperature and thought to be KWF_7 is shown in Figure 3.2. Bands can be seen at 716 (strong), 665, 615, 535, 435, 327 and possibly 220 cm^{-1} (extremely faint). Several of the bands were very weak and the exact position of the band difficult to determine. This may partly explain the slight discrepancy between the reported bands and the bands of the synthesized material. The reason for the 15 cm^{-1} difference between the reported band at 550 cm^{-1} and the band at 535 cm^{-1} of the high-temperature material is not known. The bands at 716, 665, 435 and 327 are the most prominent and also match most closely with the reported bands. The CsWF_7 Raman spectrum shown by Beuter (31) looks very similar to the Raman spectrum in Figure 3.2 and has the three most intense bands at the 718, 444 and 330 cm^{-1} positions. Beuter assumed a symmetry which gives rise to seven allowed Raman bands for the WF_7^- species, although only six are reported. If the band at 220 cm^{-1} , which is very weak in Figure 3.2, is the expected seventh band, it may be that it was lost due to signal-to-noise constraints in the reported Raman bands.

3. Potassium hexafluorotungstate (V), KWF_6 .

a. Synthetic procedures. Some solid KF crystals (7.293 g, 125.5 mmoles) and some W metal powder (4.680 g, 25.46 mmoles) were combined in the reaction cell in order to produce KWF_6 according to the equation



The cell was then sealed, evacuated, and heated. When the cell reached 850°C , the vacuum line was closed off and WF_6 gas allowed to enter the cell. The reaction was very rapid, similar to the formation of K_2WF_8 (Equation 3.1a) described above. The reaction was allowed to continue until the WF_6 pressure no longer dropped when the supply was closed off. This process took approximately 30 minutes for the >7 g of KF reactant. The cell was then allowed to cool to room temperature before being opened in the glove box. A crystalline, clear yellow material was found in the cell which had solidified from a molten state, as seen by the formation of a meniscus with the wall of the glassy carbon crucible. The weight gain of the product (41.21 g total, 42.35 g required for KWF_6 ; yield >97%) and visually estimated consumption of the W metal (which could not be readily separated from the yellow material) agreed with the formation of KWF_6 . Subsequent reactions produced yields >99%.

The major loss of product was due to the formation of K_2WF_8 , identified by Raman spectroscopy, which seemed to have vaporized and condensed on the cell top before the reduction step could take place. The addition of excess W metal powder did not affect the formation of the product, as determined by subsequent reactions. However, the progress of the reaction was dependent on

the WF_6 gas overpressure, since no further reduction product was obtained as long as the WF_6 overpressure was maintained until the material solidified. A displacement of 0.250 ml was obtained upon addition of 1.0190 g of the yellow material to benzene, giving an experimental density of 4.08 g/ml.

The yellow product was observed to decompose slowly with trace moisture in the glove box to a dark blue material indicative of the well-known "tungsten blues", such as W_2O_5 and W_4O_{11} . The decomposition was more rapid when the material was placed in a glass vial for storage. No decomposition could be seen when the material was kept in the capped reaction vessel. Nalgene storage bottles preserved the material for several months without significant discoloring. To seal the compound in glass, some of the product crumbs were packed in the glass vessel and allowed to sit for several hours. The product crystals were removed after they turned dark. Clean crystals were then immediately placed in the glass vessel and sealed under vacuum. These crystals did not show any discoloration even after one year. If crystals were added and sealed without the process of adding the crystal crumbs first, the crystals would turn dark even when sealed under vacuum. It was assumed the darkening was due to adsorbed moisture on the glass walls. Heating the glass for several days in an oven to remove moisture before bringing it into the glove box did not eliminate the darkening of the crystals to any great extent.

KWF_6 was first synthesized by Hargreaves and Peacock (32) according to the reaction



which immediately liberated iodine, even at $-60\text{ }^{\circ}\text{C}$. This was followed by gradual heating to $200\text{ }^{\circ}\text{C}$ while maintaining a vacuum to remove volatile materials. The material was described as tending towards brown crystals, but since an X-ray powder pattern was obtained rather than an X-ray crystal structure, it is assumed the crystals were not very large. Crushing some of the yellow material synthesized by the high-temperature method above also gave it a light brown-to-tan appearance rather than the clear yellow.

Approximately 0.1 g of the suspected KWF_6 was placed in a quartz tube and observed while heating under vacuum. The material appeared to decompose as it began to melt around 450°C . This was not surprising since this material requires the WF_6 gas over-pressure for its formation as described above. The decomposition was very rapid, leaving blue tungsten oxides and white WOF_4 (determined by Raman spectroscopy) on the glass surface.

Hargreaves and Peacock (32) found that their KWF_6 began to decompose above 250°C followed by rapid attack of the glass. This slightly lower decomposition temperature would seem reasonable since their material is assumed to have had a much larger surface area than the large, essentially single crystals of the high-temperature synthesized material.

b. Raman spectrum. The WF_6 species is expected to be octahedral in structure with 6 normal vibrational modes, 3 of which (ν_1 , ν_2 and ν_5) are Raman active. The modes ν_1 and ν_2 are both symmetric stretches while ν_5 is a symmetric bending mode. The Raman spectrum of the KWF_6 material is shown in Figure 3.3. The main band, ν_1 , falls at 702 cm^{-1} and ν_5 at about 225 cm^{-1} . The

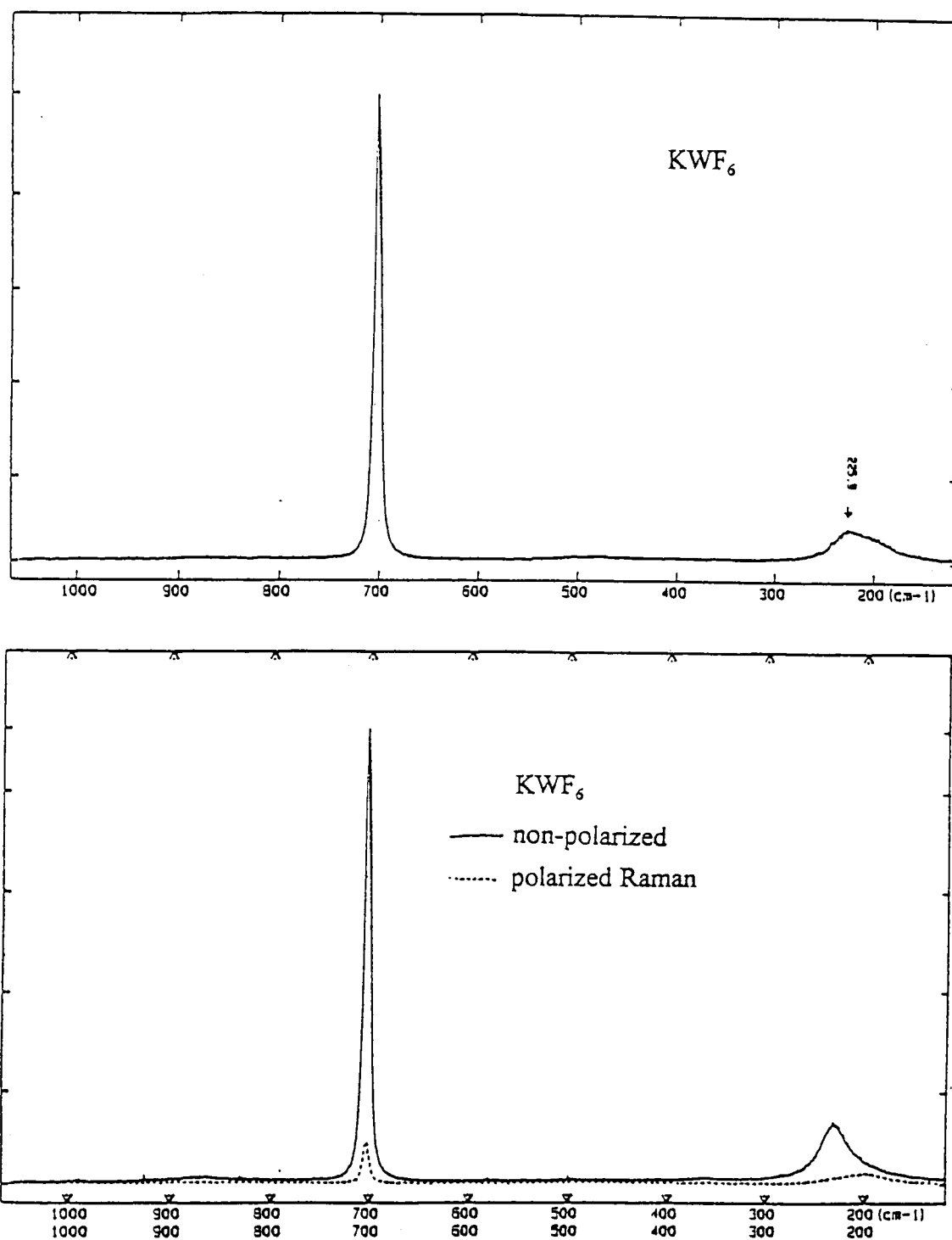


Figure 3.3. Raman spectra of KWF_6 . Lower figure shows polarized and non-polarized Raman spectrum of solid KWF_6 .

ν_1 band for WF_6^- has been reported by Anderson and coworkers as 695 cm^{-1} (33). Although it is not clear what cation was associated with their tungsten anion, it was most likely the tetra-n-butyl ammonium cation since its iodide salt (the other reactants being WF_6 and MeCN) was involved in the reaction. The gas phase Raman spectrum of WF_6^- has been reported by Shamir and Malm (34) as 707 cm^{-1} for ν_1 , $\sim 470\text{ cm}^{-1}$ for ν_2 and 215 cm^{-1} for ν_5 . Since these reported bands generally (except for ν_2 , which is dealt with below) agreed with the bands in Figure 3.3, the yellow material was assigned as KWF_6 .

No ν_2 band for the KWF_6 was seen, which, contrary to the tentative assignment by Shamir and Malm (34), was expected to be in the 600 cm^{-1} region by analogy with similar compounds such as MoF_6^- and TaF_6^- . A ν_5 band did appear consistently at 225 cm^{-1} . However, the 225 cm^{-1} band for the potassium complex was partially resolved into 2 bands in some samples, with a new, smaller band observed at 200 cm^{-1} . One of them was most likely due to a normally inactive vibration that was allowed due to crystal effects. To determine if one of the bands originated from an asymmetric vibration, the sample was subjected to a polarized beam from the Ar^+ laser. To obtain the spectrum the crystalline sample was first irradiated while the Raman spectrum was collected and displayed in 1 second intervals. A polarizing lens was placed in line with the 514 nm beam and rotated until the maximum intensity of the ν_1 Raman band was obtained. A Raman spectrum was then recorded for 100 seconds, after which the polarizing lens was rotated 90° and a second Raman spectrum recorded. Overlaid plots of the two spectra can be seen in Figure 3.3. The intensity of the

band at 225 cm^{-1} can be seen to essentially diminish into the baseline, indicating this band was polarized and nontotally symmetric in origin. The bands at 200 cm^{-1} and 702 cm^{-1} can be seen to have diminished significantly ($<3/4$ the original peak intensity), but not completely, indicating that these two peaks were depolarized, giving rise to symmetric vibrations. This is consistent with the assignment of the band at 200 cm^{-1} to the ν_5 vibration rather than the band at 225 cm^{-1} , which may be a normally Raman inactive band. Since the Na, Rb, and Cs complexes described below probably have some nontotally symmetric vibrations in the same region as well, reliance upon the frequency assignments in the literature for the ν_5 band should be treated with caution. The Raman spectra of all four compounds can be seen in Figure 3.4.

c. X-ray powder pattern. Several attempts to obtain crystal structures of the KWF_6 salt revealed nearly crystalline long range order from the X-ray photographs, though not crystalline enough to obtain a structure. The source of the disorder is not known, but a much slower rate of cooling from the molten state may allow suitable crystals to form. The crystal lattice has been reported (32) from X-ray powder patterns as tetragonal with unit cell parameters $a = 10.21\text{ \AA}$ and $c = 10.09\text{ \AA}$ and with metal ions in the CsCl-type lattice. The symmetry assumed by Burgess and Peacock (35) was an octahedral coordination of tungsten by fluoride with a KSbF_6 structure type.

4. Sodium hexafluorotungstate (V), NaWF_6 .

a. Synthetic procedures. NaF , W metal powder and WF_6 gas were

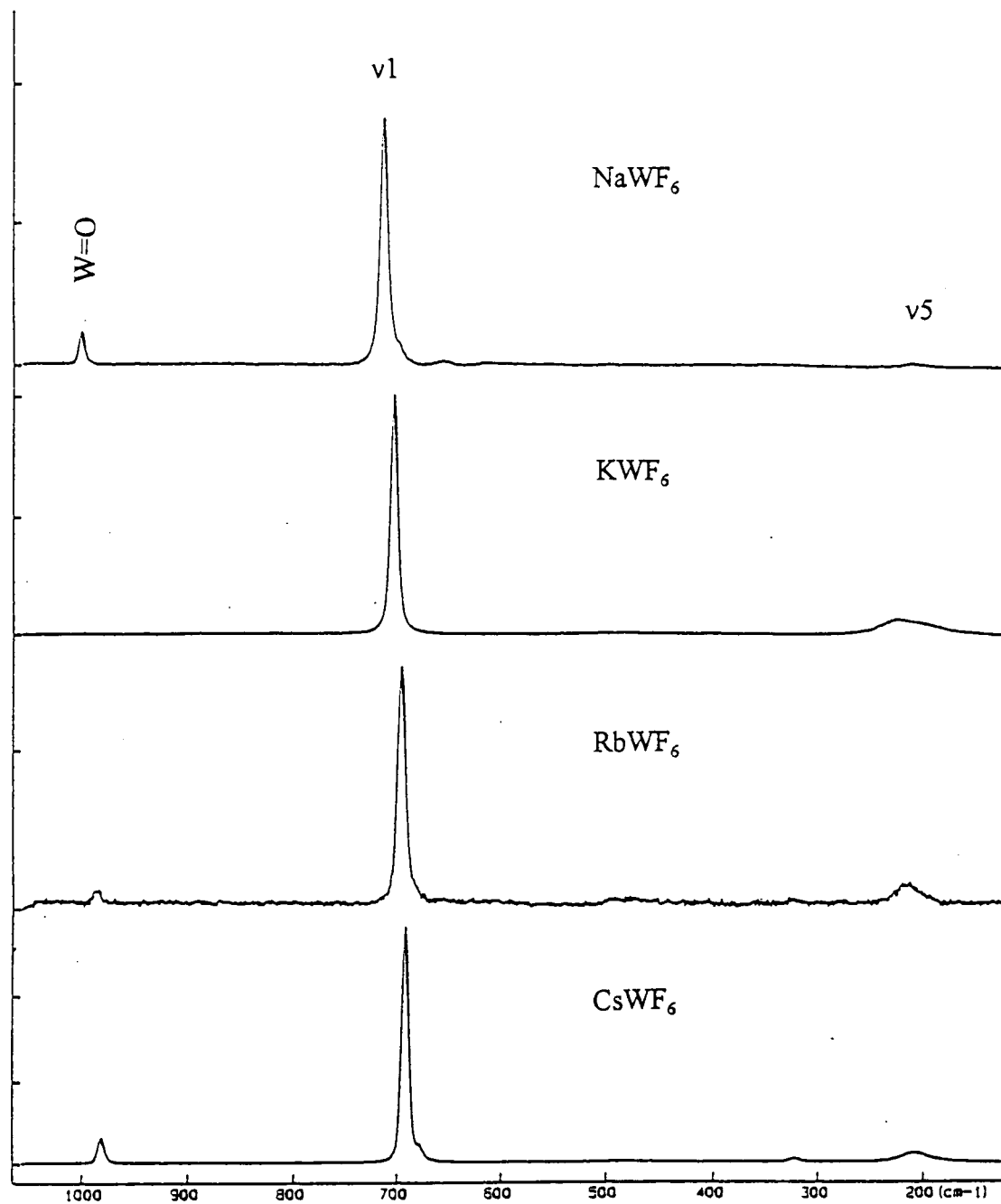
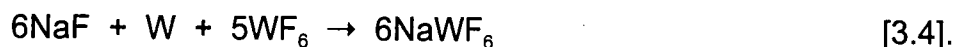


Figure 3.4. Comparison of Raman spectra of MWF_6 compounds (where M = Na, K, Rb and Cs).

combined in the same manner as the KWF_6 according to the following reaction:

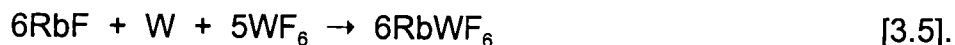


This reaction was performed at 1050°C due to the high melting point of NaF (993°C), although the WF_6 gas was let in at approximately 850°C . After the reaction was allowed to proceed for 1 hour at 1050°C , the cell was cooled down to 850°C for 2 hours while maintaining the WF_6 gas over-pressure. The WF_6 gas pressure could still be seen to decrease at the 850°C temperature when the supply was closed off, though much more slowly than at 1050°C , so it was assumed that the reaction took place at the lower temperature as well. The overall rate of this reaction was much slower than reaction [3] above for the formation of KWF_6 since the rate of decreasing WF_6 pressure went from 30 in. Hg to 15 in. Hg in about 20 minutes, and the reaction continued for several hours instead of 30 minutes. The product was a translucent yellow crystalline material which decomposed in the glove box similar to KWF_6 , though over several days rather than 1 day. A mixture of 4.6 g (110 mmoles) of NaF and 3.752 g (20.41 mmoles) of W gave a product (with some excess W metal) weighing 34.982 g upon addition of WF_6 . The weight gain of the expected product would be 35.542 g, which is within the theoretical range for the formation of NaWF_6 , giving a product yield >98%. Some product may have been lost due to the condensation of a white material on the cell top, which was assumed to be Na_2WF_8 and possibly some WOF_4 . NaWF_6 was previously synthesized by Hargreaves and Peacock (32) in the same manner as reaction [3b] above, except NaI was used in place of the KI.

b. Raman spectrum. The Raman spectrum of the material was similar to that for KWF_6 , as shown in Figure 3.4a. A strong band, ν_1 , which was expected to have a slightly higher frequency than that for KWF_6 (702 cm^{-1}), appeared at 712 cm^{-1} . A ν_2 band for this material was not seen in the predicted 600 cm^{-1} region, similar to the absence of this band in the KWF_6 spectrum. The bands in the 600 to 700 cm^{-1} region in Figure 3.4 were associated with the tungsten oxide band at 1001 cm^{-1} , and was most likely due to an impurity in the material. The weak band at 212 cm^{-1} was assigned to the ν_5 vibration, although some element of this band may be nontotally symmetric.

5. Rubidium hexafluorotungstate (V), RbWF_6 .

a. Synthetic procedures. RbF and W metal powder were combined in the reaction cell according to the following equation:



The cell temperature was maintained at 800°C (instead of 850°C for the formation of KWF_6) until the WF_6 gas pressure no longer decreased; the lower temperature was used since RbF melts at 795°C compared to 858°C for KF . The product formed was a clear yellow crystalline compound, though slightly lighter in color than KWF_6 , and the material decomposed in the inert atmosphere glove box in the same manner as was seen for KWF_6 . A mixture of 5.21 g (49.9 mmol) of RbF and 5.210 g (28.34 mmol) of W produced a product (with some excess W metal) weighing 21.953 g . This agreed well with the theoretical weight of 22.788 g to produce RbWF_6 , giving a product yield $>96\%$ (assuming

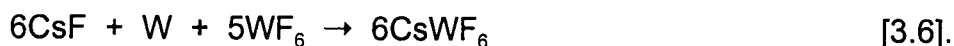
RbF to be the limiting reactant). The melting point of the product was below 800°C, since the product appeared to have frozen from a molten state by the appearance of a meniscus on the surface of the material where it was in contact with the walls of the glassy carbon crucible. The melting point of the RbWF_6 is actually expected to be below that determined for the KWF_6 , which is at 450°C, but no direct evidence was obtained to support this assumption.

The density was obtained by placing 1.0084 g of the crystalline material in a benzene filled pipet. The displaced volume was 0.24 ml, giving a density of 4.2 g/ml. This is slightly larger than the density for KWF_6 (3.9 - 4.0 g/ml). RbWF_6 has been synthesized previously by Hargreaves and Peacock (35) according to reaction [3b] above, except KI was replaced with RbI to obtain the rubidium complex.

b. Raman spectrum. The Raman spectrum of the suspected RbWF_6 is shown in Figure 3.4 where the main band, ν_1 , shows a maximum intensity at 696 cm^{-1} . This is in agreement with the expectation that the ν_1 frequency for the Rb salt would be lower than that for KWF_6 due to the greater mass of Rb than K. As with KWF_6 , the vibration expected for the ν_2 band cannot be seen, but a weak ν_5 band appears at about 212 cm^{-1} . The band at 212 cm^{-1} is slightly broad and indicates that it may consist of more than one vibration. A polarized Raman spectrum was not obtained. The band at 985 cm^{-1} was interpreted as a slight amount of oxide contamination since the W=O stretch occurs in this region. The W=O vibration is usually much more intense than the W-F vibrations, so the contamination was assumed to be only a small portion of the bulk material.

6. Cesium hexafluorotungstate (V), CsWF₆.

a. Synthetic procedures. CsF, W metal powder and WF₆ gas were combined in the reaction vessel according to the following equation:



The product was obtained as a yellow, translucent crystalline boule which appeared to be homogeneous, but was slightly lighter in color than the KWF₆ material. The surface of the boule formed a meniscus with the crucible, indicating cooling from the molten state. The product decomposed in the glove box similar to KWF₆. A mixture of 6.03 g (39.7 mmoles) of CsF and 3.21 g (17.4 mmoles) of W gave a total product weight of 18.00 g (41.8 mmoles for an expected CsWF₆ product) after the addition of WF₆. The weight of the product (with some W metal remaining) agreed fairly well with the theoretical weight expected for CsWF₆ (19.09 g, 44.3 mmoles), giving a >94% yield, assuming CsF to be the limiting reactant. Some loss of product was again due to the condensation of an unidentified white compound on the cell top, thought to be Cs₂WF₈. The melting point for this material appears to be less than 750°C since the material was observed to have frozen from the molten state when heated to that temperature. Also as with the RbWF₆, the suspected CsWF₆ is expected to have a melting point below that for KWF₆, though no direct evidence was obtained to support this assumption. The density, which was obtained with 1.0080 g of crystalline material displacing 0.21 ml of benzene, was 4.8 g/ml. CsWF₆ has been reported by Hargreaves and Peacock (32) who obtained the compound by reaction [3b] above, except the KI was replaced with CsI in order

to obtain the Cs complex.

b. Raman spectrum. The Raman spectrum of the product is shown in Figure 3.4. Vibrations ν_1 and ν_5 can be seen at 692 and 209 cm^{-1} respectively, in agreement with a structure similar to KWF_6 . The band at 981 cm^{-1} , the shoulder at $\sim 680 \text{ cm}^{-1}$, and the weak band at 323 cm^{-1} are attributed to an oxide species. CsWOF_5 has bands at 989, 689, and 331 cm^{-1} (36) where the 989 cm^{-1} band is due to the $\text{W}=\text{O}$ stretch and the 691 and 331 cm^{-1} bands are due to symmetric $\text{W}-\text{F}$ vibrations. Bands at 594 and 287 cm^{-1} are also reported by these authors for the CsWOF_5 species, but are listed as very weak and so would most likely not be seen, since even the main bands which can be seen in the spectrum of CsWF_6 in Figure 3.4 are weak. The weak band at 209 cm^{-1} is attributed to the ν_5 bending mode for the suspected CsWF_6 , but the band may also be resolved into two distinct bands with a polarized Raman spectrum as with the KWF_6 above. CsTaF_6 has a reported ν_1 band (37) at 692 cm^{-1} , and ν_2 and ν_5 are given as 581 and 272 cm^{-1} respectively.

7. Potassium heptafluorotungstate (V), K_2WF_7 .

a. Synthetic procedures. Some of the KWF_6 (12.45 g, 36.95 mmoles) obtained above and KF (2.032 g, 34.97 mmoles) were combined in a 1:1 molar ratio, with a slight KWF_6 excess, according to the following equation:



A vacuum was maintained on the reaction cell while heating to 850°C for one hour. The cell was then cooled to 800°C while still maintaining the vacuum.

These conditions continued overnight while the excess KWF_6 boiled off. This was followed by slow cooling at $25^\circ\text{C}/\text{hour}$ down to 600°C , then cooling quickly to room temperature. Orange, translucent crystals remained in the glassy carbon crucible which were stable in the glove box atmosphere. The orange product crystals were also obtained by combining KF and W metal powder in the cell and introducing WF_6 gas at 850°C . The presumed reaction was as follows:



The WF_6 gas pressure was closed off before the complete reaction could take place, where KWF_6 alone would be formed, so that instead the KWF_6 would only be formed in slight excess. The KWF_6 formed was then allowed to condense on the cooler regions of the cell, leaving the orange material in the glassy carbon crucible. Crystals suitable for the single crystal X-ray diffraction analysis were obtained from this reaction, which showed the product to be K_2WF_7 . This compound was also characterized by Raman spectroscopy and an elemental analysis was obtained for K and W .

The yields for this compound depended on the amount of excess KWF_6 that was formed, but were never greater than an estimated 50%. The melting point was estimated to be around 750 to 780°C from indirect observations. For a density measurement, 1.1027 g of the crystalline material displaced 0.285 ml of benzene giving a density of 3.87 g/ml . The density calculated from the crystal structure was 3.982 g/ml . K_2WF_7 has not been previously synthesized and represents the first MF_7^{2-} complex of the group VI transition metals (where $\text{M} = \text{Cr}, \text{Mo}$ or W).

b. Raman Spectrum. Some of the orange crystalline material was broken into pieces small enough to be loaded into the Raman cell. The Raman spectrum obtained is shown in Figure 3.5 where the main band can be seen at 642 cm^{-1} . The formation of K_2WF_7 has not been reported in the literature, so no Raman spectrum is available for a comparison. The analogous tantalum species, K_2TaF_7 , has bands in the same region and the main K_2TaF_7 band has been reported as 635 (38), 641 (37), and 645 (39) cm^{-1} . Due to the discrepancy in these reported bands, a Raman spectrum of K_2TaF_7 was obtained under the same conditions as the K_2WF_7 . The spectrum of the tantalum species is also shown in Figure 3.5. The main band agrees with that reported by Torardi et al. (39) at 645 cm^{-1} , just above the 642 cm^{-1} for the assumed K_2WF_7 . This agrees with the trend toward higher stretching frequencies as the atomic mass of the central atom decreases, although this trend is a reflection of the stretching force constant since the central atom is not moving. Torardi and coworkers also assigned the two bands at 395 cm^{-1} and 280 cm^{-1} to Ta-F bending modes. The orange material has two bands at 398 cm^{-1} and 250 cm^{-1} , which by analogy to K_2TaF_7 , can be assigned to W-F bending modes.

c. X-ray crystal structure. Suitable crystals for the X-ray crystal structure were first mounted with paratone oil and cooled with a stream of nitrogen. However, the crystals were found to shatter when cooled below 220 K (-53°C), so the crystals were instead mounted at room temperature on a glass fiber after coating them with epoxy glue. Table 3.1 shows the crystal data for this compound. The tungsten atom, as seen in the ORTEP diagram in Figure 3.6, is

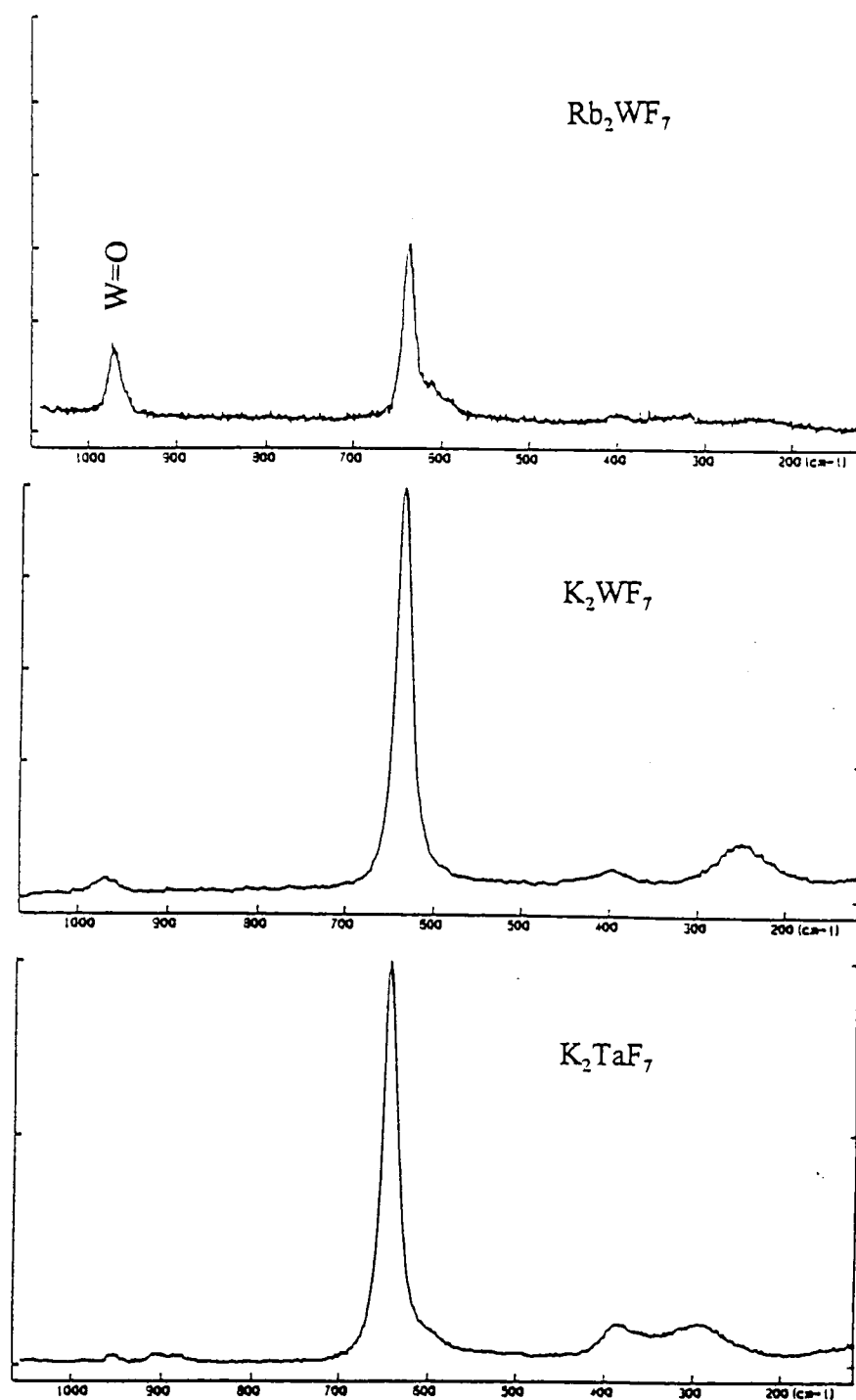


Figure 3.5. Raman spectra of K_2WF_7 and Rb_2WF_7 and comparison with Raman spectrum of K_2TaF_7 .

Table 3.1. Crystal data for K_2WF_7 .

Formula	F_7K_2W	
Formula weight	395.05	
Crystal Size (mm)	0.40 x 0.30 x 0.30	
Temperature (K)	293	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Lattice parameters	$a = 5.736(2) \text{ \AA}$	$\alpha = 90^\circ$
	$b = 11.723(4) \text{ \AA}$	$\beta = 90.00(3)^\circ$
	$c = 9.800(3) \text{ \AA}$	$\gamma = 90^\circ$
Volume, $\text{\AA}^3$	659.0(4)	
Z	4	
Density (calc)(g/cm ³)	3.982	
μ (mm ⁻¹)	18.854	
F(000)	700	
Scan type	ω -2 θ	
θ range (deg)	2.71 to 22.54	
Index ranges	$h, k, \pm l$	
Unique reflections	869 ($R_{\text{int}} = 0.0861$)	
Parameters varied	91	
R indices	0.0443 ($R_w F^2 = 0.0986$)	
Goodness-of-fit on F^2	1.078	
Absorption correction	Semi-empirical from Psi scans	

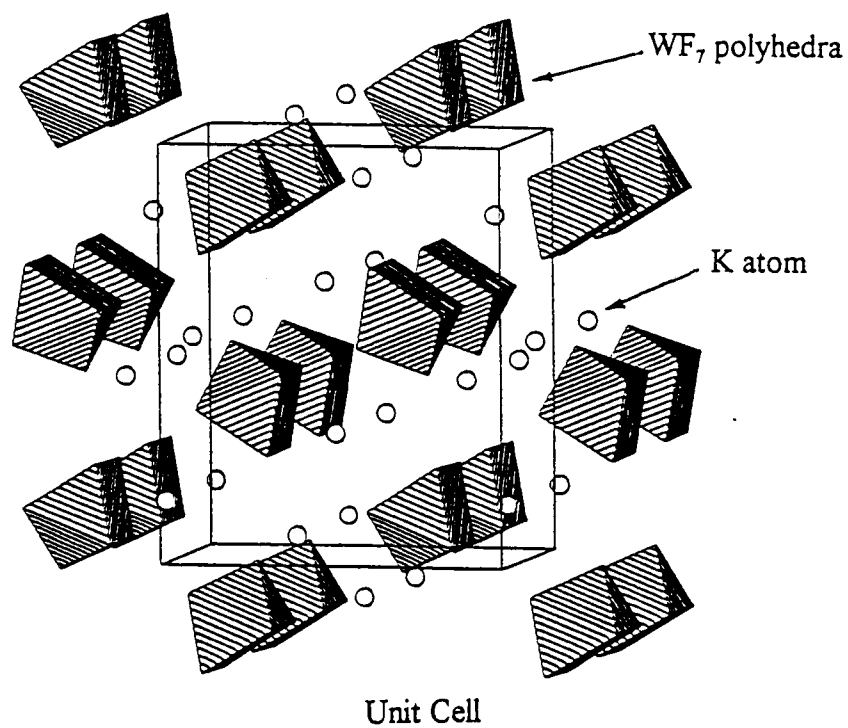
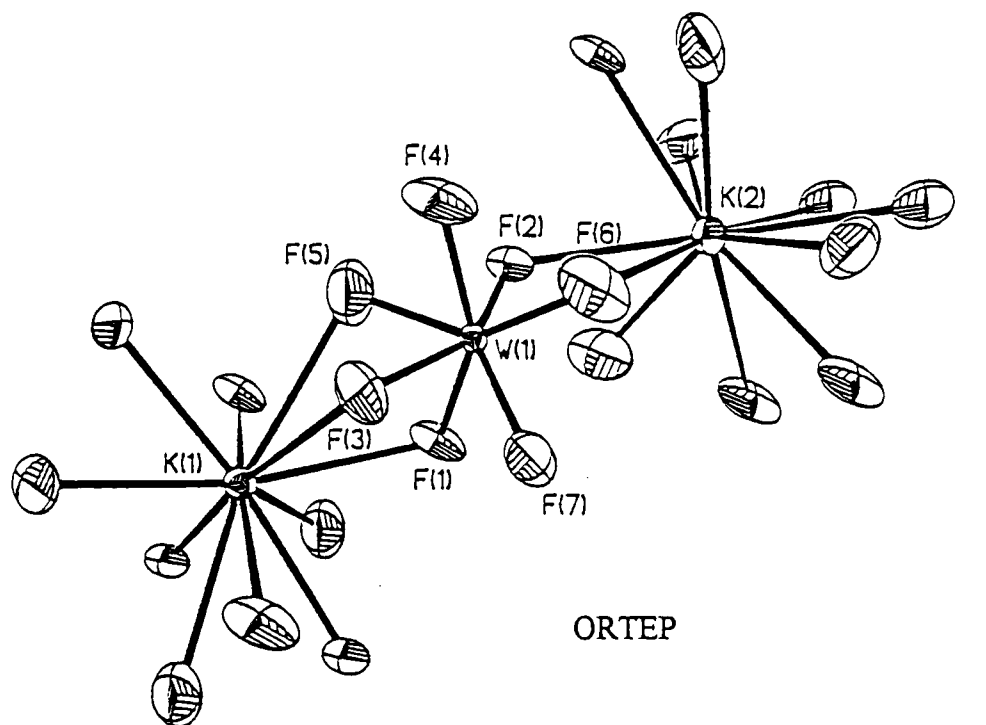


Figure 3.6. X-ray structure diagrams for K_2WF_7 .

surrounded by seven F⁻ ions in a distorted trigonal prism which is capped by the seventh fluoride on one of the rectangular faces. The W-F bond lengths vary from 1.80 to 1.95 Å, but six of the seven bond lengths range from 1.89 to 1.95 Å. Each WF₇ unit is accompanied by two crystallographically non-equivalent 11-coordinate K⁺ ions, as can be seen in Figure 3.6, with K-F bond distances ranging from 2.67 to 3.33 Å. The geometry around the K⁺ ions may be best described as a distorted cuboctahedron with one of the vertices removed. This is in contrast to the K₂TaF₇ (39) and K₂NbF₇ (40) structures, both of which contain 9-coordinate potassium ions. The unit cell can be seen in Figure 3.6, where the wedge shapes are the WF₇ polyhedra and the empty circles are the potassium ions. The full data set is shown in the appendix.

d. Elemental analysis. The potassium (19.79 wt%) was determined by atomic emission by E&R Microanalytical Laboratory, Inc. The tungsten (46.54 wt%) was determined by ICP at ORNL using Na₂WO₄•2H₂O in a NaOH solution as a standard. The tungsten fluoride samples were also treated with a few milliliters of 5% H₂O₂ to oxidize them to more soluble compounds. All solutions were stored in polyethylene bottles. The results were: %K: found 20.05%, expected 19.79%; %W: found 47.55%, expected 46.54%. The %F was determined by difference to be 32.40% (expected, 33.67%).

8. Rubidium heptafluorotungstate (V), Rb₂WF₇.

a. Synthetic Procedures. Rb₂WF₇ was synthesized according to the following reaction at 800 °C:



After allowing the reaction to continue for 1 hour, the reaction cell was cooled to room temperature and opened in the glove box. The product was a light opaque pink that appeared to be crystalline. Under the microscope the crystalline material looked more orange-colored through some faces. However, the X-ray crystal diffraction pattern, which was very weak, indicated that there was a significant amount of polycrystallinity and/or other material mixed in with the expected product. Consequently, a crystal structure could not be obtained. The pink product was estimated to be >90% of the isolated material. Along with the majority pink material, some green material formed in a small pocket, which was thought to be Rb_3WF_8 , along with some orange-brown compound which was unidentified.

The density of the pink material was 4.3 g/ml based on a displacement of 0.24 ml of benzene with 1.0291g of material. The density of Rb_2WF_7 would be expected to be slightly higher than K_2WF_7 (3.9 - 4.0 g/ml), even with an oxygen atom replacing two fluorine atoms, since the formula weight for either Rb compound would be higher than the K coordinated compound.

b. Raman Spectroscopy. The Raman spectrum of the pink material (Rb_2WF_7 in Figure 3.5) exhibits a prominent band at 637 cm^{-1} , which is in the frequency range expected for Rb_2WF_7 , i.e. a band shifted to lower frequency from the band in the corresponding K_2WF_7 spectrum (642 cm^{-1}) due to the coordination with Rb instead of K. A band at 973 cm^{-1} can also be seen which most likely corresponds to a W=O stretch, and the shoulder at 611 cm^{-1} is most

likely a W-F stretching vibration associated with the W=O vibration. Since the W=O vibration is usually much more intense than the W-F vibration, the intensities of the bands at 637 and 611 cm^{-1} assigned to W-F stretching vibrations can be compared to obtain an estimate (~ 20% oxide species) of the relative amounts of the two compounds, which are most likely a tungsten oxyfluoride (such as Rb_2WOF_5) and the assumed Rb_2WF_7 . When some of the bands for the green rubidium material were present, thought to be from Rb_3WF_8 , the small W=O band vibration was in the same region as that for a rubidium oxyfluorotungstate formed by the reaction of the suspected Rb_3WF_8 with oxide (to form Rb_3WOF_6). The mixture of tungsten fluoro- and oxyfluoro- compounds would certainly explain the weak X-ray diffraction pattern obtained as described above.

9. Potassium octafluorotungstate (V), K_3WF_8 .

a. Synthesis procedures. A mixture of 4.258 g (73.29 mmoles) of KF and 12.324 g (36.58 mmoles) of KWF_6 was combined in the reaction vessel to provide a 2:1 molar ratio respectively. The expected addition reaction was:



The cell was heated to 870°C for 15 minutes to melt the KF, then cooled to 800°C for 30 minutes. The product, upon cooling to room temperature, was a green, opaque solid which appeared to have frozen from a molten state, with some green, glassy appearing portions on the surface of the boule. As described below, Raman spectra of the material indicated K_3WF_8 with some

K_2WF_7 mixed in as well, so a calculation of the yield is not possible. The melting point of the green material was determined by direct observation to be around $780^{\circ}C$. The density was determined by placing 0.5240 g of the compound in benzene and measuring the displaced volume, 0.13 ml, which gave a density of 4.0 g/cm^3 . These data have been included since the mixture of the two compounds in the material seems to reach a repeatable equilibrium.

The synthesis of K_3WF_8 has been previously reported by Hargreaves and Peacock (29) who treated a 2:1 mixture of $W(CO)_6$ and KI with iodine pentafluoride. The excess iodine was removed by heating to $150^{\circ}C$ in a vacuum. Debye X-ray photographs revealed a rhombohedral unit cell with $a = 9.75\text{ \AA}$ and $\alpha = 86.4^{\circ}$.

b. Raman Spectrum. The Raman spectrum of the green material is shown in Figure 3.7. The main band at 598 cm^{-1} , the very weak band at 435 cm^{-1} , and the broad band at 362 cm^{-1} are associated with the green material. The band at 642 cm^{-1} in Figure 3.7 falls at the same position as that obtained for the K_2WF_7 species in Figure 3.5. In some cases the band associated with K_2WF_7 at 235 cm^{-1} could be seen as in Figure 3.7 ($K_3WF_8 \times 5$), which indicated that the green material had some K_2WF_7 mixed in with it. The bands always appeared in the same proportion, indicating some equilibrium between the two species. However, spectra obtained for the green compound diluted in FLINAK showed only the three bands associated with the green material, indicating that when cooled with excess KF the higher coordinated K_3WF_8 is preferred over K_2WF_7 .

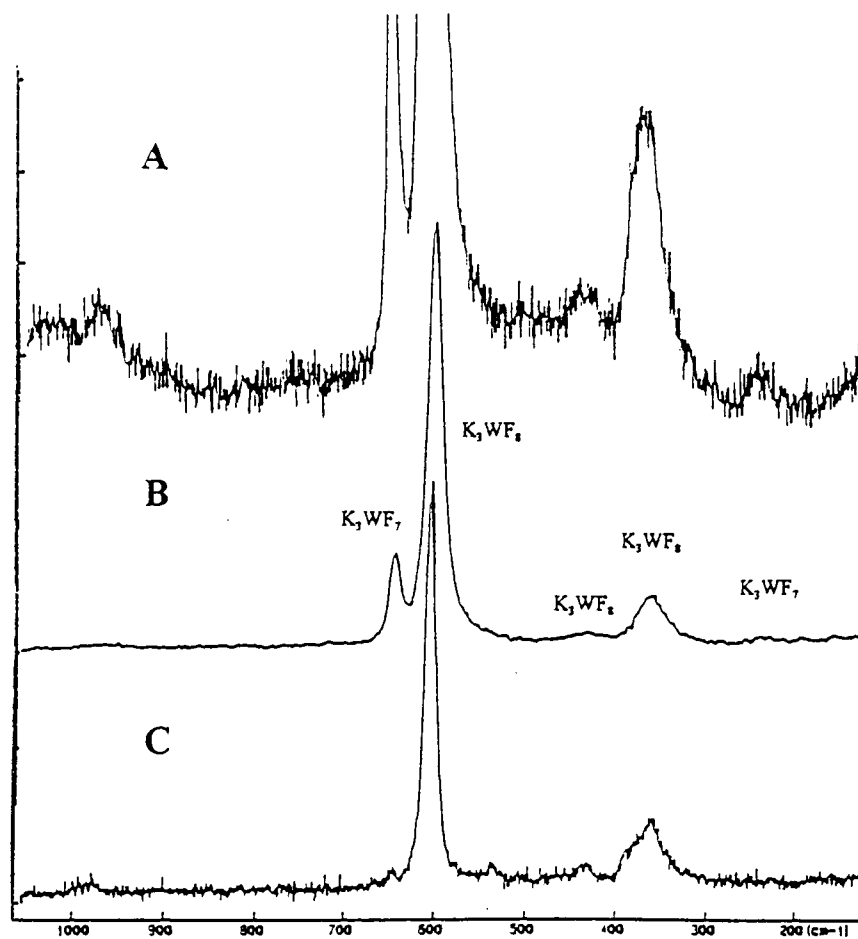


Figure 3.7. Raman spectrum of K_3WF_8 : A) K_3WF_8 (X5) showing weak bands, B) crystalline *appearing* K_3WF_8 , although found to be polycrystalline and C) K_3WF_8 in FLINAK showing a significant decrease in the bands associated with K_2WF_7 at 642, 398 (not seen) and 250 cm^{-1} .

The spectrum of K_3WF_8 in FLINAK is shown in Figure 3.7, although some slight remnant of the 642 cm^{-1} band can still be seen.

c. Discussion and Conclusion.

Some doubt as to the identity of the above green material existed since a crystal structure was first obtained of the green crystals that were found to be K_3WF_6 as described below. The green material obtained from the reaction of KWF_6 with KF was then assumed to be K_3WF_6 due to the similarity in color. However, there was no reductant in the reaction mixture that was thought to be able to cause the reduction of the W(V) to W(III) . Disproportionation of the W(V) species to lower and higher oxidation states was a possibility, but was ruled out since no products associated with a higher oxidation state tungsten species could be detected by Raman spectroscopy, such as K_2WF_8 and KWF_7 from the reaction of WF_6 and KF , and there was no significant weight loss ($<1\%$) of material after the reaction. This led to the conclusion that the green compound was actually K_3WF_8 , which is consistent with a higher coordination of the tungsten compound in the presence of a stoichiometric amount of alkali metal fluoride, and in the absence of a reducing agent.

An experiment was performed to confirm the above hypothesis in which 2.503 g of KWF_6 (7.428 mmoles), 0.889 g of KF (15.3 mmoles), and 0.919 g of W (5.00 mmoles) were combined in a glassy carbon crucible. The mixture was then heated to 850°C for 10 minutes, cooled, then opened in the glove box. The total weight before the reaction was 4.311 g of material. The total weight after the reaction was 4.319 g. The product appeared to be a homogeneous green

material with no apparent KF remaining. This suggested ~100% formation of the product. A Raman spectrum revealed only the peaks associated with the green material described above. To determine the remaining quantity of tungsten, the boule of material was then dissolved in water with the addition of some 30 wt% H_2O_2 to oxidize the tungsten species. This left a clear solution with insoluble W metal at the bottom. The W metal suspended in solution was allowed to settle before decanting the supernatant. The W was then washed with de-ionized water before drying at 125°C and weighing. The final tungsten weight was 0.852 g (4.63 mmoles).

Some conclusions can be drawn from this reaction as follows. Assuming 100% of the available KF was used to produce K_3WF_6 , then 50% of the available W should be used leaving 0.460 g (2.50 mmoles). The product would not be expected to be homogeneous since 12 moles of KF are needed for every 3 moles of KWF_6 to convert all of the KWF_6 to K_3WF_6 . Some KWF_6 would then be expected to remain in the crucible and be seen by Raman spectroscopy, or evaporate and condense on the cell top, which would be seen as a weight change in the product or by Raman spectroscopy. However, if 100% of the available KF is used to produce K_3WF_8 , then 100% recovery of the W metal would be expected and the product material should appear homogeneous.

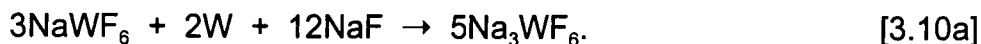
Since none of the criteria for the formation of K_3WF_6 , but all of the criteria for formation of K_3WF_8 , were found (~93% of the W metal was recovered, the product material appeared homogeneous, including the Raman spectrum, and

there was no loss of material from disproportionation), the green product material was assigned as K_3WF_8 .

To show how K_3WF_8 compares with the other potassium fluorotungstates, the main band frequencies were plotted vs. the tungsten fluoride coordination number. This is shown in Figure 3.8 where the relationship between oxidation state, coordination number and band frequency can readily be distinguished.

10. Sodium octafluorotungstate (V), Na_3WF_8 .

a. Synthetic procedures. A mixture of 23.63 g (73.65 mmoles) of $NaWF_6$, 9.445 g (51.37 mmoles, a slight excess for reaction [12] below) of W powder, and 12.43 g (296.0 mmoles) of NaF was placed in the reaction vessel according to the following reaction:



The reaction was performed at 1000 °C to melt the NaF and was allowed to continue for 30 minutes. The product material was an opaque green solid which was stable in the glove box atmosphere. However, a significant portion of the NaF remained as large chunks which could be separated from the green material. Also, the W metal was not consumed in the reaction, but remained at the bottom of the boule of material. The weight of the boule was 45.49 g, which was > 99% of the weight of the reactants, so the reaction incurred minimal loss of the reactants. The melting point seemed to be below at least an estimated 850°C since the material had melted when heated to this temperature. By analogy with the green material shown to be K_3WF_8 , the green material from this

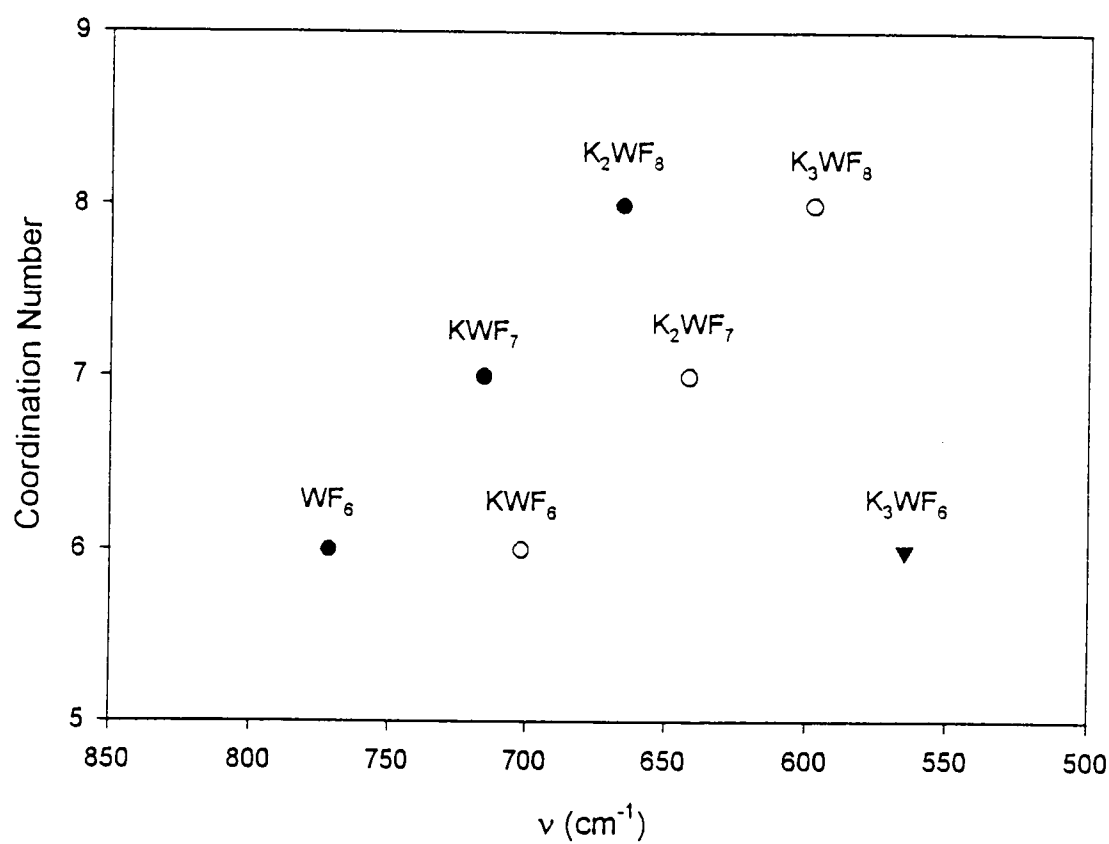


Figure 3.8. Main band frequency shift with change in oxidation state and fluoride coordination number.

reaction was assumed to be Na_3WF_8 . The reaction which occurred would then be:



This would explain the remaining NaF and W from the mole ratios of reactants used in equation [12]. No condensation of the material on the walls of the cell could be seen. A slight condensation of a white powder was observed on the top of the reaction cell which was thought to be Na_2WF_8 , but was not characterized.

b. Raman spectrum. The Raman spectrum of the material can be seen in Figure 3.9. The overall spectrum is very similar to that for the K_3WF_8 , as can also be seen in the figure, therefore the product was assumed to be Na_3WF_8 . The main band at 614 cm^{-1} , which was analogous to the ν_1 band for K_3WF_8 , was shifted toward a higher frequency than the ν_1 band for the potassium salt analog, as expected for a lighter cation. The band at 614 cm^{-1} exhibited an odd peak shape, being very sharp at the top, but broadening more normally near the base. It is not known why this band was shaped in such an odd fashion. No band at the expected frequency for Na_2WF_7 could be seen, as was observed in the case of the potassium analog in Figure 3.7. The bands at 372 and 411 cm^{-1} were also similar to the bands at 362 and 435 cm^{-1} for K_3WF_8 . A striking similarity can be seen when the bands for Na_3WF_8 are compared to those for Na_3TaF_8 , which are reported as 614 , 411 , and 371 cm^{-1} (41).

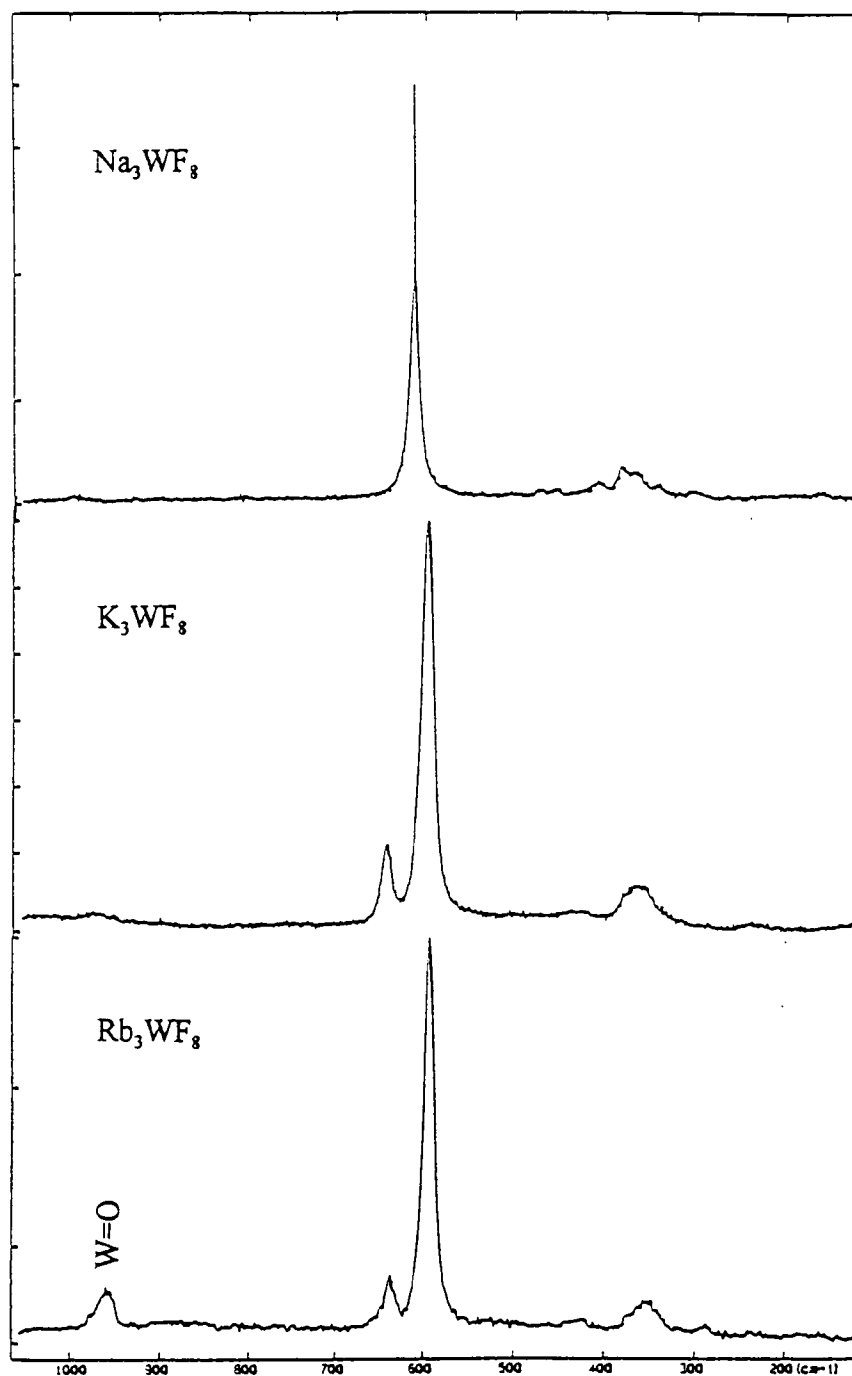


Figure 3.9. Similarity of M_3WF_8 Raman spectra (where $M = Na, K$ and Rb).

11. Rubidium octafluorotungstate (V), Rb_3WF_8 .

a. Synthetic procedures. A small portion of the product obtained from the synthesis of Rb_2WF_7 [reaction 3.10] had a bright green appearance and was thought to be Rb_3WF_8 . This would seem reasonable since the Na and K analogs of the WF_8^{3-} compounds are both green. The yield for this product was less than 5%, but much higher yields would be expected from the following reaction at high temperature:



The green material appeared as an opaque, bright green powdery substance which was removed by scraping with a spatula. No other characterization was performed other than the Raman spectrum as described below.

b. Raman spectrum. The Raman spectrum of the green material is shown in Figure 3.9 (Rb_3WF_8) along with the spectra for Na_3WF_8 and K_3WF_8 . The spectrum of the green material is strikingly similar to that for the green K_3WF_8 , as seen in Figure 3.9, including the relative intensities of the bands at 642, 598, 428 and 362 cm^{-1} in the K_3WF_8 spectrum compared to the bands at 638, 595, 428 and 353 cm^{-1} in the Rb_3WF_8 spectrum. The bands for the rubidium coordinated compound were shifted toward a slightly lower frequency than those for the potassium coordinated compound, as would be expected for the salt containing a heavier cation. The band at 638 cm^{-1} can be attributed to the presence of Rb_2WF_7 , similar to the presence of K_2WF_7 in K_3WF_8 . The bands at 956 and 288 cm^{-1} can be attributed to an oxide species such as Rb_3WOF_6 from

slight oxide contamination of the RbF starting material, since the RbF was only dried at high temperature and not purified further.

12. Potassium hexafluorotungstate (III), K_3WF_6 .

a. Synthetic procedures. The green K_3WF_8 material (5.03 g, 11.1 mmoles) was heated with KF (1.32 g, 22.7 mmoles) and excess W metal powder (4.57 g, 24.9 mmoles) to 810°C while maintaining a vacuum. After allowing the reaction to continue overnight, the cell was cooled and the contents examined in the glove box. The bulk of the material had turned a dark brown, indicating formation of a new mixture of species. This brown material was shown by a Raman spectrum to consist of a mixture of K_3WF_8 and a new, unidentified compound in approximately equal proportions. The spectrum is described below.

Some green, crystalline appearing material, which had grown at the surface of the dark brown boule, was found to be amorphous or polycrystalline when X-ray photographs were obtained. A Raman spectrum was the same as the spectrum seen in Figure 3.7, indicating the material was K_3WF_8 .

Above the main boule of brown material, at the ends of KF dendrites that had condensed from the vapor state, translucent green crystals could be seen that had also condensed from the vapor state. An X-ray crystal structure obtained from these green crystals revealed the compound K_3WF_6 with a calculated density of 3.890 g/cm³. The yield of the K_3WF_6 material was estimated at < 1%. This led to the conclusion that the unknown portion of the

brown mixture was K_3WF_6 , making the brown material a mixture of K_3WF_8 and K_3WF_6 .

In a subsequent reaction, a mixture of 14.80 g (32.7 mmoles) of the K_3WF_8 material, 5.268 g (90.67 mmoles) of KF, and 5.20 g (28.3 mmoles) of W metal powder was heated to 800°C in the reaction cell, except this time without relieving the pressure buildup. The reaction cell was left for 3 days before it was slowly cooled to room temperature and opened in the glove box. A dark brown material could be seen which had 3 separate layers. The bottom (third) layer was medium brown and appeared to have rapidly condensed from the vapor state, as seen by the dendritic form of the crystals and the gas pockets between the material and the bottom of the glassy carbon crucible. Some portions of this layer had small tungsten metal clusters as well as shiny, flat, tungsten metal layers (as identified by X-ray photoelectron spectroscopy, XPS), approximately 0.5 cm² on the surface and less than 0.1 mm thick, embedded throughout the material. The brown material easily broke away from these tungsten metal layers. These tungsten layers were not present before the reaction occurred, indicating some decomposition of the product.

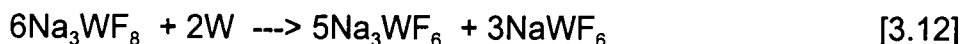
The *second* layer from the top was a thin, crystalline, translucent dark brown material. An apparent X-ray crystal structure was obtained from this portion and is described further below.

The *top* layer appeared to be a phase separation from the second layer since the second layer began to appear cloudy white with a slight green hue until the compound was completely opaque. This was interpreted as an increasing

amount of white KF(which was added in excess for formation of K_3WF_6) and green K_3WF_8 which were excluded from the second layer by density separation. At the surface of the boule, what appeared to be green crystals of K_3WF_8 (identified by Raman spectroscopy, which also revealed bands associated with K_2WF_7) had formed at the surface, although X-ray photographs showed them to be polycrystalline. All three layers gave similar Raman spectra containing the fingerprint bands for K_3WF_8 and a separate set of bands at lower frequency.

The mixed brown material containing potassium was seen to condense in the same region on the cell walls as the green K_3WF_8 material, and indirect observation of the melting point indicated a similar melting point to K_3WF_8 alone, although the melting point of the individual unknown component of the brown mixture could not be determined since it was not isolated in pure form.

Substitution of K^+ with Na^+ gave essentially identical reaction results. When 5.30 g (13.1 mmoles) of Na_3WF_8 and 3.10 g (16.9 mmoles) of W metal were combined in the reaction cell and heated to 850°C for 5 hours, a dark brown product was obtained. The total weight after reaction was 7.17 g (14.6% loss of material). The major loss of product was seen as a condensate on the cell top, which from a Raman spectrum proved to be $NaWF_6$. Since no NaF was added as a reactant, the following reaction was thought to occur in this case:



where the NaF required for the Na_3WF_6 product is obtained from the decomposition of Na_3WF_8 to $NaWF_6$ and NaF. A Raman spectrum described below revealed an approximately 2:1 ratio of Na_3WF_8 to Na_3WF_6 in the product

boule, indicating incomplete formation of Na_3WF_6 . This explains why there was only a 14.6% loss of material in the form of NaWF_6 as opposed to a theoretical 52% expected from complete formation of the products.

b. Raman spectrum. The Raman spectra of the potassium and sodium salts of the brown material are shown in Figure 3.10. The fingerprint bands for K_3WF_8 and Na_3WF_8 as described above can be seen at 599 and 361 cm^{-1} and 615 and 375 cm^{-1} respectively. A second set of bands associated with the unknown portion of the brown material can be seen at 565 cm^{-1} and 198 cm^{-1} for the potassium salt and one band at 585 cm^{-1} associated with the sodium salt. A very weak band at $\sim 480 \text{ cm}^{-1}$ could often be seen which was associated with the these bands for the unknown potassium analog as well. A small band at 964 cm^{-1} (980 cm^{-1} for the sodium salt) was interpreted as a small amount of oxide contamination. No spectrum of the brown material was obtained without some amount of the oxide bands and often the oxide bands were of equal or slightly greater intensity than the bands at 565 and 585 cm^{-1} . Since the W=O vibration was generally much more intense than the W-F vibration, the tungsten oxide was assumed to be a minor constituent in the sample. The band usually seen at 642 cm^{-1} , due to K_2WF_7 in the K_3WF_8 spectrum (Figure 3.9), was no longer visible. This reinforces the conclusion that some K_2WF_7 was present in the green K_3WF_8 sample, rather than decomposition of K_3WF_8 to K_2WF_7 from the heat generated by the Raman laser during data accumulation.

The Raman bands of the unknown component were believed to be associated with K_3WF_6 . The relationship between the ν_1 , ν_2 and ν_5 Raman

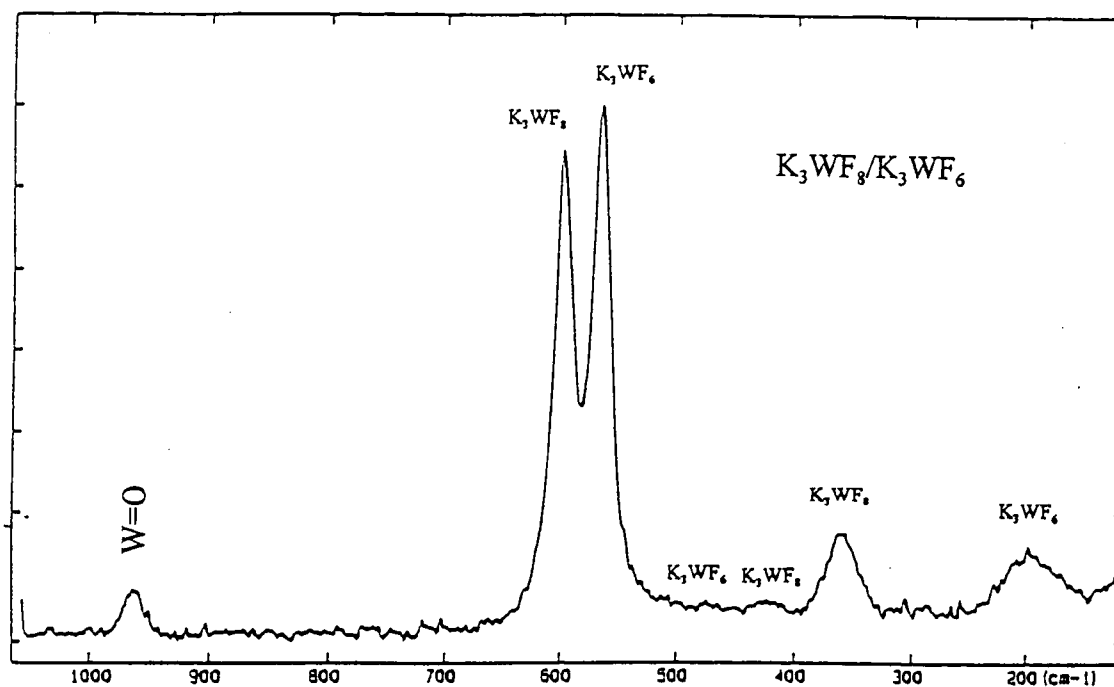
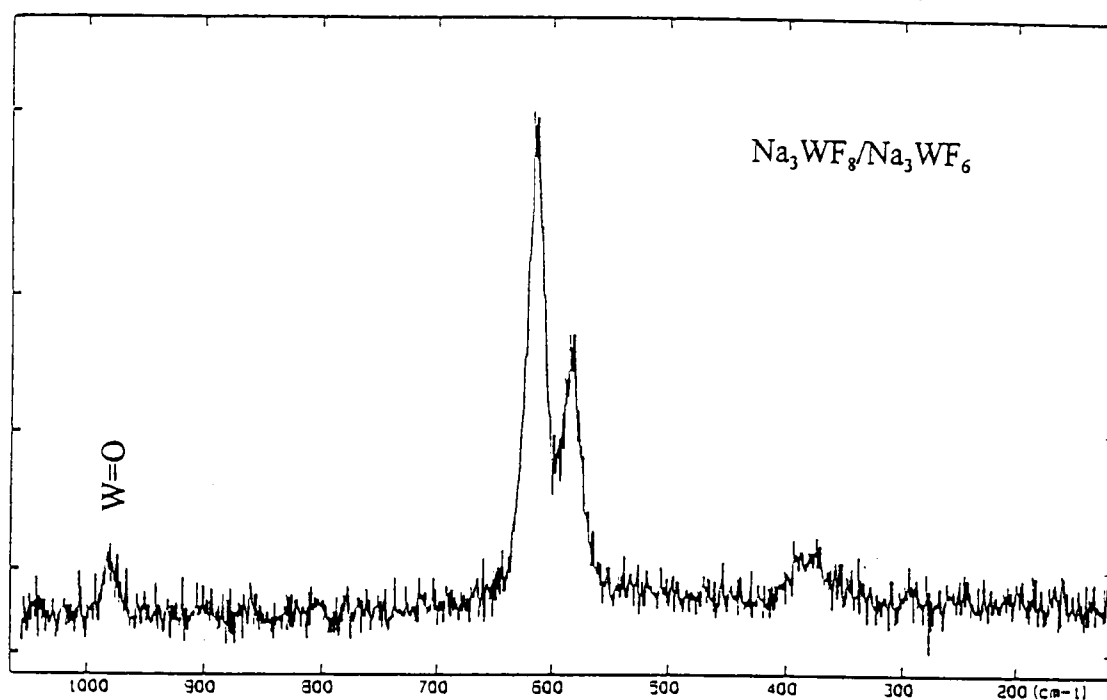


Figure 3.10. Raman spectra of $\text{Na}_3\text{WF}_8/\text{Na}_3\text{WF}_6$ and $\text{K}_3\text{WF}_8/\text{K}_3\text{WF}_6$ mixtures.

frequencies of the WF_6 , KWF_6 and suspected K_3WF_6 can be seen in Figure 3.11. The compounds were normalized as 1, 2 and 4 respectively, with K_2WF_6 (no Raman bands) assigned as 3. [The WF_6 bands at 770, 676 and 321 cm^{-1} were obtained from those reported by Bosworth, Clark and Rippon (42). The band from the spectrum of the $[\text{Cu}(\text{WF}_6)(\text{CH}_3\text{CN})_3]_2$ dimer described below at 610 cm^{-1} was used as the ν_2 band for KWF_6 , along with the bands at 702 and $\sim 225\text{ cm}^{-1}$ for ν_1 and ν_5 described above. The bands at 565, 480 and 198 cm^{-1} associated with the unknown component above were assigned to the ν_1 , ν_2 , and ν_5 Raman bands of the assumed K_3WF_6]. The trend in the frequencies of the ν_1 bands is surprisingly linear with an r^2 value of 0.999996, although no linear relationship could be predicted. All three bands reveal a good correlation between the known molecules with octahedral fluoride coordination and the identity of the unknown as K_3WF_6 with octahedral fluoride coordination. This supports the conclusion that the brown material was composed of a mixture of K_3WF_6 and K_3WF_8 .

c. X-ray crystal structure.

K_3WF_6 . Suitable crystals of the green material formed in low yield at the ends of the KF dendrites as described above were mounted and cooled under a stream of nitrogen to -100°C . No decomposition of the crystals could be seen over several days during data collection. Refinement of the data revealed a cubic unit cell containing alternating WF_6 and KF_6 octahedra in a NaCl-like arrangement, with an empirical formula K_3WF_6 . The unit cell for the compound is shown in Figure 3.12 (ORTEP diagram) where two different potassium

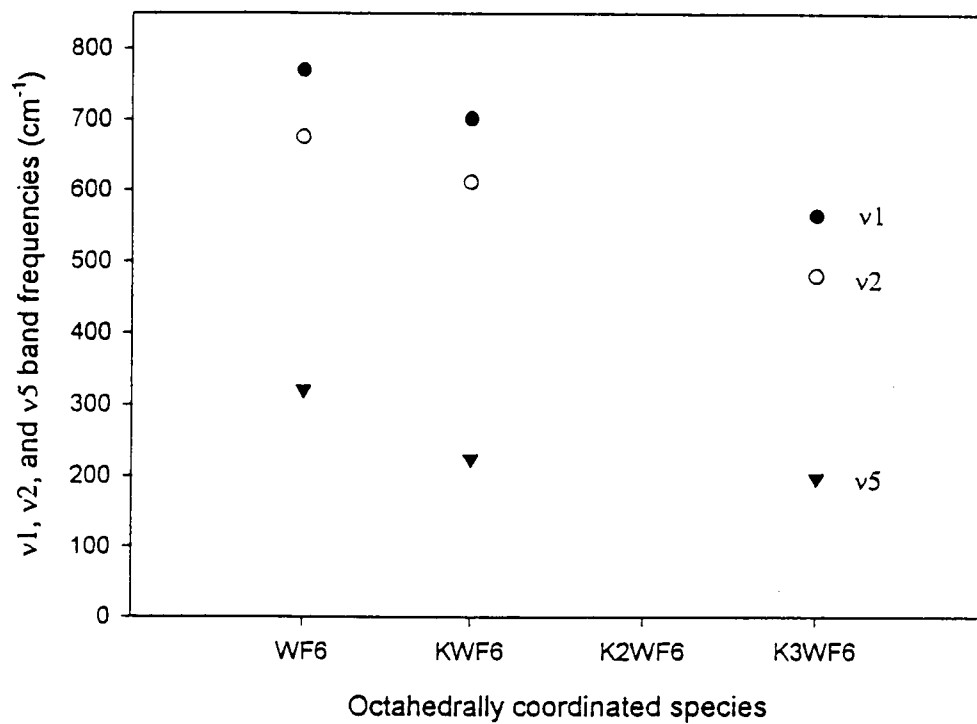
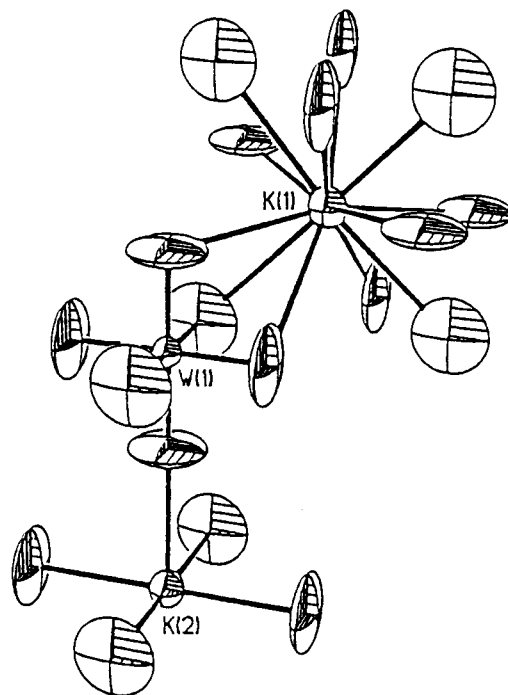
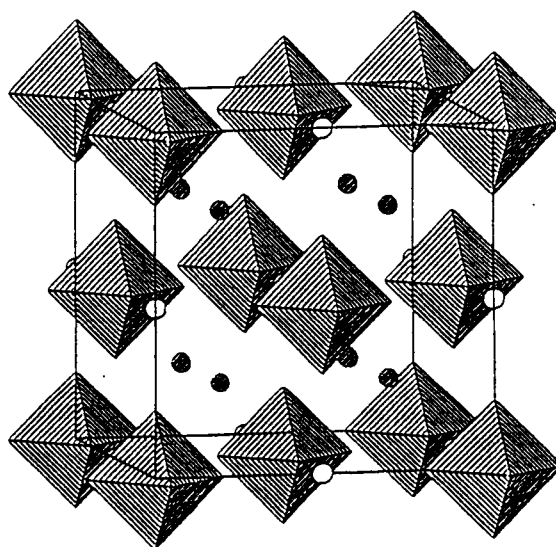


Figure 3.11. Relationships of main Raman frequencies for octahedrally coordinated tungsten fluorides.



ORTEP



Unit Cell

Figure 3.12. X-ray structures for K_3WF_6 .

coordination sites can be seen. A view of the entire cubic unit cell is also shown in the Figure. The W-F bond distances were 1.81 Å and the K-F bond distances for the KF_6 octahedra were 2.65 Å. There were an additional eight K^+ ions per unit cell, which were coordinated to 12 F^- ions in a distorted cuboctahedral array with K-F distances of 3.8607 Å. A peak of $1.13 \text{ e}^{-3} \text{ Å}$ remained in the final difference Fourier map. It was located 2.17 Å from the tungsten atom at (0.1719, 0.1719, 0). This peak was chemically unreasonable for a W-F bond, and was considered to be noise.

The structure of K_3WF_6 is isomorphous with that of the molybdenum analog K_3MoF_6 reported previously by Toth and coworkers (43). The initial model for refinement of the K_3WF_6 was based on the coordinates for the K_3MoF_6 species as reported by these authors. The crystal data for K_3WF_6 are tabulated in Table 3.2. The full data set including bond lengths and bonds angles can be seen in the appendix.

Brown mixture. The apparent crystal structure of the brown mixture was not distinguishable from that for K_3WF_6 , except for a slightly smaller unit cell, 8.879 Å as opposed to 8.916 Å for K_3WF_6 . However, since the Raman spectrum showed two distinct species in approximately equal amounts, the X-ray structure was not considered as completely accurate. An X-ray powder diffraction showed a slight splitting of the peaks, revealing two distinct unit cells with slightly different sizes, the larger agreeing with the unit cell size of K_3WF_6 .

d. Discussion and conclusion.

Since the brown material 1) X-ray diffraction data were consistent with the

Table 3.2. Crystal data for K_3WF_6 .

Formula	F_6K_3W
Formula weight	415.15
Crystal Size (mm)	0.32 x 0.24 x 0.22
Temperature (K)	173
Crystal system	cubic
Space group	Fm3m
Lattice parameters	$a = 8.916(2) \text{ \AA}$ $\alpha = 90^\circ$ $b = 8.916(2) \text{ \AA}$ $\beta = 90^\circ$ $c = 8.916(2) \text{ \AA}$ $\gamma = 90^\circ$
Volume, $\text{\AA}^3$	708.78(14)
Z	4
Density (calc)(g/cm ³)	3.890
μ (mm ⁻¹)	18.093
F(000)	740
Scan type	ω -2 θ
θ range (deg)	3.96 to 22.35
Index ranges	$h, k, \pm l$
Unique reflections	40 ($R_{\text{int}} = 0.0856$)
Parameters varied	7
R indices	0.0465 ($R_w F^2 = 0.1381$)
Goodness-of-fit on F^2	1.275
Absorption correction	Semi-empirical from Psi scans

presence of K_3WF_6 , 2) the vibrations of the unknown component were located in the frequency region consistent with K_3WF_6 and 3) the K_3WF_6 crystals were obtained from condensation above the brown mixture, the unknown component of the brown mixture was assigned to be K_3WF_6 (and Na_3WF_6 for the sodium salt), making the brown crystalline material an approximately 50/50 mixture of K_3WF_8/K_3WF_6 .

13. $[Cu(WF_6)_2(CH_3CN)_3]_2$ dimer.

a. Synthetic procedures. Approximately 50 ml of acetonitrile and 30 ml of WF_6 (added by condensation) were combined in the nickel/SS reaction cell along with 8.0 g of KF in an effort to produce reduced tungsten compounds at a lower temperature. The cell was then sealed with a copper gasket and heated to $120^\circ C$ for 3 days without releasing the pressure buildup. When the cell was cooled and opened in the glove box, a green-white flaky powder had formed and filled the majority of the cell space. No liquid was left in the reaction cell and green translucent crystals had formed at the interior bottom. These were removed by chipping with a sharp metal tool and were used to obtain a crystal structure for this compound.

The crystal structure revealed copper as a major component in the compound, indicating that the copper gasket (which showed extensive corrosion where it was in contact with the cell interior) contaminated the reaction mixture, producing a copper/tungsten compound with +2 and +5 oxidation states respectively, and with empirical formula $C_6H_9CuF_{12}N_3W_2$. When heated very

slowly up to 170°C under a vacuum, the green material lost what was interpreted as WF_6 and CH_3CN and left a red-brown residue. Since the boiling point of these two compounds is much lower than 150°C, especially under vacuum, they would be expected to evaporate as soon as the material decomposed. When heated too fast, the material boiled before 170°C was reached and left a copper colored residue along with some blue tungsten oxides from reaction with the glass. Under a microscope this red-brown residue was seen to consist of some brown material mixed with what appeared to be an equal amount of copper colored material in the form of small, powdery clusters.

Both the green and red-brown material were soluble in acetonitrile, which when decanted, left a copper colored residue thought to be elemental copper. The decanted portion reacted with the glass vial producing a dark blue color, the blue being indicative of tungsten oxides. The brown residue began to decompose around 200 - 300°C. This may be from the decomposition of WF_4 , which is reddish-brown in color (8).

The density was measured by placing 1.222 g of the green crystals in a benzene-filled pipet. The displaced volume of 0.410 ml gave a density of 2.98 g/cm³. This agreed well with the calculated density obtained from the X-ray crystal structure of 3.015 g/cm³.

b. Raman spectrum. The Raman spectrum of the green material is shown in Figure 3.13. The bands at 949/956 and 409 cm⁻¹ match those for CH_3CN (acetonitrile). A spectrum of neat CH_3CN in the region of interest for the W-F vibrations can also be seen in the Figure, where the band at 918 cm⁻¹ is

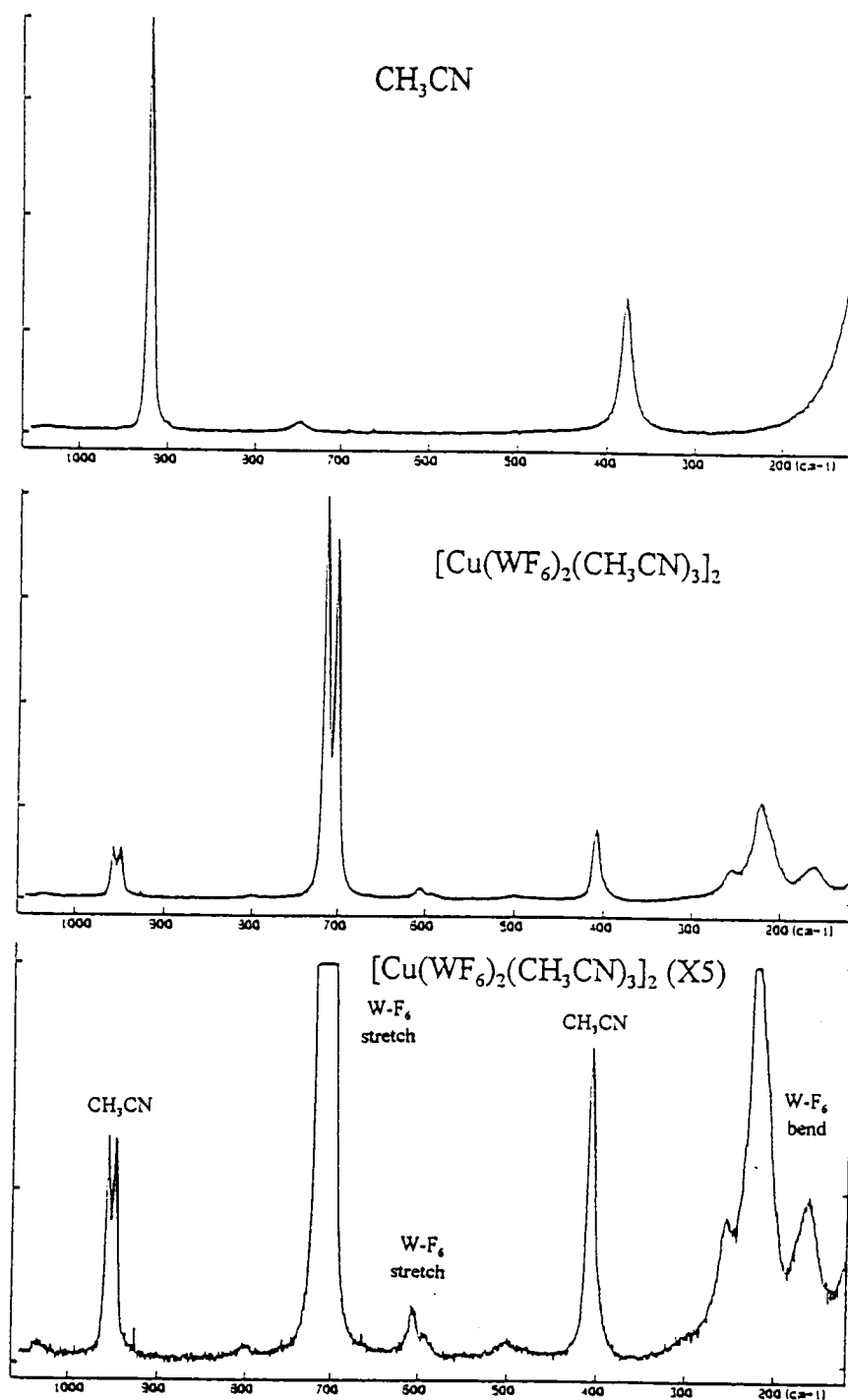


Figure 3.13. Raman spectra of CH₃CN and the [Cu(WF₆)(CH₃CN)₃]₂ dimer.

assigned to a symmetric C-C vibration and the peak at 380 is assigned to a symmetric C-C=N bending vibration (44). (Eight vibrations are expected for a compound with a three-fold axis of symmetry, all of which are expected to be Raman active, but only the two fall in the W-F vibration region of interest and so are the only ones considered here). The CH₃CN bands in the spectrum of the green compound are shifted toward higher frequency than the bands in the neat CH₃CN, reflecting the coordination of the nitrile group to the copper atom. Although not listed by Herzberg (44) as a band in the Raman spectrum of CH₃CN, the very weak band at 750 cm⁻¹ in the spectrum of neat acetonitrile can also be seen shifted toward higher frequency (800 cm⁻¹) in the spectrum of the green compound.

The splitting of the bands at 949/956 cm⁻¹ can be attributed to the two different coordination sites of the CH₃CN to the copper atom (see the crystal structure below). The crystal structure also reveals WF₆⁻ octahedra at two different coordination sites. The first has two W-F-Cu bonds while the second has only one W-F-Cu bond. These different coordination environments are proposed to account for the splitting of the ν_1 bands into two peaks observed at 702 and 715 cm⁻¹. The band at 702 cm⁻¹ matches well with that for WF₆⁻ coordinated with K⁺ (Figure 3.3), along with the band at 222 cm⁻¹. WF₆⁻ coordinated with Na⁺ (Figure 3.4) has a band at 714 cm⁻¹, so the assignment of these two bands to the ν_1 frequency of the WF₆⁻ species is reasonable.

Since the ν_1 band is split, it can be assumed that the ν_2 symmetric stretch and the ν_5 symmetric bending mode of the octahedral WF₆⁻ species are split as

well. The band at 222 cm^{-1} is interpreted as splitting into the 256 and 161 cm^{-1} vibrations, although the 256 cm^{-1} vibration may be related to the nontotally symmetric portion of the ν_5 vibration as described in the Raman of KWF_6 above. The ν_2 band has been reported by Shamir and Malm (34) as 470 cm^{-1} , but these authors listed this as a questionable band assignment. In contrast to these authors, the band at 607 cm^{-1} in Figure 3.13 (dimer X5) is interpreted as the ν_2 vibration for the WF_6^- species for the reasons described below. Although this band was not seen in any of the spectra of the Na, K, Rb or Cs coordinated complexes as shown above, the band is predicted to fall in this region since, by comparison, the CsTaF_6 species ν_2 band falls at 581 cm^{-1} , and CsTaF_6 and CsWF_6 (see above) both have ν_1 peaks at 692 cm^{-1} . This indicates that the TaF_6^- and WF_6^- species likely have similar ν_1 assignments and so would be expected to have similar ν_2 assignments. Also, ν_2 for WF_6 falls at 676 cm^{-1} and would be expected to shift approximately 70 cm^{-1} toward a lower frequency when the tungsten oxidation state is reduced from +6 to +5, similar to the shift for ν_1 , which decreases from 772 cm^{-1} to 702 cm^{-1} . The band at 607 cm^{-1} also appears to be split with one band at 607 and another at 595 cm^{-1} . A shoulder on the 607 cm^{-1} band at about 610 cm^{-1} may also be present. The suggested splitting of the bands in this region looks very similar to the splitting of the bands in the 222 cm^{-1} region and is attributed to different coordination environments as well.

c. X-ray crystal structure. The structure of the dimer is shown in Figure 3.14 where an 8-membered ring can be seen with alternating W-F-Cu-F bonds.

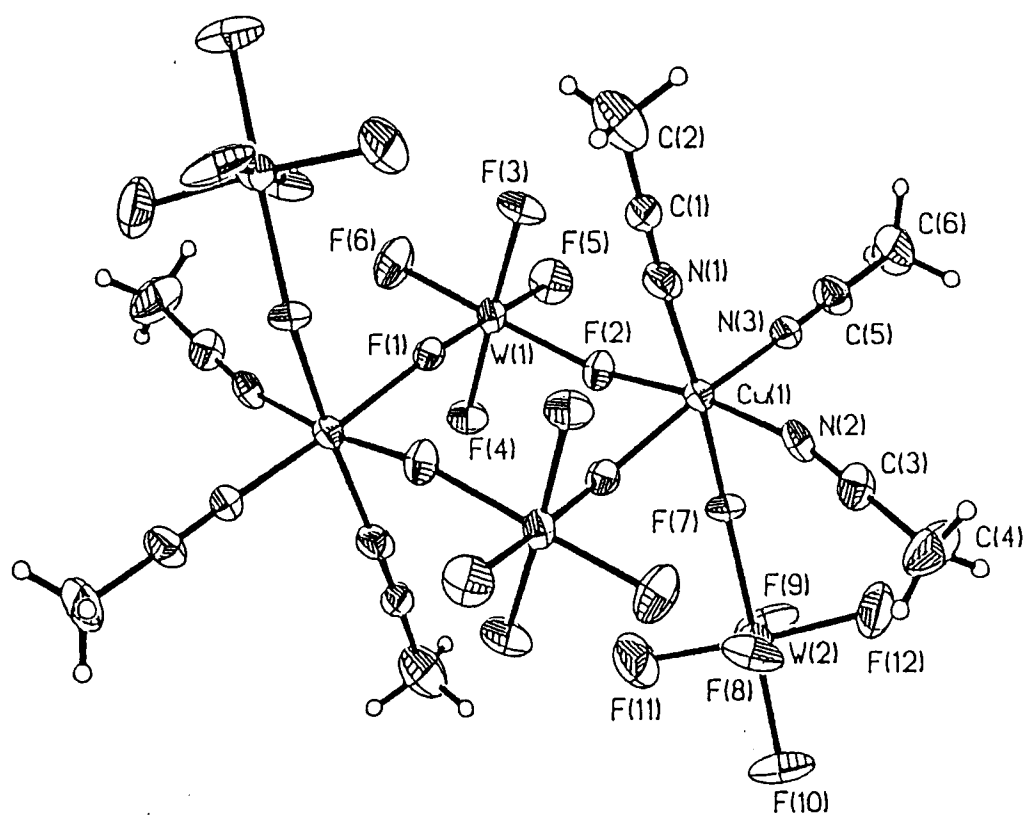


Figure 3.14. ORTEP for the $[\text{Cu}(\text{WF}_6)(\text{CH}_3\text{CN})_3]_2$ dimer.

The W and Cu atoms are both octahedrally coordinated, the W with six F atoms and the Cu with three F atoms and three CH₃CN groups coordinated through the nitrogen atom. The two groups of three CH₃CN ligands are *facially* oriented with respect to the individual Cu atom, and are *trans* to each other with reference to the 8-membered ring. Also, four of these CH₃CN ligands are equatorial with respect to the ring, while the other two are axial. Two of the WF₆ octahedra are bridging between the two Cu atoms and complete the ring, while the other two are terminal axial positions in a *trans* arrangement with respect to the ring. There is also some non-planarity in the ring as seen by a puckering of the F atoms along the W-F-Cu bonds.

The crystal was encased in paratone oil and X-ray data obtained at -100°C for several days with no visible sign of decay of the crystal. The crystal system was found to be monoclinic with unit cell dimensions $a_0 = 12.189\text{\AA}$, $b_0 = 14.054\text{\AA}$, and $c_0 = 11.033\text{\AA}$. The crystal data for this compound are shown in Table 3.3. The full data set can be seen in the appendix.

D. Discussion of the Synthesis and Characterization of the Tungsten Compounds.

1. Synthetic procedures.

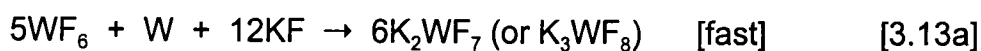
a. Reduction/oxidation steps. During the synthesis of KWF₆ the WF₆ gas and W metal were added to the KF in excess. The limiting reagent in this case then became the KF according to reaction [3a]. However, this did not explain

Table 3.3. Crystal data for $\text{Cu}(\text{WF}_6)_2(\text{CH}_3\text{CN})_3$.

Formula	$\text{C}_6\text{H}_9\text{CuF}_{12}\text{N}_3\text{W}_2$	
Formula weight	782.40	
Crystal Size (mm)	0.80 x 0.75 x 0.20	
Temperature (K)	173	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Lattice parameters	$a = 12.189(4) \text{ \AA}$	$\alpha = 90^\circ$
	$b = 14.054(5) \text{ \AA}$	$\beta = 114.23(3)^\circ$
	$c = 11.033(4) \text{ \AA}$	$\gamma = 90^\circ$
Volume, $\text{\AA}^3$	1723.5(10)	
Z	4	
Density (calc)(g/cm^3)	3.015	
μ (mm^{-1})	14.652	
F(000)	1404	
Scan type	ω -2 θ	
θ range (deg)	1.83 to 27.56	
Index ranges	$h, k, \pm l$	
Unique reflections	3969 ($R_{\text{int}} = 0.0876$)	
Parameters varied	216	
R indices	0.0485 ($R_w F^2 = 0.1365$)	
Goodness-of-fit on F^2	1.121	
Absorption correction	Semi-empirical from Psi scans	

why a product with an intermediate oxidation state between W (VI) and W (0), other than W(V), such as KWF_4 , was not obtained. If the reaction tended to maximize the use of fluoride, then products such as KWF_2 would be expected to be prevalent. The formation of compounds such as WF_4 and WF_5 , etc. was unlikely due to their low decomposition temperature, 200 - 300°C for WF_4 (8) and ~180°C for WF_5 (46). The MWF_6 , M_xWF_7 , and M_xWF_8 products (where M = Na, K, Rb or Cs and X = 1 or 2) obtained experimentally indicated that the W rather preferred to be octahedrally or higher coordinated with the fluorides, which would seem reasonable due to the smaller size of the fluoride ion in comparison to the other halogens. The final product was then determined by maximizing the use of the remaining alkali metal to produce KWF_6 (or MWF_6).

The oxidation of the tungsten metal starting material to W (V) undoubtedly follows a complex mechanism, but this most likely occurs in a step-wise manner. An overall reaction stoichiometry for the potassium coordinated species is as follows:



where the WF_6 and W are added in excess. The fast reaction represents multiple reduction/oxidation steps which would be very difficult to characterize individually. The slow reaction represents a reduction/oxidation process accompanied by dissociation of a seven- or eight- coordinated complex to a six- or seven- coordinated complex. This general scheme can be understood experimentally in that a mixture of KWF_6 and K_2WF_7 can be obtained after letting

the WF_6 gas into the reaction cell for approximately 20 seconds, since the initial reaction rate is very fast. Cooling below the estimated freezing point of the products took approximately 10 minutes. This fast reaction was probably limited by the rate at which WF_6 gas was delivered to the reaction, as seen by the large drop in the supply line pressure when the WF_6 gas supply was let into the reaction cell.

b. Reaction of the tungsten species with the reaction vessel. No reaction with the interior of the glassy carbon crucible by any of the high temperature synthesized material could be seen, such as corrosion by fluoride or the formation of tungsten carbides. Even minute scratches on the inside bottom and sides of the glassy carbon crucible, caused by spatula scraping, remained after many reactions with no sign of degradation. The imprint of the scratches could be seen on the solidified material where it was in contact with the crucible walls while cooling. The exterior of the crucible, however, showed bright deposits of metallic tungsten which were assumed to have deposited from WF_6 or some other volatile tungsten species. More extensive deposition of tungsten metal was seen at higher operating temperatures. The nickel cell itself did not react to any significant degree with any of the tungsten compounds. Most likely this was due to the more negative reduction potential of the tungsten species, which would tend to reduce any nickel compounds to nickel metal. Fluoride would also have a passivating effect on the surface of the nickel.

c. Reaction rate during the tungsten compound synthesis. All the high temperature reactions in which WF_6 gas was used were very rapid, and care had

to be taken not to allow the reaction to proceed too quickly. When the reaction did proceed too quickly, the reactants would tend to bubble over the top of the glassy carbon crucible and spill into the nickel container. This spilled material would then usually react with any excess WF_6 gas to produce KWF_6 and K_2WF_7 , which, when cooled, would freeze and stick to the deposited tungsten metal on the exterior walls and bottom of the crucible and to the nickel cell material. This made removal of the crucible from the reaction cell very difficult. Many times this would cause the crucible to crack on the bottom, rendering the crucible unusable for further reactions.

Limiting the rate of WF_6 gas flow was the simplest method to control the reaction rate, although a lower temperature was used as well. In the latter case, the reaction vessel was filled with WF_6 gas before the melting temperature of the KF was reached. The rate of the reaction was much slower, as seen by the much slower rate of consumption of the WF_6 gas, which was monitored by the pressure change in the WF_6 gas supply line. Since the reaction was normally most vigorous with the molten KF during the first few minutes of the reaction, the bubbling over was reduced significantly by this method.

d. Applications of the synthetic method. Based on the results described here, it is thought that any quantity of the higher-yield products, i.e., K_2WF_8 and KWF_6 , can be produced by this high temperature method of synthesis, and this process would also lend itself well to the formation of other, yet unsynthesized and previously synthesized, transition and rare earth metal fluorides in various oxidation states.

2. Discussion of the Raman spectra of the tungsten compounds.

Table 3.4 summarizes the peak frequency assignments for all the compounds discussed in this chapter. Relationships between the various tungsten compounds are described under individual headings below.

a. MWF₆ compounds. Since all four MWF₆ compounds (where M = Na, K, Rb or Cs) were obtained in a pure, crystalline or nearly crystalline state, and the Raman spectra obtained under the same conditions, some comparisons between the various compounds according to the coordinating cation were made. A graph of the ν_1 band frequency vs. the coordinating alkali metal cation for NaWF₆, KWF₆, RbWF₆ and CsWF₆ can be seen in Figure 3.15. A general trend toward lower frequencies with heavier second sphere alkali cations can be readily seen. As shown previously, Figure 3.4 reveals the similarity of all four spectra of the compounds at the ν_1 and ν_5 bands. The ν_2 band is conspicuously absent from all four spectra. As mentioned in the section dealing with the Raman spectrum of the Cu(WF₆)₂(CH₃CN)₃ dimer, ν_2 may be in the 600 to 615 cm⁻¹ region for these compounds, but is most likely obscured due to crystal effects.

b. W(V) compounds. The main bands (ν_1) for several W(V) compounds are plotted vs. the individual compounds in Figure 3.16. The main band for WF₅ was obtained from the work by Hildenbrand (47) who calculated an estimate of the frequency. The band frequencies can be seen to follow what appears to be a predictable path.

Table 3.4. Raman band frequencies for tungsten compounds studied in this work and related fluoride compounds. (s=strong, m=medium, w=weak, vw=very weak).

Compound	ν (cm ⁻¹)				References
1. a. K ₂ WF ₈	667 s	417 w	385 w		31
	667 s	419 w	389 w		This work
b. Rb ₂ WF ₈	657 s	406 w	383 w		31
c. Cs ₂ WF ₈	656 s	406 w	385 w		31
2. a. Na ₃ WF ₈	614 s	(411?) w	372 w		This work
b. K ₃ WF ₈	598 s	435 w	362 w		This work
c. Rb ₃ WF ₈	595 s	428 w	353 w		This work
3. KWF ₇	718 s	665 vw	620 vw	550 vw	31
	438 vw	330 vw			
	716 s	665 vw	615 vw	535 vw	This work
	435 vw	327 vw	(220 vw)		
4. a. K ₂ WF ₇	642 s	395 vw	255 w		This work
b. K ₂ TaF ₇	635 s				38
	641 s				37
	645 s	395 w	280 w		39
	645 s	396 w	290 w		This work
c. Rb ₂ WF ₇	637 s				This work
M_xWF₆ compounds					
	ν_1	ν_2	ν_5		
5. a. NaWF ₆	712 s	(600 vw) ^a	(212 vw) ^b		This work
b. KWF ₆	702 s	(600 vw) ^a	200 vw		This work
c. RbWF ₆	696 s	(600 vw) ^a	(212 vw) ^b		This work
d. CsWF ₆	692 s	(600 vw) ^a	(209 vw) ^b		This work
e. CsTaF ₆	692 s	581	272		37
f. WF ₆ ⁻					
(in CH ₃ CN)	695	---	---		33
(gas phase)	707	470	215		34
6. a. Na ₃ WF ₆ ?	585 s	---	---		This work
b. K ₃ WF ₆ ?	565 s	480? vw	198 w		This work

^a Estimated frequencies obtained from the [Cu(WF₆)₂(CH₃CN)₃]₂ dimer.

^b These bands most likely contain totally and nontotally symmetric vibrations.

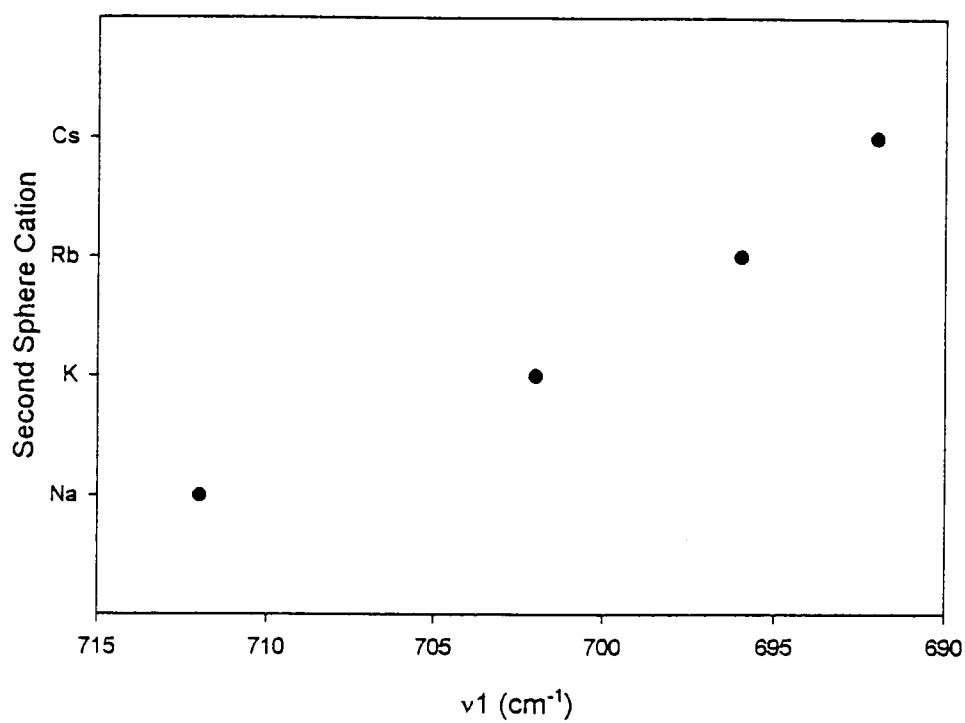


Figure 3.15. Relationship between ν_1 bands for MWF_6 species (where $\text{M} = \text{Na}$, K , Rb and Cs).

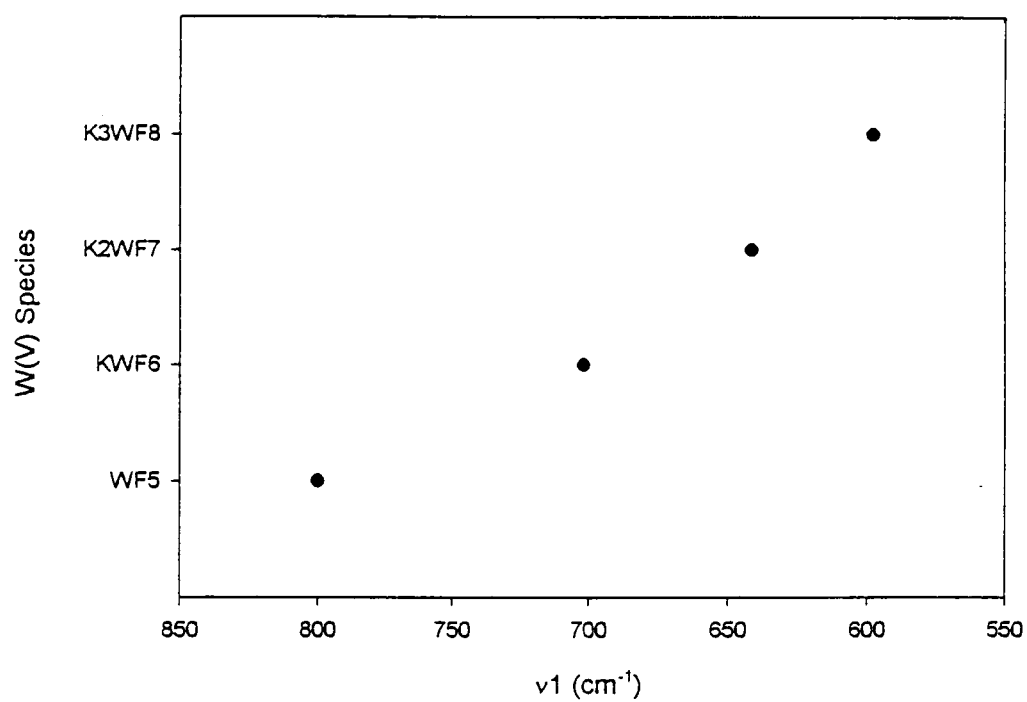


Figure 3.16. Relationship of main bands for W(V) species.

3. Physical data of the tungsten compounds.

A compilation of the physical properties along with the measured density and calculated X-ray density can be seen in Table 3.5. The densities increase as the atomic masses of the alkali metal cations increase for similar compounds. Only three of the melting points were directly observed: those for KWF_6 , K_3WF_8 , and $\text{Cu}(\text{WF}_6)_2 \cdot 3\text{CH}_3\text{CN}$. The green K_3WF_8 compound was interesting in that it began to change color on heating from the initial green to an orange color, with a complete change at approximately 400-500°C, then changing from orange to yellow at approximately 600-700°C. An explanation for this is the successive loss of F^- in the coordination sphere to give first the orange K_2WF_7 and then the yellow KWF_6 . Many of the seven- and eight- coordinated transition metal fluorides are known to go from a higher to a more stable lower coordination number complex at higher temperatures. Differential scanning calorimetry or a thermal gravimetric analysis may provide additional information on the suspected phase changes.

Table 3.5. Physical properties of some tungsten fluorides.

Compound	Color	m.p. (°C)	Density (g/cm ³)		Crystal Habit
			Meas.	X-ray Calc.	
K ₂ WF ₈	white	---	---	---	---
^a K ₃ WF ₈	white	---	---	---	Rhombohedral
^b K ₃ WF ₈	green	780	4.0	3.890	---
Na ₃ WF ₈	dark green	<850	---	---	---
Rb ₃ WF ₈	light green	---	---	---	---
KWF ₇	bright yellow	---	---	---	---
K ₂ WF ₇	orange	750-780	3.87	3.982	Monoclinic
Rb ₂ WF ₇	red-orange	<795	4.3	---	---
^c NaWF ₆	yellow	---	---	---	Cubic
^c KWF ₆	yellow	~450	4.08	---	Tetragonal
^a RbWF ₆	yellow	(<450)	4.2	---	Rhombohedral
^a CsWF ₆	yellow	(<450)	4.8	---	Rhombohedral
^b K ₃ WF ₆	green	~780	---	3.890	Cubic
^b K ₃ WF ₈ + K ₃ WF ₆	brown	~780	---	3.890	Cubic?

^a Reference (29)

^b This work.

^c Reference (35).

CHAPTER IV

CHEMICAL AND ELECTROCHEMICAL REDUCTION OF TUNGSTEN SPECIES IN FLINAK

A. Introduction.

All the reported electrochemistry (1, 4-7, 46, 47) of tungsten in FLINAK has been performed in melts containing some tungsten metal to act as a reductant. In order to characterize this chemical reduction of tungsten in FLINAK, where tungsten metal is present as a reducing agent, a series of experiments was performed in which tungsten hexafluoride gas was added to molten FLINAK at 750°C with tungsten metal powder present. The products in the solidified FLINAK were then examined by Raman spectroscopy to identify the species present by their fingerprint bands, which were characterized in the previous chapter. Several of the synthesized compounds reported in the previous chapter were also combined with FLINAK and the products examined with Raman spectroscopy.

In order to characterize the electrochemistry of tungsten in FLINAK, cyclic voltammetry was performed on dilute concentrations of several of the individual compounds that were synthesized in the previous chapter. Other electrochemical investigations were also performed on the species in FLINAK in order to further clarify the reduction mechanisms of higher oxidation states of

tungsten in this eutectic salt mixture. The synthesized addition materials (M_2WF_8 , M_2WF_7 , MWF_6 and M_3WF_8 ; $M = K, Na$) were in the form of their potassium or sodium salts so that no new cations would be introduced into the system. Special emphasis was placed on the electrochemistry of W(V) since the most clearly defined electrochemical responses were seen for the compounds in this oxidation state. K_3WF_6 was added as the brown mixture of K_3WF_8 and K_3WF_6 , and therefore could not be studied as a pure compound. The effect of added oxide (Na_2O) on the electrochemistry of these species and the electrodeposition of tungsten was also studied.

B. Experimental Details for the Reduction of Tungsten Compounds in FLINAK

1. Chemicals.

Tungsten hexafluoride gas (Cerac, 99.9%) and tungsten metal powder (Aesar, 99.9%, 100 and 300 mesh) were used without further purification. FLINAK was purified by bubbling HF through the molten material at 550 °C for 3 to 4 days, followed by an H_2/He sparge to remove excess HF and reduce metal ion species. This produced FLINAK containing <12 ppm oxide, as determined by the apparatus described in Chapter 2. The individual tungsten fluoride compounds used for addition to the FLINAK were prepared as described previously. Na_2O (Ventron, Alfa division, 98%) was used without further purification. All purified and synthesized chemicals were handled and stored in

an inert atmosphere glove box which was filled with purified nitrogen and operating at $< 2\text{ppm H}_2\text{O}$.

2. Electrode materials.

Working electrodes were constructed from platinum wire (Aesar, 0.5mm dia., 99.95%), platinum foil (Aesar, 0.05mm and 0.1mm, 99.95%), or tungsten wire (Aesar, 1.0mm dia., 99.98%). The counter electrode was generally the glassy carbon crucible (Sigridur G) used to contain the FLINAK, but glassy carbon rod (Sigridur, grade K, 1mm dia.) and tungsten wire were also used as counter electrodes. Reference electrodes were constructed of either platinum wire or platinum foil, or were made from hot-pressed boron nitride (Advanced Ceramics Corporation and Union Carbide, $\frac{1}{2}$ " dia.). A polished nickel plate was used for the electrolytic removal of metallic impurities.

3. Chemical and electrochemical reduction apparatus.

a. Chemical reduction cell. The cell and equipment used for the chemical reduction of the tungsten compounds in FLINAK was the same as that used for the synthesis of the individual tungsten compounds (Figure 3.1), including the glassy carbon crucible used to contain the FLINAK. The gas used to pressurize the system in all cases was helium.

b. Electrochemical reduction apparatus. The cell used for the electrochemical reduction of the tungsten compounds can be seen in Figure 4.1. The cell was constructed of 3" Inconel pipe to which was welded a nickel plate to

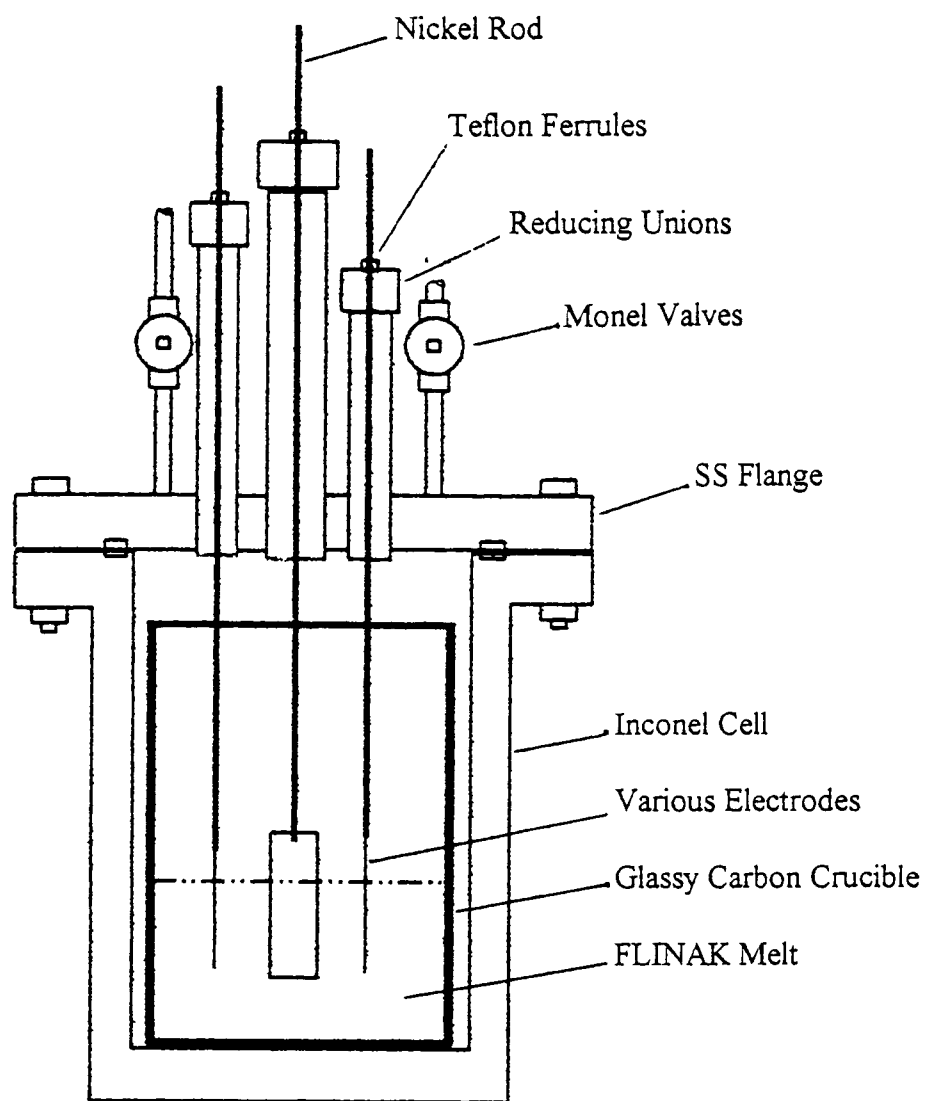


Figure 4.1. Schematic of the cell for the electrochemical studies of tungsten in FLINAK.

form the bottom. Knife edge SS flanges (Huntington Labs, Inc.) were welded to the top of the pipe to form a cap for the cell. Copper gaskets were used to seal the cell at the flange knife edges, enabling a vacuum tight atmosphere.

Stainless steel tubes were welded into the top flange to allow the insertion and removal of electrodes, the measurement of temperature, and the addition of chemical samples. These tubes were capped with Swagelock reducing unions (1" to 1/4" and 5/8" to 1/4") and cone-shaped Teflon bushings to provide vacuum tight connections as well as electrical insulation of the electrodes from the cell. The length of the tubes was sufficient to minimize the heat conduction from the cell during operation, which prevented melting of the Teflon bushings. The height of the reducing unions was staggered vertically to facilitate their removal during sample additions to the cell, since the redundant proximity of the union hex flats would otherwise prevent free rotation. Two Monel diaphragm valves (Hoke) were silver-soldered to 1/4" Monel tubing, which was in turn welded to the cell top flange in order to allow gas inlet/outlet flow and regulate the pressure/evacuation of the cell. All connections to the vacuum/pressure system were made with Monel or SS Swagelock fittings and Monel tubing (1/4"). The top of the cell usually remained cool enough that a blast of air was not necessary to prevent overheating and seizing of the bolts. The system was kept pressurized with helium gas at all times, except when a vacuum in the cell was used to remove residual hydrogen fluoride gas dissolved in the melt.

c. Electrochemical instrument. The electrochemical instrument used to acquire and record the electrochemical data was an EG&G Princeton Applied

Research (PAR) Model 273 Potentiostat/Galvanostat controlled by the PAR M270 Electrochemical Research Software. The software, which provided functions for all of the electrochemical methods used, allowed some minor data manipulation such as curve smoothing and peak area calculations.

d. Ovens. Ovens were made in-house to fit the reaction vessels by wrapping Kanthal wire around alumina tubing. The wire was then covered tightly with a blanket of quartz wool. A larger alumina tube was then slipped snugly over this assembly which compressed the quartz wool against the Kanthal wire, preventing its movement due to thermal expansion when heated to glowing temperatures. The temperature was controlled with a large-current (25 amp) Variac transformer and was monitored using an Inconel sheathed chromel-alumel thermocouple (Omega), which was pressed against the bottom of the cell. The interior temperature of the cell was measured and found to be 2 to 3 °C lower than the temperature measured on the exterior bottom.

d. Spectra. All Raman spectra were obtained with the Dilor spectrometer as described in the previous chapter. Samples were likewise enclosed in glass Raman tubes for data collection. ESCA (Electron Spectroscopy for Chemical Analysis) spectra were obtained using a Perkin-Elmer PHI5000 instrument which was calibrated using gold and copper standards.

e. Electrodes. Working electrodes were fabricated by attaching either platinum, nickel or tungsten in the form of wire, foil, or plate to the end of a 1/8" nickel rod, which provided exterior electrical connection when inserted through the Teflon bushing. The attachment was made by clamping the rod in a vise,

filing a "V" shape in the end of the rod with a metal file, then using a hacksaw to cut a notch approximately $\frac{1}{4}$ " down the length of the rod starting at the "V", leaving two prongs the width of the blade apart. The wire was then inserted into this notch and the nickel prongs pinched together with a pair of pliers. Care had to be taken not to pinch the platinum (and silver) wire too tightly since the malleable platinum wire would compress and leave a stressed, weak joint at the point of contact with the nickel. Otherwise this provided a very strong and reliable electrical connection that held up consistently under the high working temperatures and corrosive environment of the experiments. Foil and plates were also successfully attached by this method.

Spot welding was also attempted, but this was performed in the open atmosphere under high temperatures, necessitating the removal of additional oxides and other contaminants introduced during the welding process. Consequently, preference was given to the former method. Working electrodes were also fabricated from glassy carbon rod, which was attached to a small stainless steel bushing with set screws in the side. The opposite end of the bushing held the nickel rod for electrical connection. Glassy carbon counter electrodes were also fashioned in this same manner. When the glassy carbon crucible was used as the counter electrode, electrical connection was made through the main body of the cell.

Reference electrodes were either platinum foil connected to the nickel rod as above, or were constructed from boron nitride (BN) as described by Jenkins (48). However, it was found that BN often gave unreliable potential

measurements when tungsten fluorides were added to the melt. This was most likely due to the binder used to hold the BN material together, which was an oxide-containing ceramic. Since the tungsten fluorides were especially sensitive to even minute quantities of oxide, and the experiments called for the rigorous removal of any form of oxide, the BN reference electrodes were subsequently only used to establish the viability of the electrochemical cell apparatus by observing known potentials, such as the Ni^{2+}/Ni couple, and to make reasonable estimates of the metal impurities in the melt before and after electrolysis at a nickel electrode.

The electrodes were generally inserted into the cell in the inert glove box atmosphere before sealing the cell. When it was necessary to remove the electrodes outside the glove box during experiments, a positive helium flow was maintained when the cell was opened to the atmosphere. Clean electrodes inserted into the cell outside the glove box were kept in the hot helium flow, halfway into the cell, for at least one minute before the cell was resealed. Electrical contact of the electrodes with the melt was established by gently tapping the end of the nickel rod until conductance was observed by an ohmmeter attached across the nickel rod and cell body. The typical resistance of a platinum wire just touching the FLINAK surface was ~ 1.2 ohms. The point of electrical contact was then marked on the exterior nickel rod. Scale markings were then drawn above that mark, after which the wire was inserted one centimeter into the melt. Electrodes removed from the melt confirmed the one centimeter distance by measurement of the discoloration on the electrode. The

electrodes were generally two centimeters in length or more to avoid contact of the melt with the nickel support rod. The BN reference electrode was inserted into the cell until it touched the bottom of the crucible, then was raised ~5mm.

C. Chemical Reduction of Tungsten in FLINAK.

1. Addition of WF_6 and W metal.

A series of additions of WF_6 gas to FLINAK containing excess W metal powder was performed in order to ascertain the final chemical reduction products. These were the same conditions that previous studies employed, except in some of those cases the W metal was the vessel used to contain the reactants. The WF_6 gas in the present study was added in different estimated concentrations, and each reaction mixture was maintained at 750 °C for 30 minutes before the cell was cooled. Each product was weighed to determine the amount of added WF_6 more accurately, then examined by Raman spectroscopy to record the ν_1 band area ratios.

a. Procedure. Excess tungsten metal powder was combined with FLINAK samples ranging from 5 to 10 grams and heated to 750 °C. A vacuum was then pulled on the cell (Figure 3.1) to remove residual hydrogen fluoride gas dissolved in the melt. After approximately 15 minutes, the vacuum line was closed off and the valve to the WF_6 gas slowly opened, allowing the gas to flow into the evacuated cell. The WF_6 gas flow was maintained for various time intervals, but never more than 30 seconds. The reaction temperature was then

maintained for 30 minutes before cooling to room temperature. This produced reduction products in various concentrations as shown by Raman spectroscopy on the solidified samples. The weight gain of the product was recorded as the amount of WF_6 added, since the exact composition of the products was not known. Measurement of the exact quantity of WF_6 gas to add to the reaction vessel was not attempted since a portion of the gas reacted with the exterior of the glassy carbon crucible used to contain the reactants. This was indicated by a thin layer of tungsten metal deposited on the crucible and made it difficult to control the exact amount of WF_6 added to the FLINAK inside the crucible. The products inside the crucible did not adhere to the glassy carbon and were easily removed for weighing.

b. Results and discussion. The products in the reaction mixture described above were green for the higher concentrations of WF_6 added and tended to be brown at the lower concentrations. The Raman spectra of these melts, which exhibited bands resembling those in Figure 3.14b, indicated that the green color of the material was due to the presence of K_3WF_8 , and the brown color due to the presence of a mixture of K_3WF_8 and K_3WF_6 . The Raman bands associated with the sodium salt analogs (and presumably the lithium analogs as well) were not seen, indicating preferred coordination with the larger potassium cation when the melt was solidified. When some Na_3WF_8 and Na_3WF_6 mixed material was added to FLINAK, the Raman bands shifted to lower frequency to match those for the potassium coordinated species when the mixture was solidified. Raman bands associated with a lithium coordinated species would be

expected to shift to even higher frequency than the sodium coordinated species.

The only difference between the spectra obtained on samples of these products and the spectrum in Figure 3.14b was the height of the ν_1 bands (598 cm^{-1} for K_3WF_8 and 565 cm^{-1} for K_3WF_6) for the two species, which varied with the quantity of added WF_6 and reflected the concentration differences of the two products. Not surprisingly, the more green appearing products had more intense bands that were associated with K_3WF_8 (in relation to the K_3WF_6 bands).

The Raman spectra of a series samples containing various concentrations of added WF_6 can be seen in Figure 4.2, where the ν_1 band of K_3WF_8 can be seen to increase in relation to the ν_1 band of K_3WF_6 as the quantity of added WF_6 increases. Assuming similar sensitivities for the Raman signals for K_3WF_8 and K_3WF_6 , the amount of K_3WF_6 as a percentage of the total tungsten species in the FLINAK melt [$\text{K}_3\text{WF}_6/(\text{K}_3\text{WF}_6 + \text{K}_3\text{WF}_8)$ ν_1 band areas] was plotted versus the mole ratio of added WF_6 to FLINAK (Figure 4.3). A band area percentage (BAP) of 100% would indicate complete formation of K_3WF_6 , and a BAP of 50% would indicate equal amounts of K_3WF_8 and K_3WF_6 . A prominent plateau can be seen to fall at a BAP of 52% as the mole fraction of added WF_6 approaches zero. The BAP was never found to be greater than this value, not even for the crystalline material as shown in Figure 3.14b, which suggests there is some equilibrium in the molten state between the WF_8^{3-} and WF_6^{3-} species when tungsten metal is present as a reductant. It is interesting to note that the optimum plating concentrations in FLINAK reported by Baraboshkin et al. (7) fell where the BAP

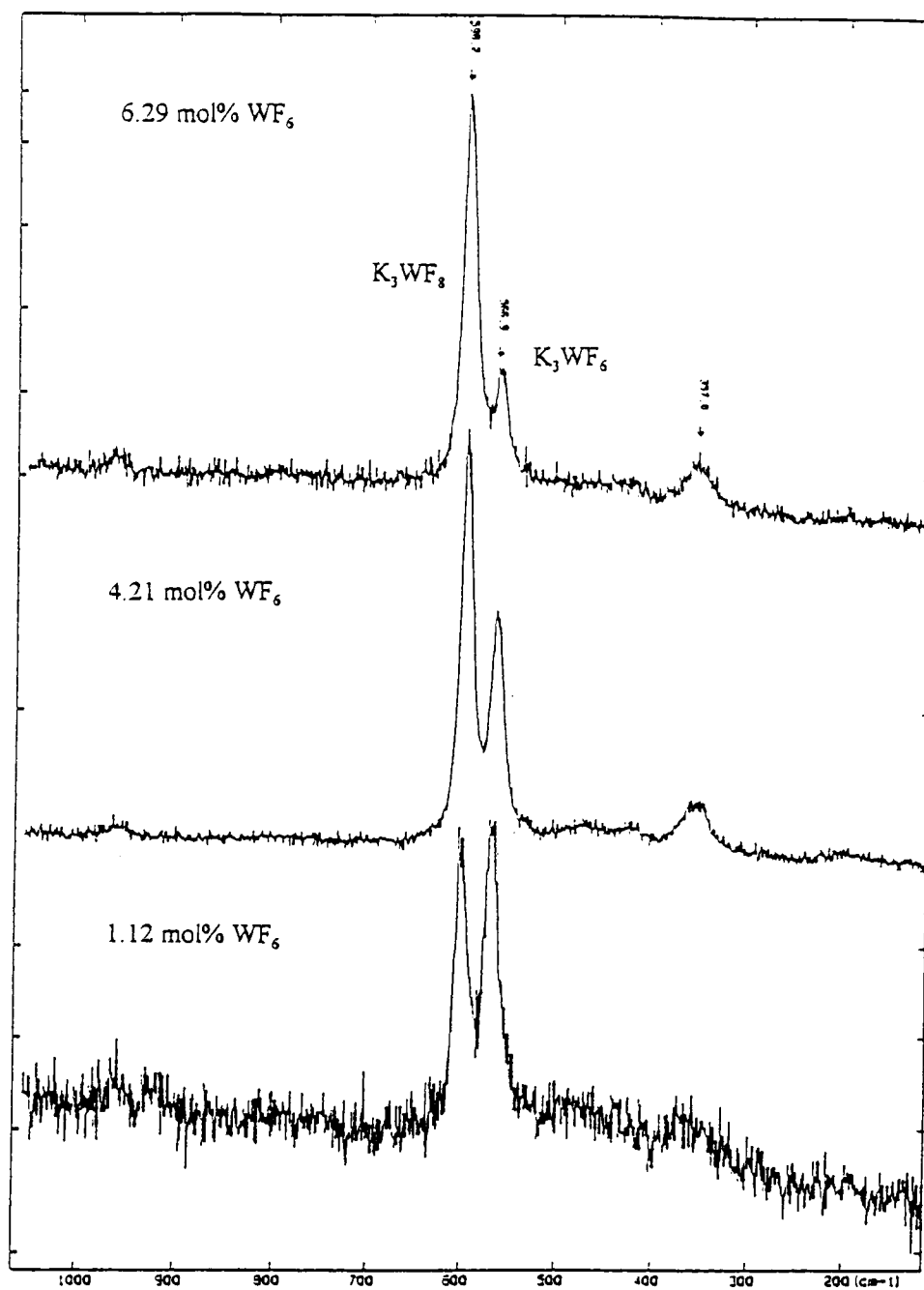


Figure 4.2. Variation in K_3WF_8 (598 cm^{-1}) and K_3WF_6 (565 cm^{-1}) Raman band intensities in a solidified FLINAK melt with increasing addition of WF_6 in a bath containing excess W metal.

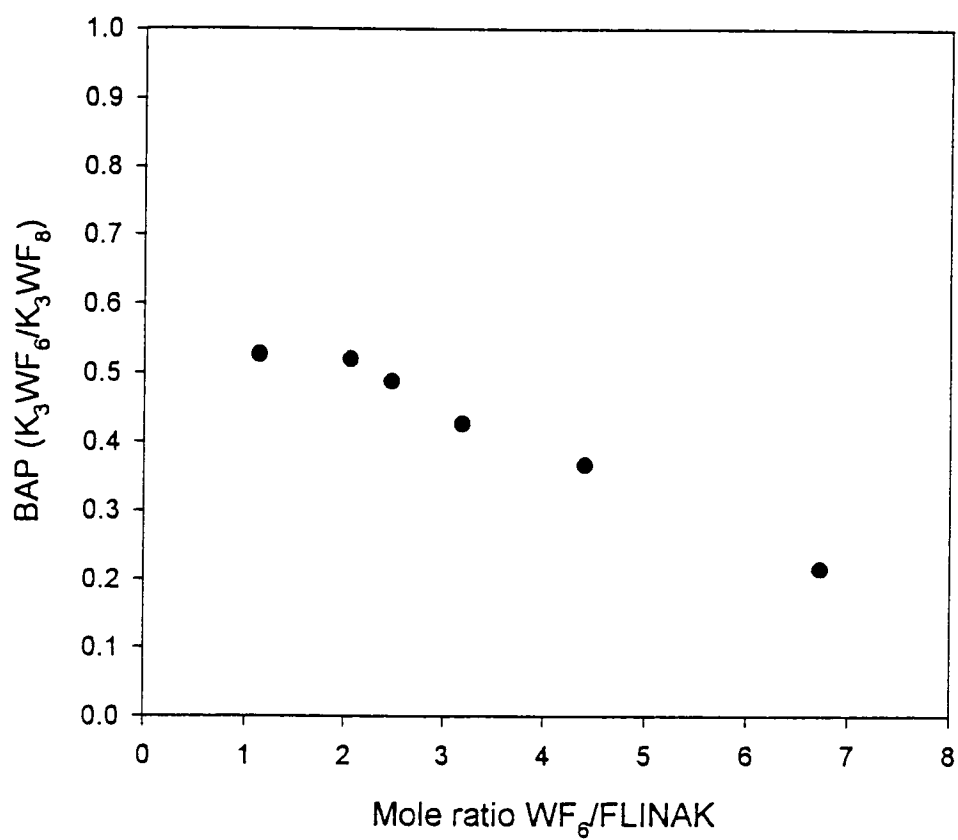


Figure 4.3. ν_1 Band Area Percentage (BAP) for $\text{K}_3\text{WF}_6/\text{K}_3\text{WF}_8$ with increasing WF_6 .

in Figure 4.3 was equal to 50 - 52%, indicating that maintaining the two species in equal proportions in the melt is a condition for obtaining the best plates.

To show that no further reduction occurs without tungsten metal present, even at lower concentrations, an experiment was performed in which some of the material from the product mixture in which a 0.04 mole ratio $\text{WF}_6/\text{FLINAK}$ was found was diluted with more FLINAK to a concentration of 0.01 mole ratio $\text{WF}_6/\text{FLINAK}$, except without the tungsten metal to act as a reductant. After heating the mixture for 30 minutes then obtaining a Raman spectrum on the solidified product, the BAP for the two samples remained essentially identical. This indicated that the ratio of K_3WF_8 to K_3WF_6 did not change, i.e., that there was no further reduction of the WF_8^{3-} species to WF_6^{3-} in the molten state. When the same experiment was repeated with W metal present to allow further reduction, a different BAP was obtained, corresponding to the 52% plateau, indicating reduction of some of the WF_8^{3-} species to the equilibrium mixture described above.

2. Addition of KWF_6 , K_2WF_7 and K_3WF_8 to FLINAK.

When 2.0 g of KWF_6 was added to 5.0 g of FLINAK and heated to 750 °C for 30 minutes, the product was a mixture of the green K_3WF_8 in FLINAK, as shown by Raman spectroscopy on the solidified melt. No band associated with KWF_6 was evident. Essentially identical results were obtained when K_2WF_7 was added to FLINAK under the same conditions. Mixtures of K_3WF_8 and FLINAK in various proportions produced only the diluted material in FLINAK when no W

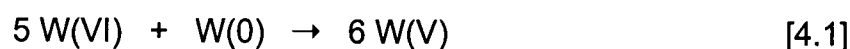
metal reductant was added, as shown by Raman spectroscopy. When the boule was allowed to cool slowly in all three cases, there was a phase separation with one portion of the boule separating into a very intense green color, due to the presence of K_3WF_8 , while the other portion appeared as a faint green. No bands from a Raman spectrum were found for the faint green material, indicating the species was very low in concentration. When W metal was added to any of the reaction mixtures, the K_3WF_6 Raman bands appeared and brown colored mixtures were obtained as described above.

3. Discussion of the chemical reduction.

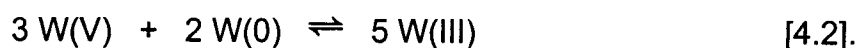
Since the reactions described above were essentially the same as previous experiments performed in the FLINAK melt and LiF-KF eutectic (1, 4-7, 46, 47), some comparisons and conclusions can be made with regard to the chemical reduction schemes. In all previous studies of tungsten in these alkali fluoride salts, the reported oxidation states of the tungsten species were from +4 to +4.5, implying a mixed oxidation state system from which the tungsten metal was plated. This agrees well with the spectroscopy of the reduction products with excess tungsten metal, which indicates two separate species in approximately equal portions at the lower concentrations. Senderoff and Mellors (46) proposed this +4.5 mean valence was the result of a polynuclear complex with tungsten and fluoride. However, the above results suggest that the melts contain two separate species, WF_8^{3-} and WF_6^{3-} . Furthermore, Figure 4.3 indicates that in dilute solutions these two species are in equal proportions,

which would give a mean valence of +4, but in more concentrated solutions the mean valence begins to increase as the amount of WF_8^{3-} increases in relation to WF_6^{3-} . This increasing disparity in concentration of the two species with increasing total tungsten species concentration would explain the difference in reported mean valences.

From the present studies it is thought that the chemical reduction of the mixture of WF_6 and W metal in FLINAK at 750°C proceeds according to the following overall reaction:



followed by the equilibrium process:



D. Electrochemical Reduction of Tungsten in FLINAK.

1. FLINAK background voltammograms.

a. FLINAK background. A background cyclic voltammogram for FLINAK can be seen in Figure 4.4. The reduction limit of the melt occurred at the reduction potential of Li^+ , which has been reported (49) as -2.2 V at a pyrolytic graphite working electrode versus the platinum quasi-reference electrode in FLINAK at 500 °C . Voltammetric studies by Clayton and coworkers (50) showed this to be at -2.14 V vs the Ni^{2+}/Ni reference, indicating a shift of +60 mV from the

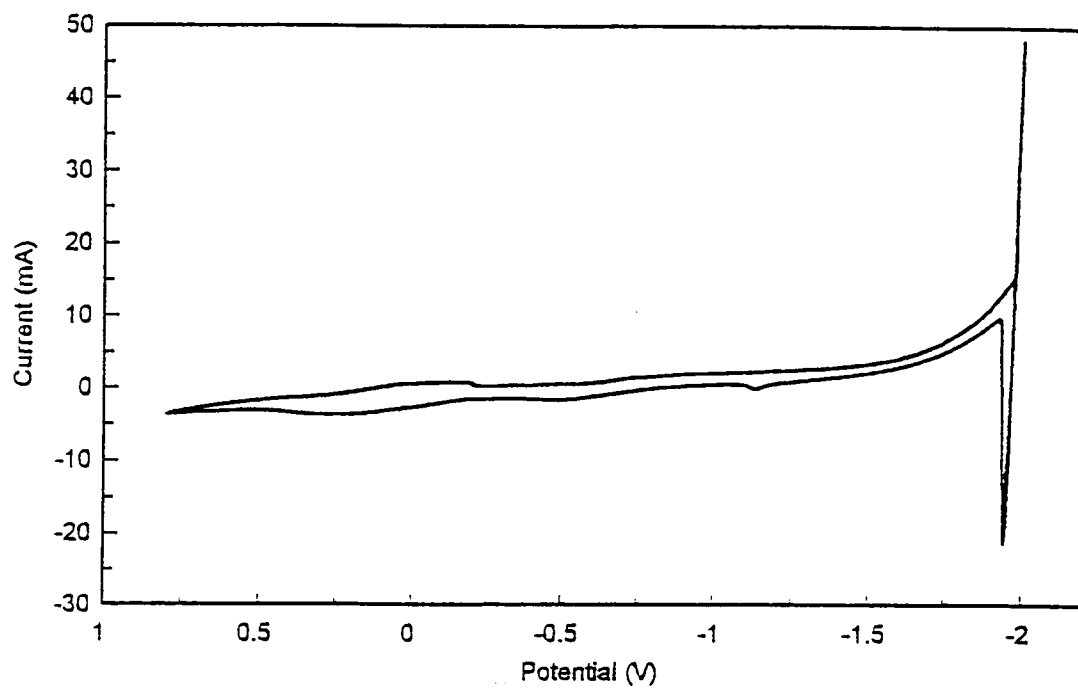


Figure 4.4. Background cyclic voltammogram for FLINAK.

platinum quasi-reference electrode. All potentials in this study have been reported against the platinum quasi-reference electrode, except where noted.

b. Metal ion impurities. The metal ion impurities, which were the major source of interference on the voltammograms after the HF purification to eliminate oxide, were removed by electrolyzing the FLINAK at a nickel plate cathode with an applied potential of -1.5 V to -1.8 V. The glassy carbon crucible acted as the counter electrode. This generally produced smooth voltammograms, and when current peaks did remain after the electrolysis, they were usually very small and negligible in comparison to the much larger currents (at least two orders of magnitude) obtained from the tungsten addition compounds. When the background currents were large enough to cause interference and could not be removed, the FLINAK was discarded. The location of the redox potentials for the major impurities vs. a BN reference electrode containing the Ni^{2+}/Ni couple (51) suggested iron ($\text{Fe}^{3+}/\text{Fe}^{2+}$, $E^\circ = -0.2 \text{ V}$; Fe^{2+}/Fe , $E^\circ = -0.39 \text{ V}$), chromium (Cr^{2+}/Cr , $E^\circ = -0.681 \text{ V}$) and sometimes nickel ions ($E^\circ = 0.0 \text{ V}$) as the major sources of contamination. Some of the peaks could not be assigned to specific redox couples.

c. Residual hydrogen fluoride (HF) gas. Following the HF purification, the FLINAK was sparged with a H_2/He mixture to strip off residual HF and reduce metal ion impurities to the metal. When the sparge was discontinued before all the residual HF was removed, the voltammograms exhibited a reduction wave with large oscillations, similar to a reduction with the formation of a gas. This was assumed to be reduction of H^+ in the FLINAK melt causing the formation of

H₂. This H₂ would then react with tungsten species in the melt causing reduction to metallic tungsten. The reaction scheme is as follows:



When a vacuum was pulled on the cell for 15 minutes, the reduction wave was significantly lowered, indicating the reducible species had a high volatility in the molten FLINAK. The best results in eliminating residual HF were obtained when the FLINAK batch was freeze/thawed under vacuum.

In order to further characterize the electrochemistry of HF in FLINAK, several portions of the FLINAK containing residual HF were added to a larger batch of FLINAK at 540 °C which had been treated with a vacuum and exhibited no reduction wave associated with H⁺. Cyclic voltammograms at a platinum wire working electrode vs. a platinum flag reference were obtained after each HF sample addition (Figure 4.5). A plot of the reduction current at -350 mV vs. the added sample weight was linear (Figure 4.5 inset) with a slope of 0.36 mA/g (SD = 0.0061), and indicated that the HF in the FLINAK could be quantified voltammetrically. Note that the background current was not subtracted from the *I*_{max} values plotted in the inset of Figure 4.5.

The absence of "diffusion tails" on the voltammograms in Figure 4.5 suggests the presence of significant convective stirring in the cell. This could be due to the formation of H₂ gas bubbles during the HF reduction process or to a significant temperature gradient in the melt. Using the Randles-Sevcik equation and an estimate of the diffusion coefficient of 10⁻⁴ to 10⁻⁵ cm²/s with a 0.10 V/s

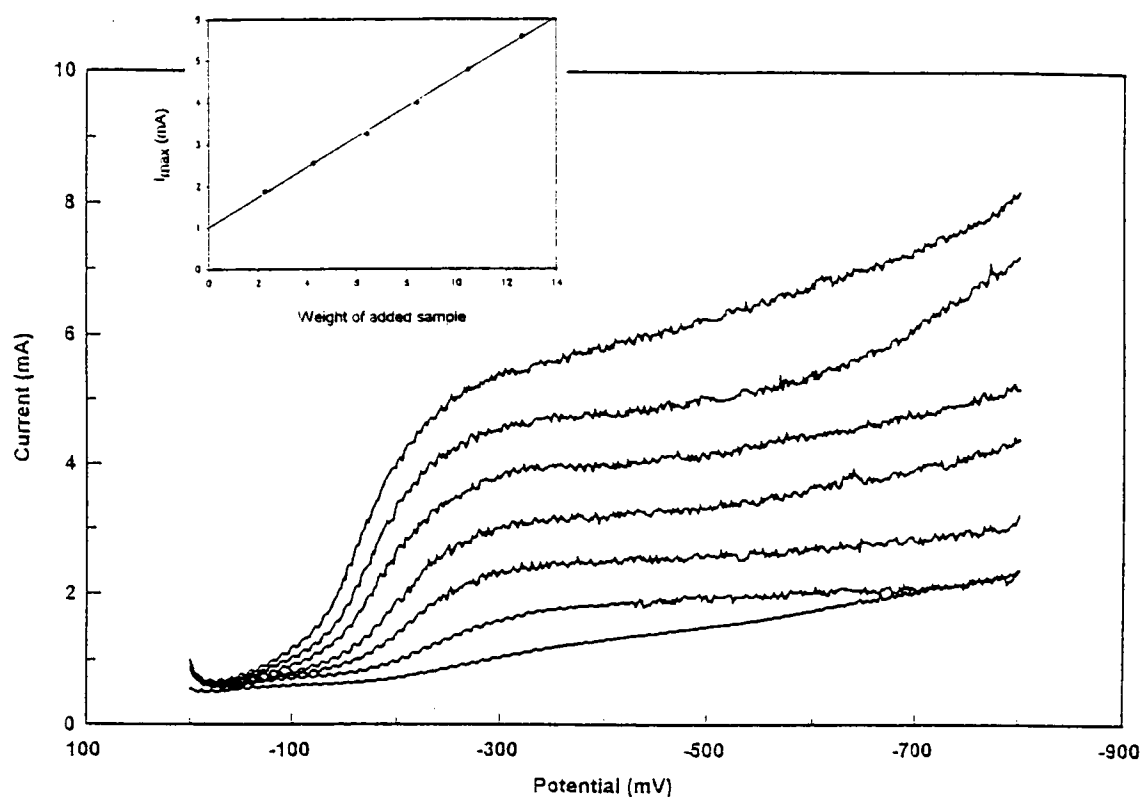


Figure 4.5. Voltammograms showing the reduction of HF in FLINAK. 500°C, 100 mV/s scan rate, $A_{\text{pt}} = 0.157 \text{ cm}^2$. Inset: Plot of the maximum current at -325 mV vs. the added sample weight.

scan rate and electrode surface area 0.157 cm^2 , placed the lowest wave in Figure 4.5 (approximately 2 mA) at about 10 to 60 ppm H^+ (mg/L). The density of FLINAK at 500°C is 2.17 g/ml (48).

2. Reduction of tungsten species in FLINAK.

a. Addition of K_2WF_8 . A sample of K_2WF_8 weighing 0.10 g was added to the cell containing 95.243 g of FLINAK at 750°C (density $\sim 1.95 \text{ g/ml}$)(52), making the mixture approximately 4.9 mM in tungsten ions. The coordination number of the tungsten in the melt at this temperature was not known, but was assumed to be an ion coordinated with seven or eight fluorides; or, less likely, WF_6 dissolved in the FLINAK.

1.) Cyclic voltammograms. A cyclic voltammogram was obtained of this mixture using a platinum wire working electrode (Figure 4.6, curve a; only the initial sweeps in the negative potential direction are shown). A reduction wave, R_1 , began at approximately -0.10 V vs. a platinum flag quasi-reference electrode, and plateaued at approximately -0.20 V . A second reduction wave, R_2 , followed at approximately -0.6 V . Successive additions of K_2WF_8 in 0.10 g quantities (Figure 4.6, curves b-e) showed the growth of yet another reduction wave, R_0 , as a shoulder on R_1 , with a peak at approximately -0.1 V . The R_1 and R_2 peaks also shifted slightly toward more negative potentials with successive sample additions. These voltammograms were very similar to those encountered with addition of K_3WF_8 described below.

An anodic current, Ox_1 , in the form of a stripping wave on the reverse

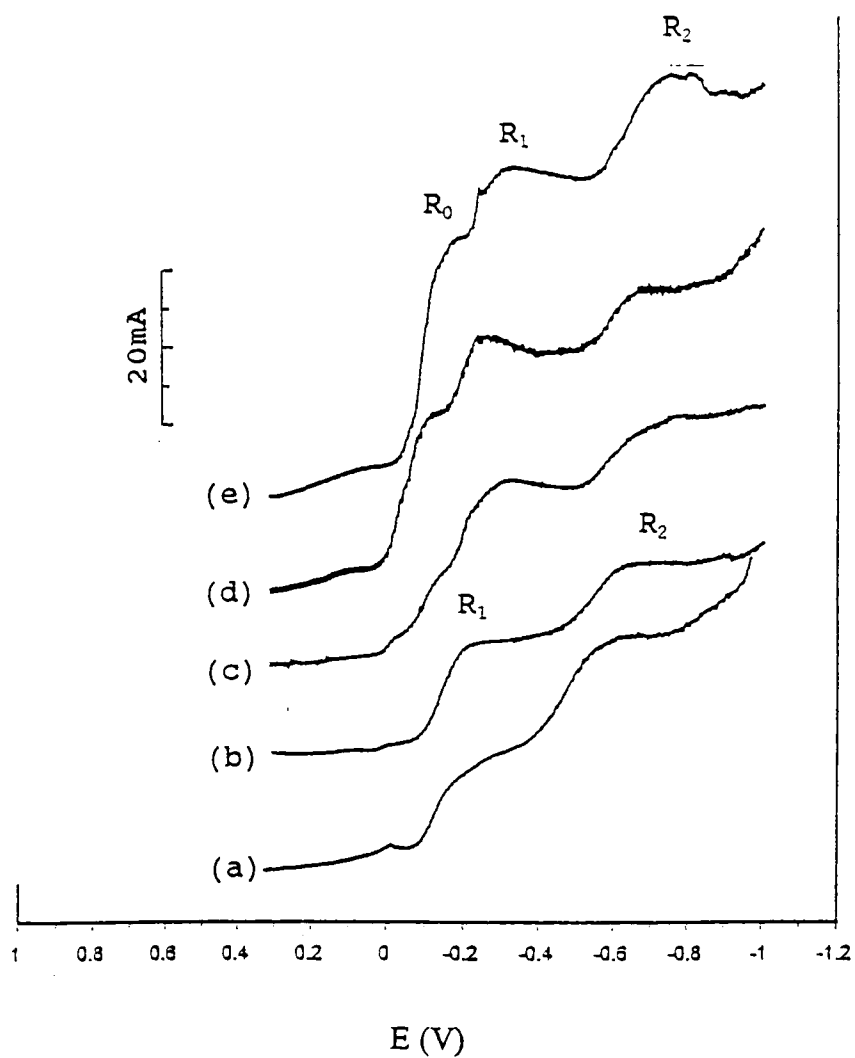


Figure 4.6. Reduction waves for K_2WF_8 in FLINAK at $730^\circ C$. $A_{pt} = 0.157 \text{ cm}^2$, scan rate = 100 mV/s . Molarity of tungsten species = a) 0.151 M , b) 0.303 M , c) 0.454 M , d) 0.605 M and e) 0.756 M .

sweep could also be seen (Figure 4.7, curve A1), corresponding to a species formed during the reduction process. Integration of the I-E curves showed an essentially equal number of coulombs for the reduction waves and corresponding oxidation waves (i.e. 152 mC and 148 mC respectively, Figure 4.7 curves B1 and A1), indicating oxidative stripping of some species reduced at the surface of the electrode. The number of electrons transferred for the reduction or oxidation step could not be gleaned from this experiment.

The peak at R_2 did not increase in proportion to the peak at R_1 upon successive additions of K_2WF_8 , but remained essentially the same height in relation to wave R_1 . This led to the conclusion that this peak was due to a species produced by the reaction of K_2WF_8 with an impurity in the melt, most likely oxide, or due to an oxide impurity in the addition compound. The latter case was supported by a Raman spectrum of the addition material, which revealed a small peak associated with a $W=O$ vibration at $\sim 990\text{ cm}^{-1}$. Since addition of an oxide impurity in the sample would cause the current at R_2 to increase in proportion to R_1 , the impurity is likely to have originated from the melt.

2.) Addition of oxide. Assignment of wave R_2 to reduction of an oxide-containing species was confirmed by successive additions of Na_2O to the melt containing the concentration of tungsten species seen in Figure 4.6e. Cyclic voltammograms collected after each oxide addition can be seen in Figure 4.7, where the peak at R_2 can be seen to increase to a maximum at an O^{2-}/K_2WF_8 ratio of 0.71. The peaks at R_0 and R_1 remained relatively unchanged until the

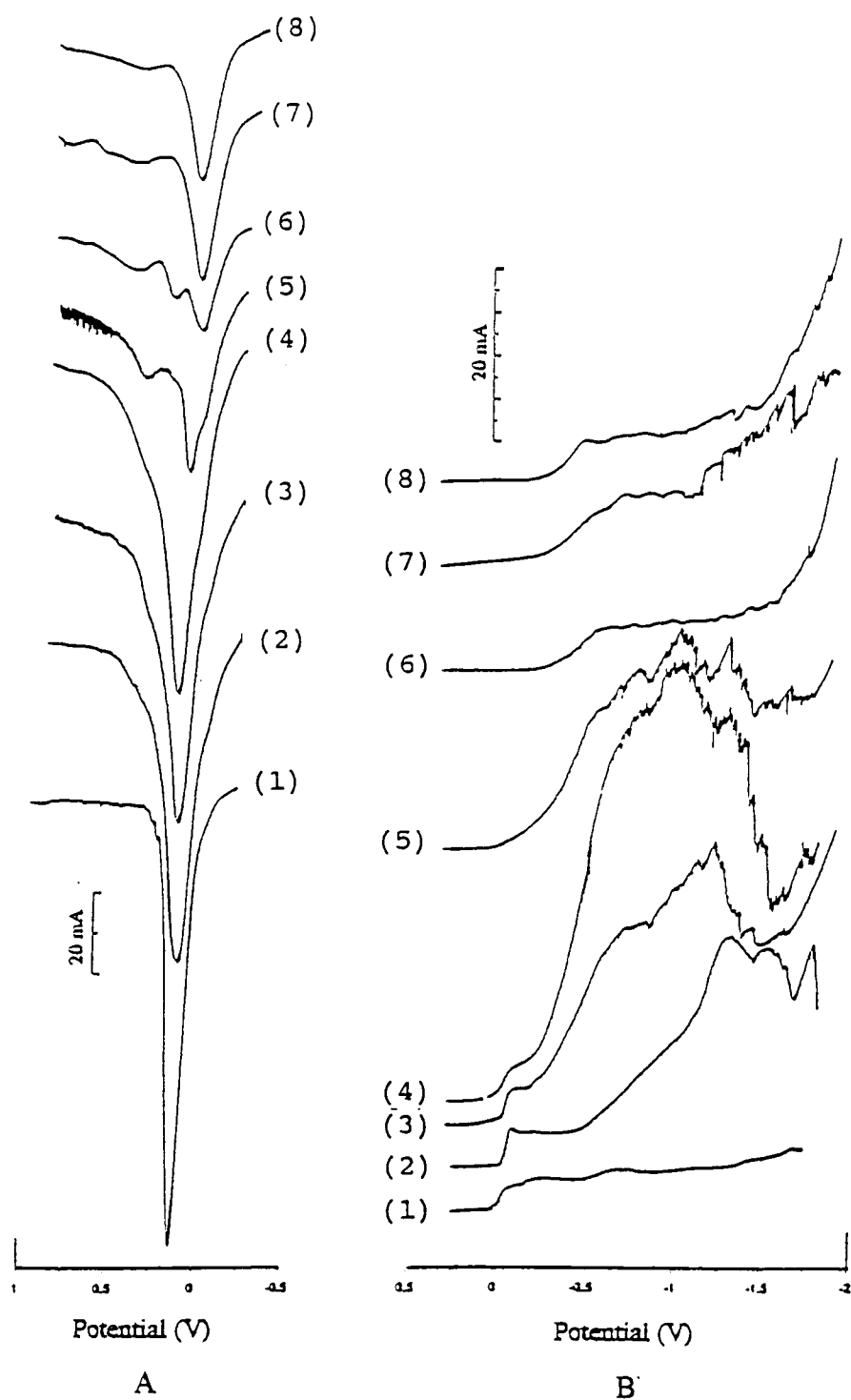
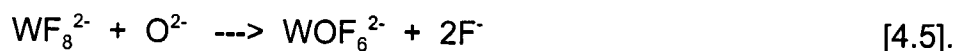
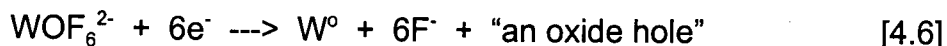


Figure 4.7. Oxidation (A) and reduction (B) waves for K_2WF_8 in FLINAK with addition of Na_2O . Mole ratio $O^{2-}/K_2WF_8 = 1)$ 0.0, 2) 0.177, 3) 0.444, 4) 0.170, 5) 0.95, 6) 1.32, 7) 1.61 and 8) 1.94. $A_{pt} = 0.157 \text{ cm}^2$, scan rate = 100 mV/s.

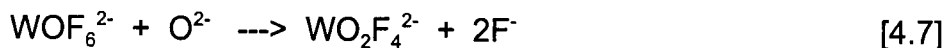
O^{2-}/K_2WF_8 ratio reached 1.0. The species present at this time was thought to be a mono-oxofluoro complex from the following displacement reaction



where the species WOF_6^{2-} gives rise to R_2 . The reduction to tungsten metal in this case would be as follows



where W^0 is metallic tungsten and the oxide hole is a discontinuity in the tungsten crystal. Above the 1.0 O^{2-}/K_2WF_8 ratio the two peaks began to disappear and were gradually replaced by a reduction wave at -0.4 V, when the O^{2-}/K_2WF_8 ratio approached 2.0. This suggested further ligand displacement according to the reaction



The anodic waves corresponding to the cathodic waves for the oxide addition are also shown. The stripping peak at 0.2 V remained until the O^{2-}/K_2WF_8 ratio reached 1.0, i.e., up to addition 4 and 5, the stripping wave can still be seen, although it is not as sharp or ideal. At O^{2-}/K_2WF_8 ratios greater than 1.0 the stripping peak at 0.2 V disappeared and was replaced by a peak at 0.1 V, which appeared initially as a very slight shoulder before oxide was added, and was associated with the reduction wave at -0.4 V. Addition of oxide above a ratio of 2.0 caused the elimination of the reduction peak altogether, leaving a continuously sloping curve until the solvent limit was reached. This may be due to the formation of an insoluble tungsten oxyfluoride.

3.) Cathodic deposition. A black deposit was obtained from an attempted deposition at -1.0 V for 60 seconds at 700°C from the melt that gave the cyclic voltammogram in Figure 4.6e (and Figure 4.7B1). The deposit was easily washed off with water, leaving behind the platinum metal. The presence of W metal on the electrode could not be detected from an ESCA spectrum. It should be noted that, upon completion of the electrolysis, the electrode was not immediately removed from the melt. This would allow the W(VI) species remaining in the FLINAK to react with any W metal deposited on the surface of the electrode, possibly producing low valent tungsten species at the surface, which would decompose upon exposure to moisture. The high reactivity of W(VI) with W(0) was not known at the time of the experiment, and since the sharpness of the oxidation wave suggests stripping of a W deposit, this could explain the absence of W in the ESCA spectrum.

b. Addition of KWF_6 and K_2WF_7 . The voltammograms of samples of KWF_6 and K_2WF_7 in FLINAK were the same as those seen for K_3WF_8 described below. This agreed with the finding that the Raman spectra of these compounds solidified in FLINAK had the same bands as K_3WF_8 as discussed above.

c. Addition of K_3WF_8 .

1.) Cyclic voltammograms. The addition K_3WF_8 to FLINAK at 600°C produced two distinct reduction waves (Figure 4.8) at a platinum wire working electrode. The first wave, R_1 , occurred between -50 and -200 mV, depending on the concentration of tungsten species; the second wave, R_2 , occurred between -400 and -550 mV. However, in many other instances the wave at R_2 could not

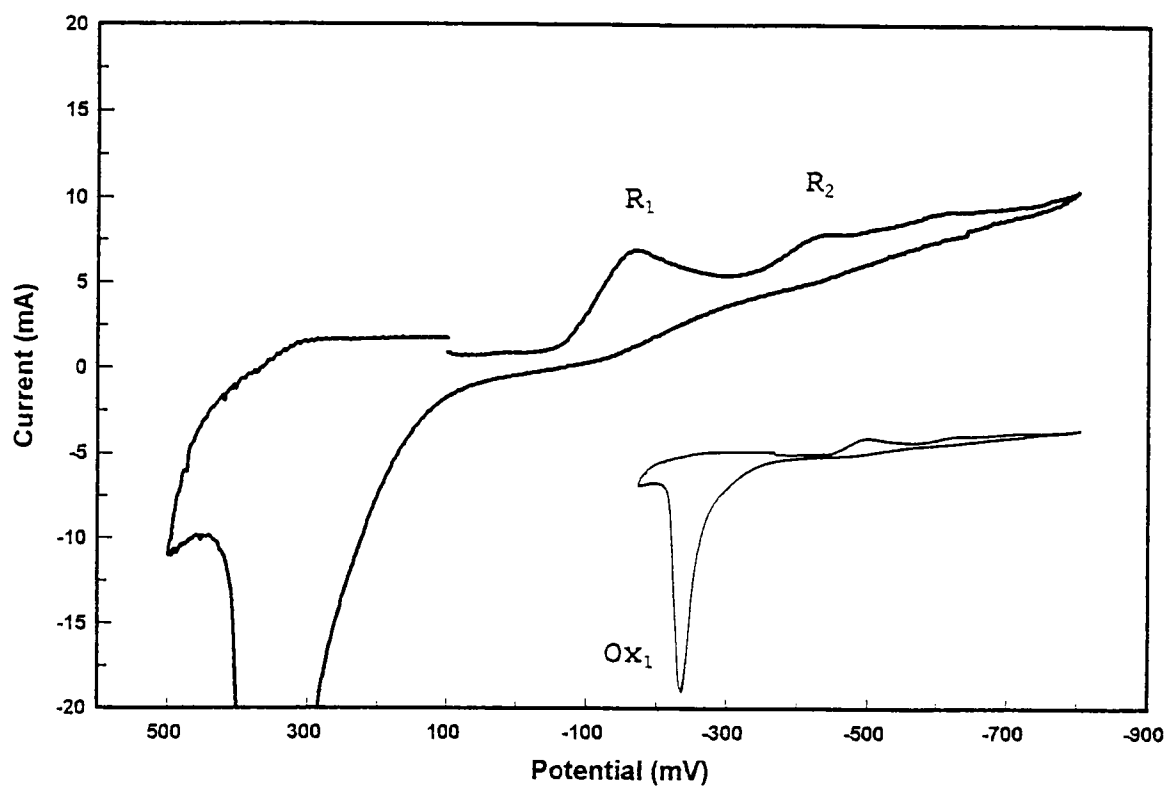


Figure 4.8. Cyclic voltammogram of K_3WF_8 in FLINAK, 540°C. $A_{Pt} = 0.157 \text{ cm}^2$, scan rate = 100 mV/s, Pt quasi-reference electrode, glassy carbon crucible counter electrode.

be seen, or was greatly diminished, and so was thought to be associated with a reaction with a contaminant in the system.

An anodic current could also be seen in the 300 to 400 mV range which appeared to be a stripping wave due to the sharply peaked current response. The stripping wave appeared at a potential that was ca. 100-200 mV more positive than seen in Figure 4.7. However, neither the cathodic nor anodic peak currents appeared at a stable potential, so some standard additions of K_3WF_8 were performed followed by voltammetry after each addition in order to establish the waves associated with the species produced from this compound in the molten FLINAK. The reason for this lack of reproducibility may be related to the platinum flag used as a quasi-reference electrode, which can become spoiled by surface contaminants that change the activity of the electrode, which in turn changes the reference potential.

Figure 4.9 shows reduction waves from cyclic voltammograms at increasing concentrations of K_3WF_8 at 536°C in FLINAK, in which the oxide concentration was less than 12 ppm. Note the decreased intensity of the R_2 wave in these voltammograms. The R_1 waves shown in Figure 4.9 reveal a shift of the peak toward more negative potentials with increasing K_3WF_8 concentration. However, the peak potential is expected to shift toward positive potentials with increasing concentration for a reversible deposition process (53). This suggests some possible quasi-reversible or irreversible character to the process. The current response of the wave from each sample addition traced the same path until the current limit for the previous concentration was reached.

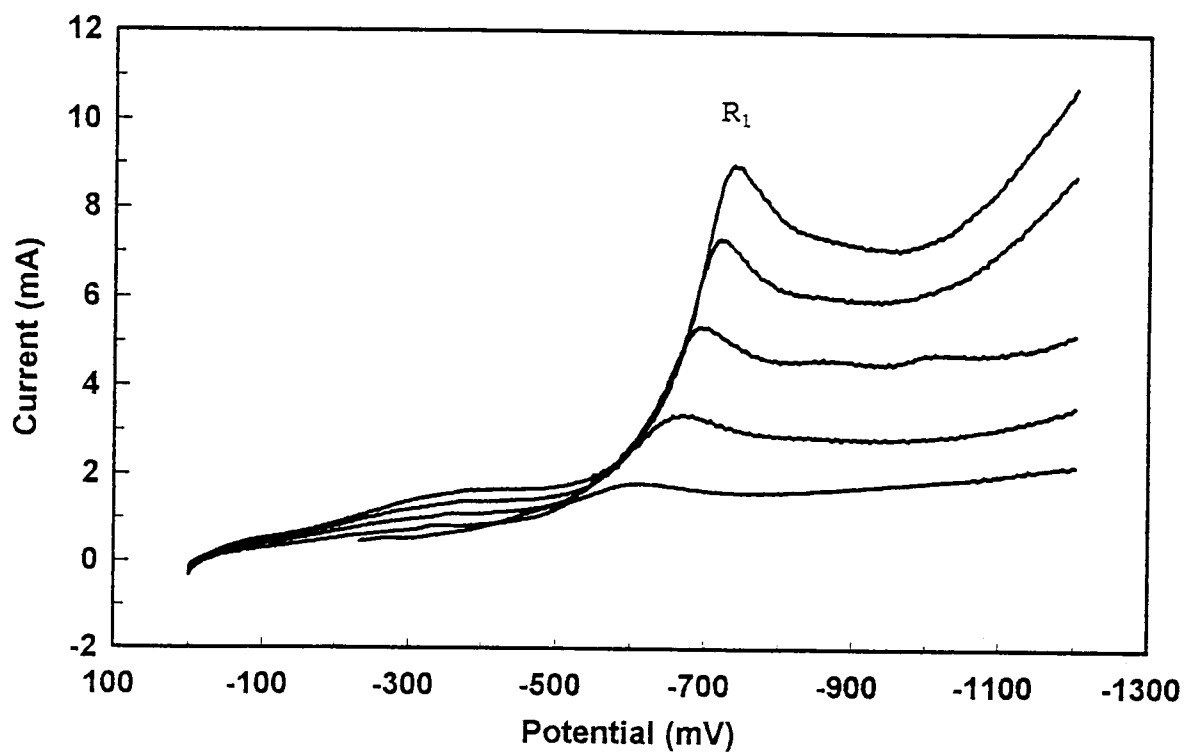


Figure 4.9. Reduction waves in FLINAK with increasing K_3WF_8 concentration. 536°C, platinum working electrode ($A = 0.157 \text{ cm}^2$), platinum quasi-reference, glassy carbon counter electrode. Scan rate = 100 mV/s.

This phenomenon was not clearly understood, although the peak current for wave R_1 was linear with increasing concentration with a slope of 3.52 ± 0.08 mA/mmol.

When the R_2 wave was present, it did not increase in proportion to the R_1 wave with an increase in concentration. This suggested a reaction of the species reduced at wave R_1 with some contaminant in the melt, which would decrease the concentration of K_3WF_8 and form the species reduced at R_2 . This can be seen by the current for wave R_1 in Figure 4.10 at 0.5 mmol added K_3WF_8 . The point corresponding to this first sample addition does not conform to the linear current response obtained at higher concentrations. The contaminant in this case was thought to be oxide, forming a tungsten oxyfluoride, i.e.,



Upon successive additions of K_3WF_8 , the current response for R_2 did not change in relation to wave R_1 , indicating a one time (or possibly equilibrium) formation of the species reduced at wave R_2 . The current at wave R_2 then "rides" the current at wave R_1 . Other experiments with the same compound in some of what was found to be the purest FLINAK by oxide analysis showed the linear slope of the current at wave R_1 to pass through the origin, with no effect from contaminants on the first sample addition. Wave R_2 could not be seen in this case. For this reason, the study of the electrochemistry was focused on wave R_1 .

At temperatures above 675°C a wave, R_0 , at the foot of wave R_1 appeared and increased with increasing temperature (Figure 4.11). This wave was thought to be reduction of a WF_7^{2-} species from the temperature induced equilibrium

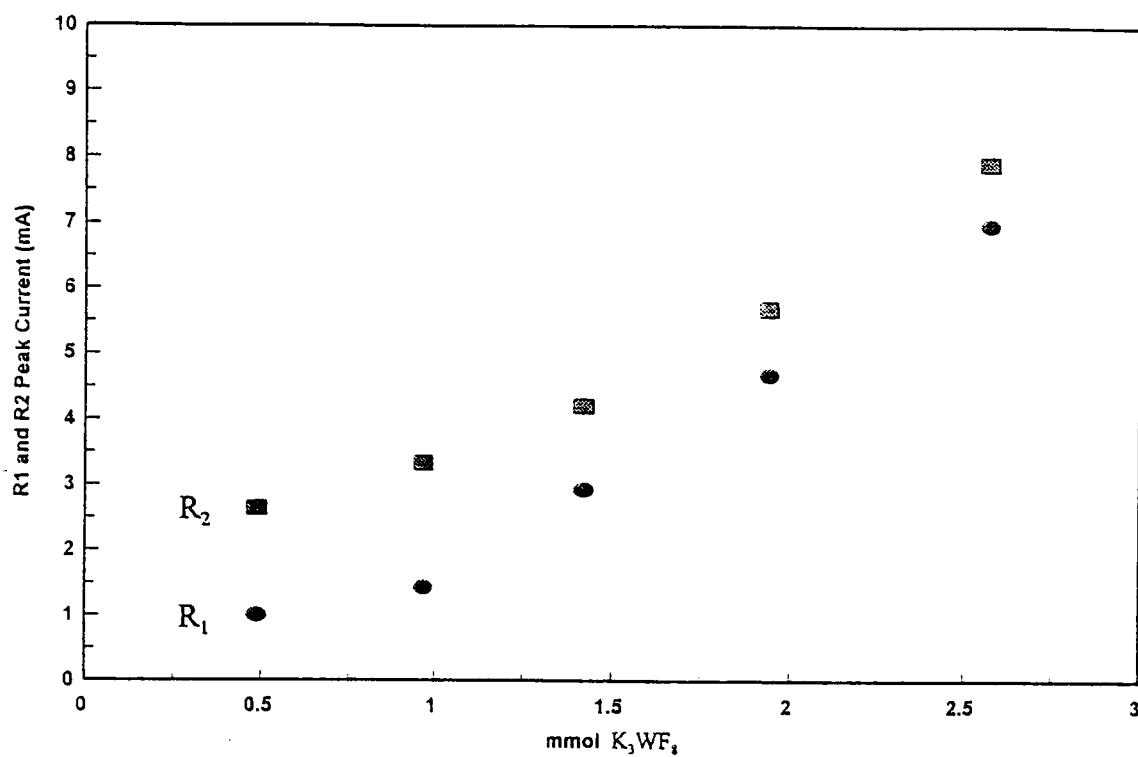


Figure 4.10. Variation in waves R_1 and R_2 with increasing K_3WF_8 concentration.

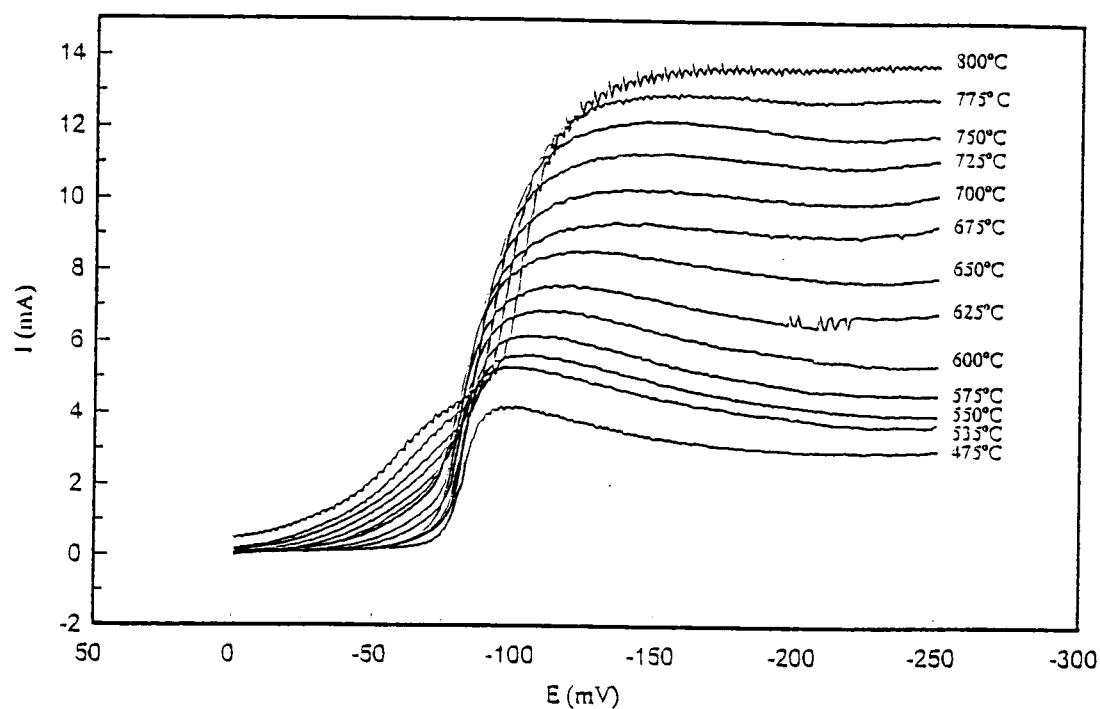


Figure 4.11. Voltammograms showing the effect of increasing temperature. 475 to 800°C. $A_{\text{Pt}} = 0.157 \text{ cm}^2$, $C_{\text{W(V)}} \text{ (at } 500^\circ\text{C)} = 5.20 \times 10^{-5} \text{ M}$ (0.0990 mol%), scan rate = 100 mV/s.



with WF_8^{3-} being preferred at lower temperatures. However, another possible interpretation arises from the approximate height difference of waves R_0 and R_1 , which appear to be in a 2:3 ratio. This could indicate reduction of a W(V) species to W(III) at wave R_0 , followed by a reduction of W(III) to W(0) at wave R_1 . This would agree with the finding that, with tungsten metal present as a reductant, W(V) and W(III) exist in equilibrium in FLINAK. An inconsistency with this particular interpretation is the observation that, when the potential was swept in stages into the wave at R_0 , the resultant oxidation wave on the reverse sweep had the appearance of a stripping wave. This indicates deposition on the electrode surface rather than a wave controlled by diffusion of an electroactive species to the surface of the electrode, such as $\text{W(III)} \rightarrow \text{W(V)} + 2\text{e}^-$.

In the following discussions, the waves at R_0 and R_1 will be considered to consist of the reduction of W(V) to W(0) in a single five electron step at R_1 in order to simplify the quantitative analysis of the voltammetry.

ΔE_p . The peak potential separation of a specific redox couple, $\Delta E_p (=|E_{p,c} - E_{p,a}|)$, is an indicator of the reversibility of a process. For Nernstian reactions the following equation is used (54)

$$\Delta E_p \cong 2.3RT/nF \quad [4.10].$$

At 500 and 700°C the peak separation should be 153/n mV and 193/n mV, respectively, or considering a five-electron reduction 30.6 and 38.6 mV, respectively, for a wave exhibiting Nernstian behavior. However, at higher

temperatures, four oxidation waves could be seen, Ox₁ - Ox₄, and two reduction waves, R₀ and R₁. Cyclic voltammograms for the reduction and oxidation waves at 475, 600, 700 and 800°C can be seen in Figure 4.12. The peak potentials at temperatures ranging from 475 to 800°C are tabulated in Table 4.1. The R₀ peak potentials were estimated since the wave appears as a shoulder on wave R₁. Due to the multiplicity of oxidation waves, assignment of reduction and oxidation waves to specific redox couples could not be performed. The peak potential separation between R₁ and all of the oxidation waves was much greater than expected for a five-electron reduction, the lowest being 136 mV. The peak potential separation was within range for R₀ and Ox₄, and Ox₄ did begin to appear when R₀ appeared, but it is not wise to make any meaningful comparisons between them since R₀ appeared as a shoulder and did not have a well-defined peak potential.

Reversible and irreversible diffusion coefficients. The peak current, i_p , for a reversible deposition process is described by the equation (53)

$$i_p = (6.35 \times 10^6) T^{-1/2} n^{3/2} A C^0 D^{1/2} \nu^{1/2} \quad [4.11]$$

where T is the temperature in Kelvin, n the number of electrons transferred, A the electrode area in cm², C⁰ the bulk concentration in mol/cm³, D the diffusion coefficient in cm²/s, ν the scan rate in V/s, and i_p in amperes. Assuming a five-electron transfer for wave R₁, the average value for the diffusion coefficient calculated at different concentrations at 700°C was $2.66 \times 10^{-6} \pm 0.15$ cm²/s. The peak current for an irreversible deposition process is described by another equation which considers sluggish electrode kinetics (53):

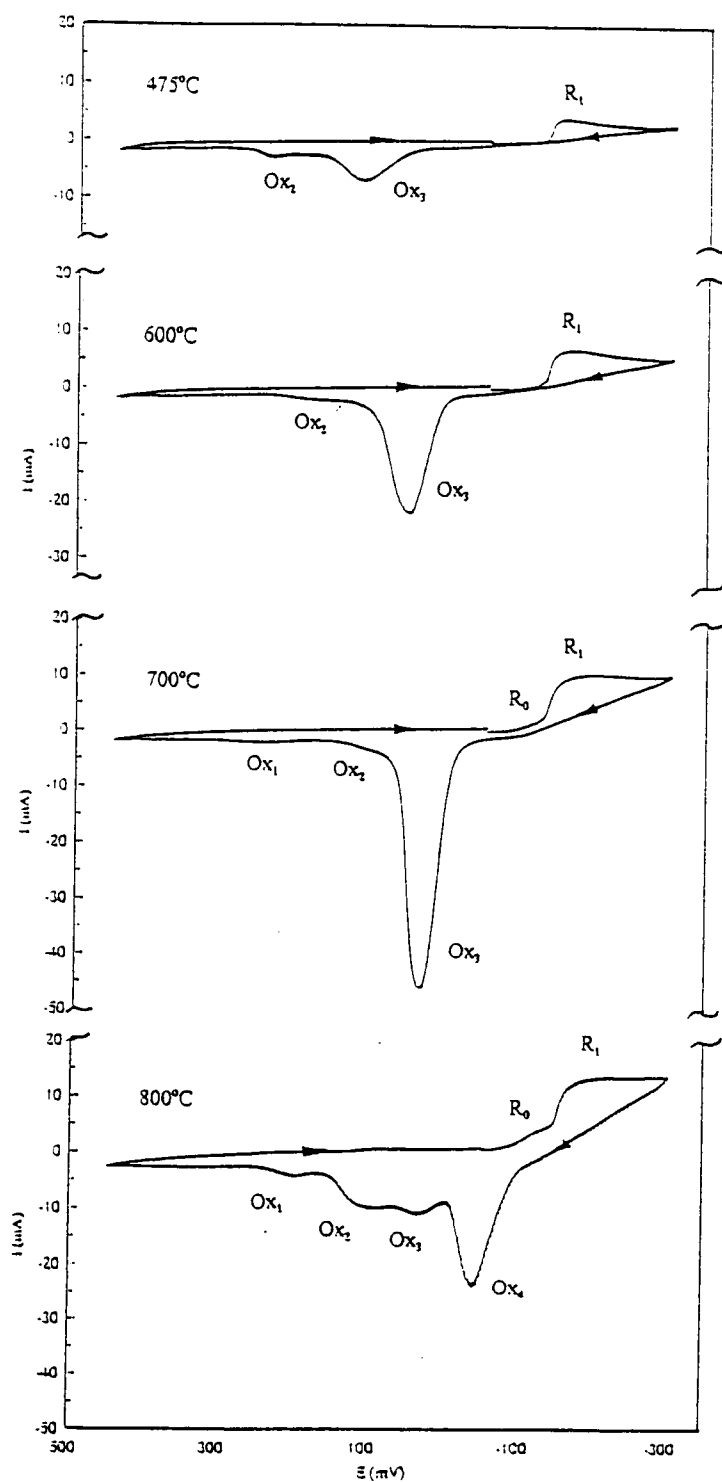


Figure 4.12. Reduction and oxidation waves for K_3WF_8 in FLINAK at $T = 475$, 600, 700 and 800°C. $A_{pt} = 0.157 \text{ cm}^2$, $C_{K_3WF_6} = 0.0520 \text{ M}$ at 500°C (0.0990 mol%), scan rate = 100 mV/s.

Table 4.1. Values for E_p in mV for cathodic and anodic waves from 475 to 800°C. Scan rate = 100 mV/s, platinum wire working electrode ($A = 0.157 \text{ cm}^2$), platinum flag reference electrode.

T (°C)	R_0	R_1	Ox_1	Ox_2	Ox_3	Ox_4
475	---	-90	---	251	122	---
535	---	-95	---	183	104	---
550	---	-103	---	151	92	---
575	---	-105	---	152	80	---
600	---	-110	---	175	61	---
625	---	-115	---	150	59	---
650	---	-123	---	128	53	---
675	---	-135	275	110	51	---
700	---	-139	250	110	46	---
725	-70	-148	230	110	40	12
750	-75	-150	220	110	25	-5
775	-75	-159	210	110	32	-11
800	-75	-170	200	110	30	-32

$$i_p = (5.16 \times 10^5) T^{-1/2} n(\alpha n_a)^{1/2} A C^0 D^{1/2} \nu^{1/2} \quad [4.12]$$

where α is the transfer coefficient and n_a the number of electrons involved in the rate determining step. Assuming $\alpha n_a = 0.5$ and $n = 5$, the average diffusion coefficient calculated using this equation was $4.01 \times 10^{-5} \pm 0.24 \text{ cm}^2/\text{s}$ at 700°C . Polyakova and coworkers (16) applied this same equation to the tantalum deposition process, which they found to be irreversible at scan rates above 500 mV/s. They found the temperature dependence of the diffusion coefficient for the tantalum species, TaF_7^{2-} , follows the equation

$$\log D = -2.55 - 2044/T \quad [4.13],$$

which at 700°C is $2.23 \times 10^{-5} \text{ cm}^2/\text{s}$. This is consistent with the irreversible case for the tungsten deposition.

$|E_p - E_{p/2}|$ parameter. Electrode processes can also be described by the difference between the peak (E_p) and half-peak ($E_{p/2}$) potentials from a linear sweep voltammogram (LSV) according to the following equations (53)

$$|E_p - E_{p/2}| = 0.770 RT/nF \quad [4.14]$$

for a reversible deposition process and

$$|E_p - E_{p/2}| = 1.857 RT/\alpha n_a F \quad [4.15]$$

for an irreversible deposition process, where the parameter R is 8.314 V•Coul/mol•K, T the temperature in Kelvin, and F the Faraday constant (=96485 Coul/equivalent). However, the reduction peaks did not have the appearance of well-defined diffusion-controlled processes, especially at temperatures above $\sim 600^\circ\text{C}$. The experimental $|E_p - E_{p/2}|$ values at temperatures from 475°C to 800°C were obtained from the voltammograms seen in Figure 4.11. A plot of

these values along with the theoretical $|E_{p/2} - E_p|$ values obtained from reversible and irreversible deposition processes, assuming $n=1$ and $\alpha n_a=0.5$, respectively, is shown in Figure 4.13 where the experimental and (theoretical) reversible $|E_{p/2} - E_p|$ values can be seen to converge above $\sim 675^\circ\text{C}$.

Reversible deposition model. The theoretical curve resulting from a reversible deposition process was solved by Berzins and Delahay (55) who gave the current as

$$i = (2n^{3/2}F^{3/2}/\pi^{1/2}R^{1/2}T^{1/2})AC^0D^{1/2} \nu^{1/2} \Phi[(\sigma t)^{1/2}] \quad [4.16]$$

where $\sigma = nF\nu/RT$ and t is the time in seconds. At 25°C , Φ reaches a maximum and gives equation 4.11. Figure 4.14 shows a comparison of the theoretical curve at 475°C to the experimentally obtained curve for wave R_1 . The wave at 475°C was chosen since there was no significant current associated with wave R_0 as seen at the higher temperatures ($> \sim 600^\circ\text{C}$), and the peak was more well-defined. The general shape of the experimental curve indicated some association with a reversible deposition process, but the experimental curve had some current at the foot of the wave which would not be expected for a reversible deposition. There was also some tailing of the decay current, but this was thought to be associated with convection due to thermal gradients.

Activation energy of diffusion. A diffusion controlled process is indicated by a slope of 0.5 from a plot of $\log I_p$ vs. $\log \nu$. However, Maestre and coworkers (56) showed that for simple nucleation waves a plot of $\log I_p$ vs. $\log \nu$ should have a slope of 0.6, and a plot of $\log E_p$ vs. $\log \nu$ should have a slope of 0.4 for a two-dimensional phase-change process. Plots of $\log i_p$ vs. $\log \nu$ for

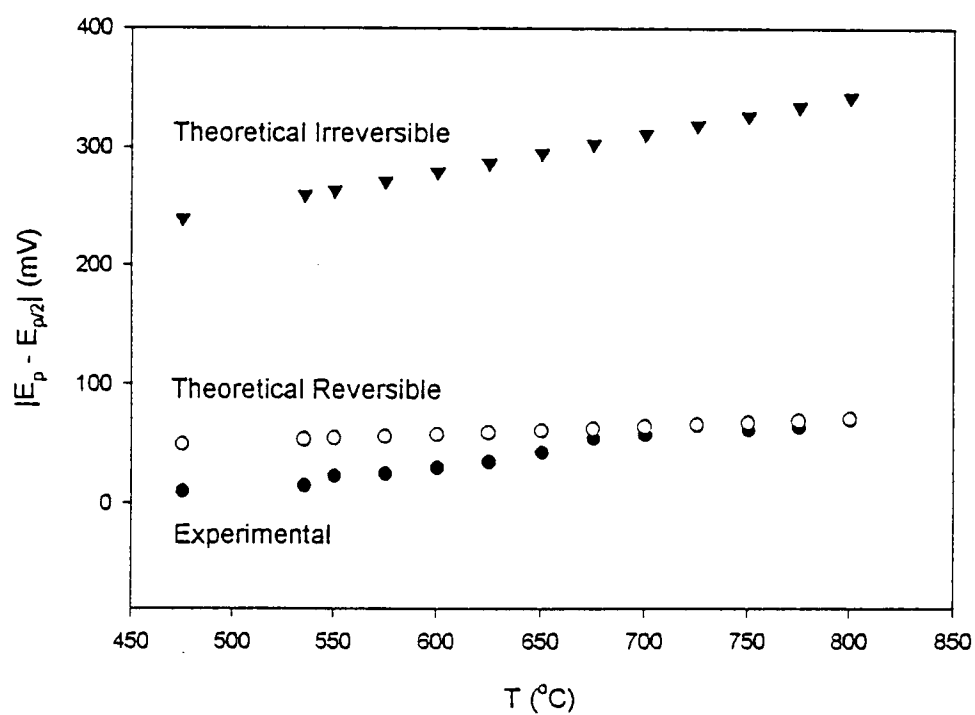


Figure 4.13. Experimental variation of $|E_p - E_{p/2}|$ with increasing temperature for K_3WF_8 in FLINAK. The theoretical reversible and irreversible responses are shown for comparison.

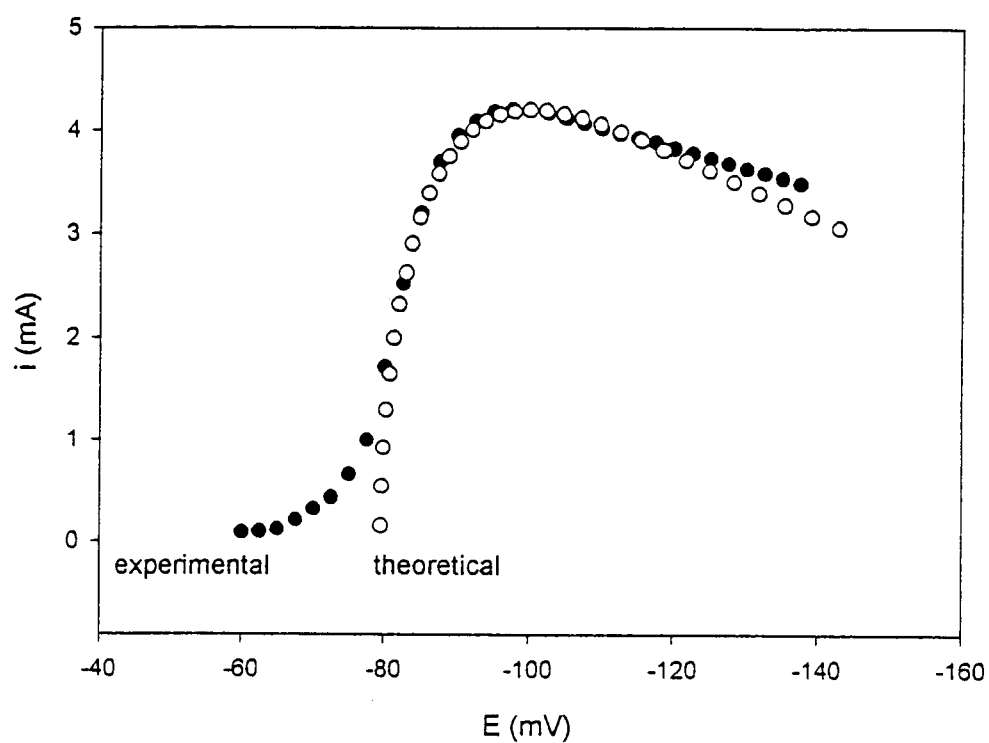


Figure 4.14. Comparison of an experimental voltammogram for wave R_1 (K_3WF_8 in FLINAK, 475°C, 100 mV/s scan rate) with a theoretical voltammogram for a reversible deposition process.

wave R_1 at 500°C and 700°C can be seen in Figure 4.15a with slopes 0.489 and 0.443 respectively. Plots of $\log E_p$ vs. $\log v$ were not linear (Figure 4.15b). In this case, assuming near diffusion control, the activation energy (E_{act}) of diffusion can be extracted from the temperature dependence of the peak current (i_p) from the following equation (54) for an irreversible reaction

$$i_p = 0.496T^{1/2}nFAC^0v^{1/2}(\alpha_n F/R)^{1/2}D^{1/2} \quad [4.17]$$

where C^0 is the bulk concentration of the electroactive species, α_n is a dimensionless kinetic parameter, A the area of the electrode in cm^2 , and D the diffusion coefficient in cm^2/s . Assuming n , A , α_n , and C^0 are constant and rearranging we have

$$i_p T^{1/2} = \text{constant} \cdot D^{1/2} \quad [4.18].$$

Obtaining the natural logarithm of equation 4.6 after substituting $D^0 e^{-E_{act}/RT}$ for D yields the following equation

$$\ln i_p T^{1/2} = \ln (\text{constant}) - E_{act}/2RT \quad [4.19]$$

from which E_{act} can be extracted by obtaining the slope from a plot of $\ln i_p T^{1/2}$ vs. T^{-1} . Figure 4.16 shows plots from 525 to 800°C for $i_p T^{1/2}$ vs. T^{-1} for two separate experiments. The activation energies calculated from the slopes of these plots were 41.7 ± 1.4 kJ/mole and 58.9 ± 1.4 kJ/mole. Activation energies obtained by Polyakova and coworkers (16) for the tantalum deposition process from the TaF_7^{2-} and TaOF_5^{2-} species in FLINAK were similar at 39.1 and 43.9 kJ/mol, respectively.

Slopes of E_p vs. $\log v$. When the slope of the linear portion of the plot of $-E_p$ vs. $\log v$ was obtained, as seen in Figure 4.17, the α_n values at 500°C and

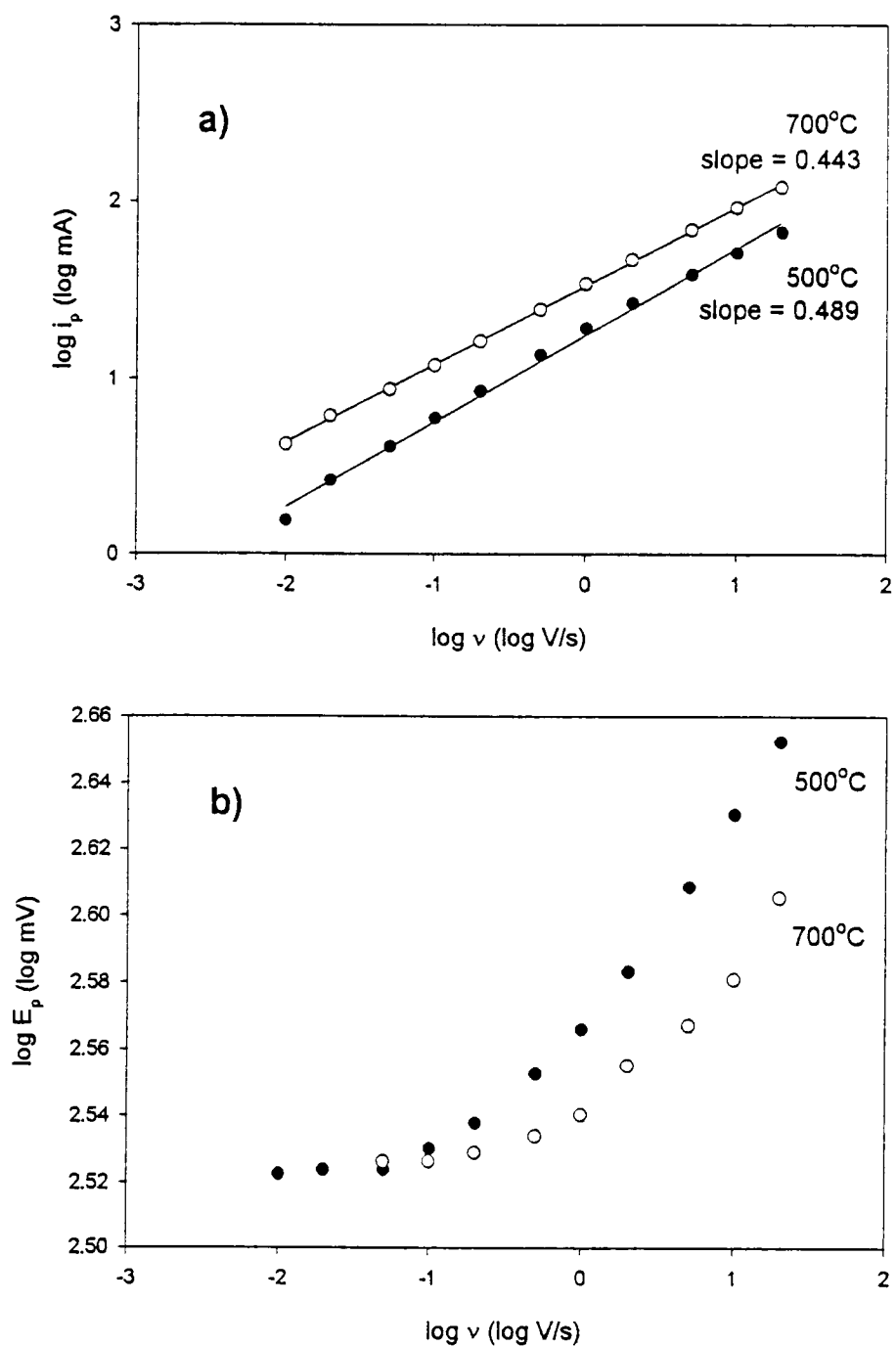


Figure 4.15. a) Variation of $\log i_p$ with $\log v$ and b) variation of $\log E_p$ with $\log v$ at 500 and 700°C. Platinum working electrode, platinum quasi-reference, glassy carbon counter electrode.

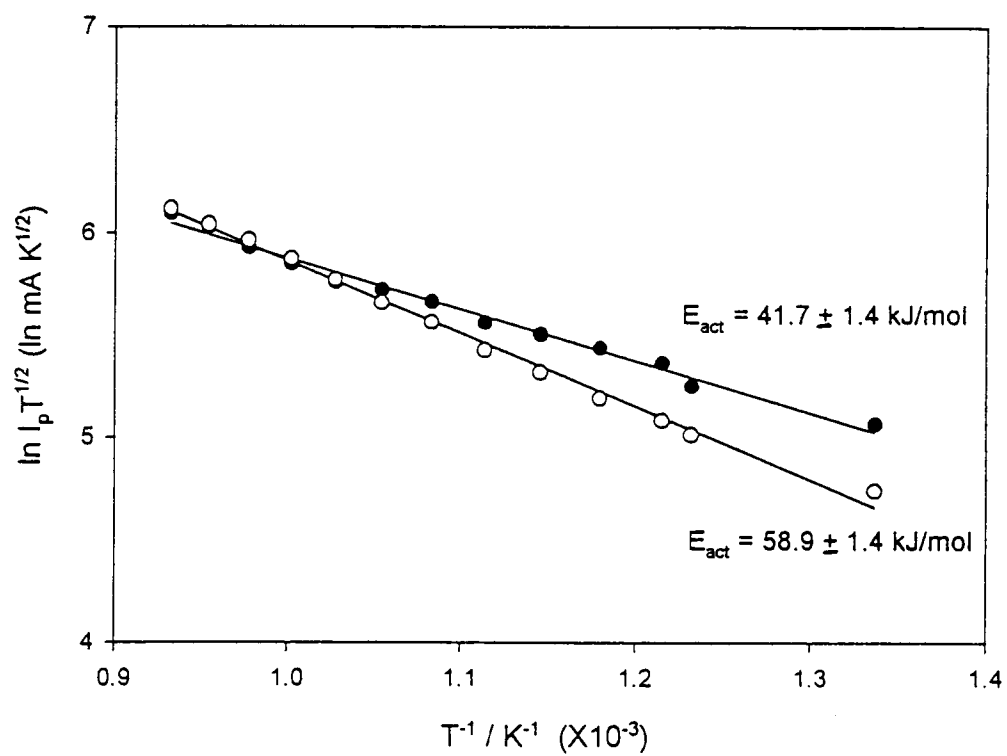


Figure 4.16. Variation of $\ln I_p T^{1/2}$ with T^{-1} for $T = 475$ to 800°C . $\text{SR} = 100 \text{ mV/s}$.

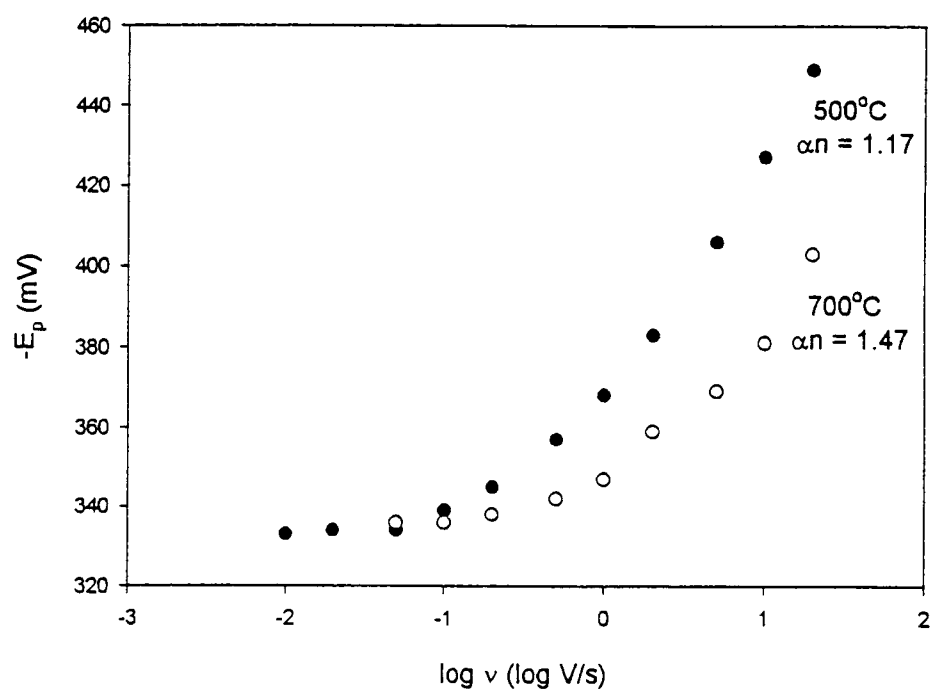


Figure 4.17. Variation of E_p with $\log v$ at 500 and 700°C.
 $A_{pt} = 0.157 \text{ cm}^2$, 0.013 mol% K_3WF_8 in FLINAK.

700°C were 1.17 and 1.47, respectively, using the equation (53)

$$K = 2.303 RT/2\alpha n_a F \quad [4.20]$$

where K is the slope. Since αn_a should be less than 1.0, it can be deduced that the shape of the waves is affected by more than simple diffusion. It is thought that nucleation (the formation and growth of crystallization sites), and to a lesser extent convection, play a role in the reduction process as well. However, the increasing slope of the curves in Figure 4.17 indicates a transition from diffusion to activation control of the electrode process at sweep rates between 0.1 to 1 V/s.

Coulometry. In order to further characterize the number of electrons transferred in the wave at R_1 , a coulometric experiment was performed in which the potential at a large surface area electrode (11.1 cm²) was stepped beyond the peak at R_1 for a predetermined time to reduce a large portion of the electroactive species. Cyclic voltammograms were obtained before and after the coulometric potential step. The difference in the peak currents at wave R_1 for these two voltammograms was then related to a linear plot of current vs. species concentration, which indicated the quantity of species reduced at wave R_1 . This quantity could then be related to the number of coulombs of charge passed on a chronoamperogram obtained during the reduction step, and hence the number of electrons transferred could be calculated.

These experiments, which did not give definitive results, were complicated by the instability of the reference electrode potential. However, the cyclic voltammograms before and after the electrolysis step were not significantly

shifted from one another, so the actual potential was not considered to have drifted significantly from the applied potential. Another problem was the reaction of the anode oxidation product with the species being reduced at the cathode, reforming the original species. The oxidation product could not be isolated from the reduction product since it was the main current carrier. This produced a variety of results for the number of electrons transferred for the wave at R_1 , none of which gave a definitive answer. The experimental "n-values" ranged from 1.4 to 5.5 mole e^- per mole W.

Pulse voltammetry. A series of chronoamperometric experiments was performed to obtain a comparison of the number of electrons transferred for the waves at R_1 and R_2 . The Cottrell plots for the slope of the chronoamperogram (displayed as I vs. $t^{1/2}$) curves were plotted against the applied potential (Figure 4.18) to mimic a pulse voltammetry experiment. The applied potential was stepped in 50 mV increments while allowing the cell contents to re-establish equilibrium at open circuit after each potential step. The chronoamperograms, however, exhibited a second linearly sloping region when potentials associated with the wave at R_1 were reached, rather than one clear slope. The first slope, when plotted, reached a steady state of $\sim 12.2 \text{ mA}\cdot\text{s}^{1/2}$ when the potential steps were in the region for the waves at R_1 and R_2 , and was considered to be part of the background current. The second slope increased rapidly to a plateau of $\sim 49.8 \text{ mA}\cdot\text{s}^{1/2}$, associated with R_1 , followed by a second plateau at $\sim 58.2 \text{ mA}\cdot\text{s}^{1/2}$, associated with R_2 . Measurement of the first plateau from the background current, and the second plateau from the first plateau, suggested the

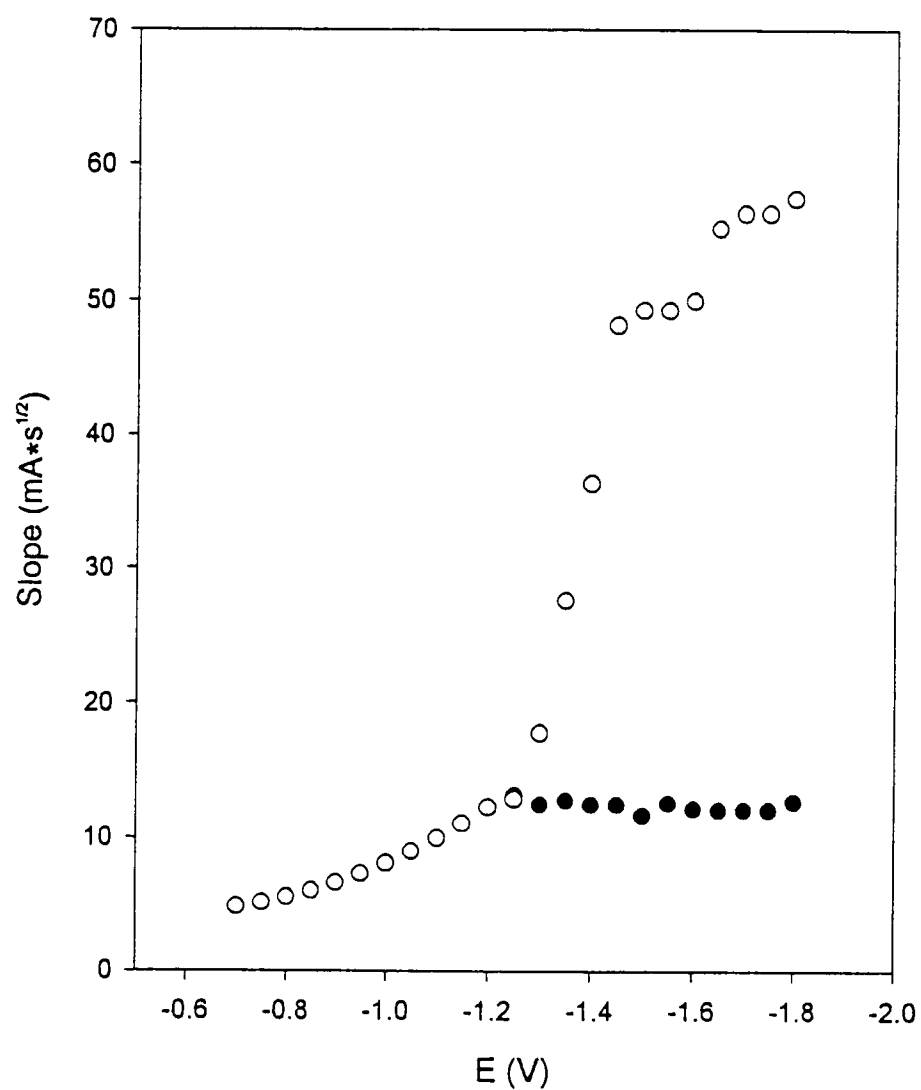


Figure 4.18. Slopes (vs. E) obtained from a plot of I vs. $t^{1/2}$. Temperature = 700°C , $A_{\text{pt}} = 0.157 \text{ cm}^2$, 0.05 V increments, $9.08 \times 10^{-2} \text{ M}$ in K_3WF_8 .

ratio of wave R_1 to wave R_2 was 4.5. Most likely this reflects the concentration ratios between the two species, and is consistent with the assignment of the R_2 wave to reduction of a $W(V)$ species possessing a coordinated oxygen ligand.

2.) Effect of oxide. Cyclic voltammograms were also taken of the WF_8^{3-} species in the FLINAK over several days to show any decay in the material. Cyclic voltammograms at 0, 3, 20 and 70 hours elapsed time are shown in Figure 4.19 where a peak, R_2 , at -500 mV can be seen to increase with time. This was thought to be due to contamination by oxygen slowly leaking into the electrochemical cell. The wave at R_1 shows a significant decrease in current corresponding to an increase in the wave at R_2 . The number of coulombs for this wave at R_2 was nearly twice as large as the loss of coulombs for the wave at R_1 , so some contribution to the decay product from the wave at R_2 was assumed. Addition of oxide to a fresh batch of K_3WF_8 in FLINAK gave the same peak as the wave at R_2 (Figure 4.20), showing that the decay was indeed due to oxide contamination.

3.) Electrodeposition. An electroplating experiment was performed from a bath consisting of 0.3 M K_3WF_8 in FLINAK at 750 °C by applying a -0.30 V potential step for 300 seconds at a 1.0 cm X 1.0 cm platinum foil cathode. When the electrode was removed, a black deposit was observed which formed bubbles when immersed in 1:1 HCl. Once free of the black deposit an ESCA spectrum indicated the presence of tungsten on the surface of the electrode. As can be seen in Figure 4.21, no other lines apart from copper and oxygen (due to the retaining clips of the sample holder) were evident in the spectrum.

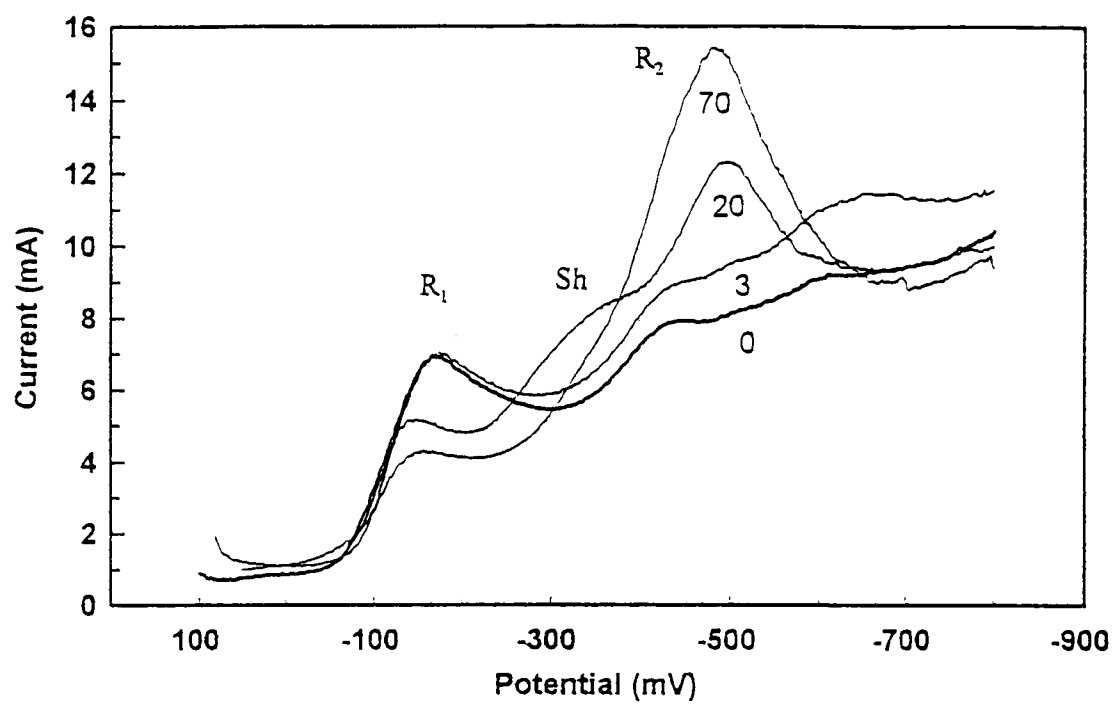


Figure 4.19. Reduction waves for K_3WF_8 in FLINAK after 0, 3, 20 and 70 hours elapsed time. Sh = shoulder.

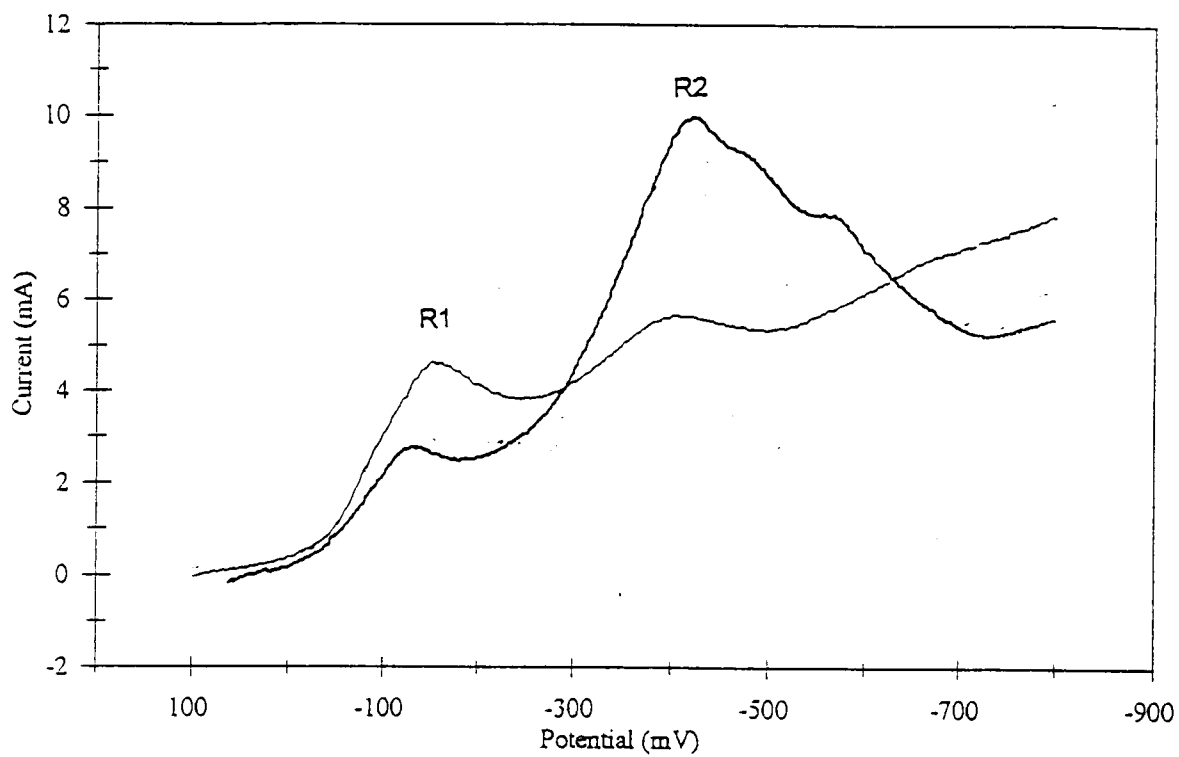


Figure 4.20. Change in waves R_1 and R_2 with addition of oxide. K_3WF_8 in FLINAK, 700°C . $A_{Pt} = 0.157 \text{ cm}^2$, scan rate = 100 mV/s . O^{2-}/K_3WF_8 ratio = a) ~ 0.0 , b) 0.76 .

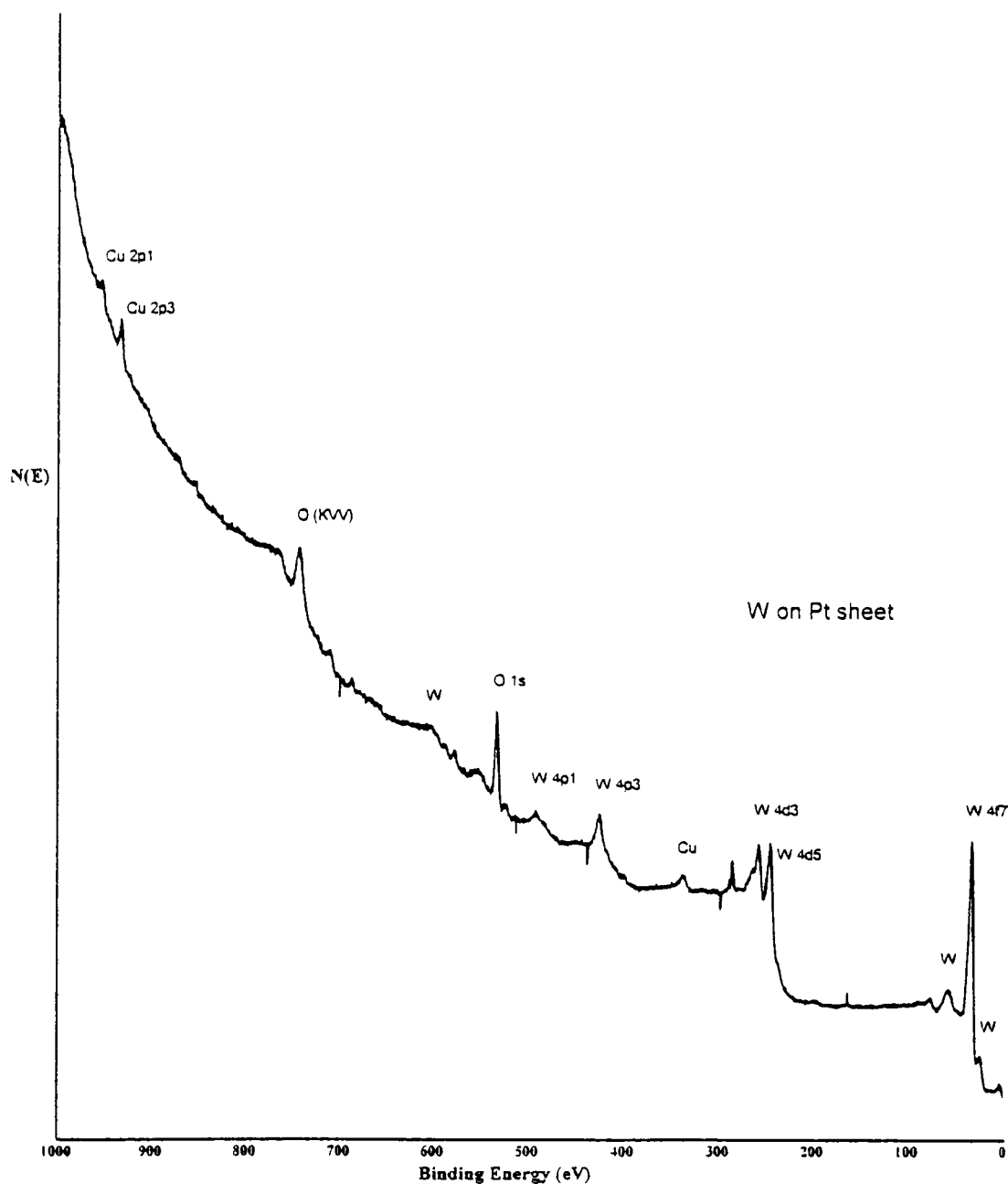


Figure 4.21. ESCA spectrum of tungsten deposit on platinum foil electrode. No evidence for platinum can be seen, indicating complete coverage by tungsten. EV/s = 0.5, Time/Step = 50 ms, Source = Mg, Work Function = 4 eV, Pass Energy = 178 eV.

d. Addition of the K_3WF_8 / K_3WF_6 mixed brown material.

1.) Cyclic Voltammograms. Cyclic voltammetry was performed on a mixture of 74.28 g of FLINAK combined with 0.9659 g of the K_3WF_8 / K_3WF_6 crystalline mixture. The cyclic voltammograms exhibited two or three poorly defined reduction waves. In Figure 4.22 B, 0.0% oxide, a shoulder appears between the waves labeled R_1 and R_2 . The corresponding anodic sweep revealed a well-defined stripping peak, Ox_2 , at +390 mV with a small shoulder, Ox_1 , at about +200 mV (Figure 4.22 A, 0.0% oxide).

Tentative wave assignments are given with wave R_1 thought to be associated with the species that gave rise to wave R_1 when K_3WF_8 was added to the melt (see Figure 4.8), i.e., the reduction of the WF_8^{3-} species. The shoulder on R_1 was thought to be the reduction of the WF_6^{3-} species and wave R_2 was thought to be associated with an oxide species. Although wave R_2 did seem to disappear with added oxide, this was difficult to determine since the voltammogram had a continuous upward slope. This behavior is similar to the results described above when oxide was added to the melts containing K_3WF_8 .

2.) Addition of oxide. When the same melt was titrated with Na_2O , the cyclic voltammograms (Figure 4.22, curves 2-4) showed a decrease in wave R_1 with each oxide addition. The shoulder on wave R_1 did not immediately decrease at the same rate as wave R_1 , but could not be seen when the oxide/tungsten species ratio reached 0.65.

The anodic waves shifted toward more positive potentials with increasing oxide concentration, until a 1:1 mole ratio of oxide to tungsten species was

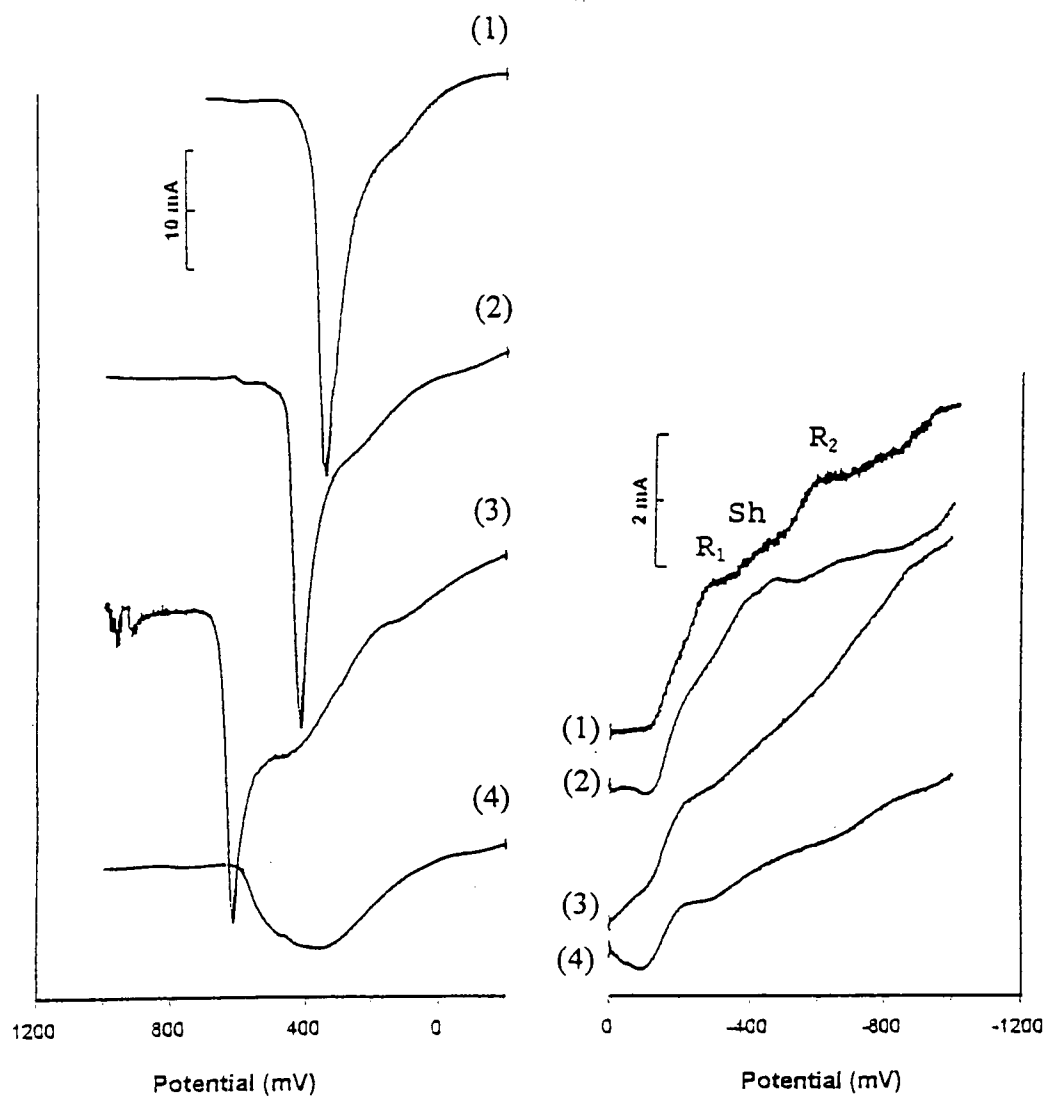


Figure 4.22. Oxidation (left) and reduction (right) waves of the K_3WF_8/K_3WF_6 mixture in FLINAK with addition of Na_2O . A) anodic waves and B) cathodic waves at O^{2-}/W species mole ratio (1) 0.0, (2) 0.15, (3) 0.65 and (4) 1.0. Sh = shoulder.

reached. At that point the sharp stripping peak, Ox_2 , could no longer be seen. The shift was not thought to be due to the reference electrode in this case, since R_1 did not shift, and the Li^+ limit did not shift appreciably from the Li^+ limit in the FLINAK background voltammogram (compare Figure 4.4 with 4.23). A possible reason for this shift toward more positive potentials, especially for the stripping peak at Ox_2 , is most likely the deposit of a tungsten oxyfluoride species over a previously deposited or codeposited tungsten layer, causing a kinetic barrier to the re-oxidation of the tungsten until the tungsten oxyfluoride species was stripped off the surface. Addition of oxide beyond a 1:1 ratio began to eliminate wave R_1 and the sloping reduction curve altogether, and produced a peaked reduction wave near the Li^+ limit when a ratio of ~2:1 oxide/(K_3WF_8/K_3WF_6) was reached (Figure 4.23).

From these oxide studies, it became evident that Ox_1 , in the voltammogram with no added oxide, was due to some initial oxide species in the melt, either added as a contaminant in the K_3WF_8/K_3WF_6 addition sample or a reaction of the addition sample with some oxide contaminant previously in the melt. Anodic stripping waves with much smaller Ox_1 shoulders, and hence much cleaner melts, were later obtained from baths containing the K_3WF_8/K_3WF_6 mixture with no added oxide, but they were not under the same experimental conditions as these oxide studies (electrode area, species concentrations, etc.) and so were not used in the Figure.

3.) Crossover waves. When the cyclic voltammetric potentials in melts containing the tungsten species with no added oxide were swept beyond

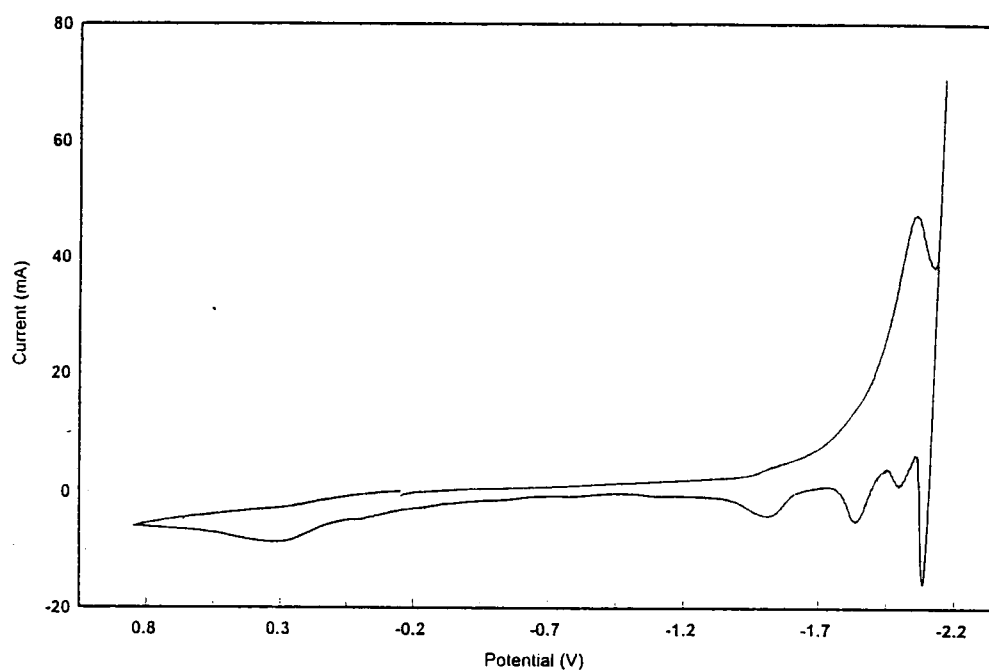


Figure 4.23. Cyclic voltammograms of $\text{K}_3\text{WF}_8/\text{K}_3\text{WF}_6$ in FLINAK containing a 2:1 mole ratio oxide/W species.

approximately -600 mV before the return sweep, the voltammograms exhibited a higher *reduction* current at the same potentials on the return sweep followed by a “crossing over” the initial current curve when the potential sweep neared the oxidation region (Figure 4.24). This was most likely caused by the formation of an initial surface layer, which then made it more energetically favorable for subsequent deposition, which in turn increased the current, i.e. smaller overpotentials are necessary for depositing tungsten onto tungsten than for depositing tungsten onto platinum. This is a very common phenomenon in the electrodeposition of metals.

Also, when the potential was swept to -200 mV and then delayed at that limit for 10-20 seconds before allowing the return sweep, similar higher currents were obtained along with crossing over when the potential scan was reversed. This further indicated that the formation of the more energetically favorable surface was a time-based (i.e., depended on nucleation and deposit growth), as well as potential-dependent phenomenon. Delay times shorter than 5 s at -200 mV (for this concentration), or approximately -50 to -100 mV beyond wave R_1 , did not usually produce the higher currents and cross-over phenomenon.

4.) Electrodeposition. Deposition experiments were performed in the melt with no added oxide at -800 mV potential step for 60 seconds on platinum foil electrodes. The plates, when removed from the cell and cleaned in distilled water followed by sonication, revealed a dull grey area where the electrode was in contact with the melt. The platinum normally remained shiny when removed from the FLINAK when no deposition was performed.

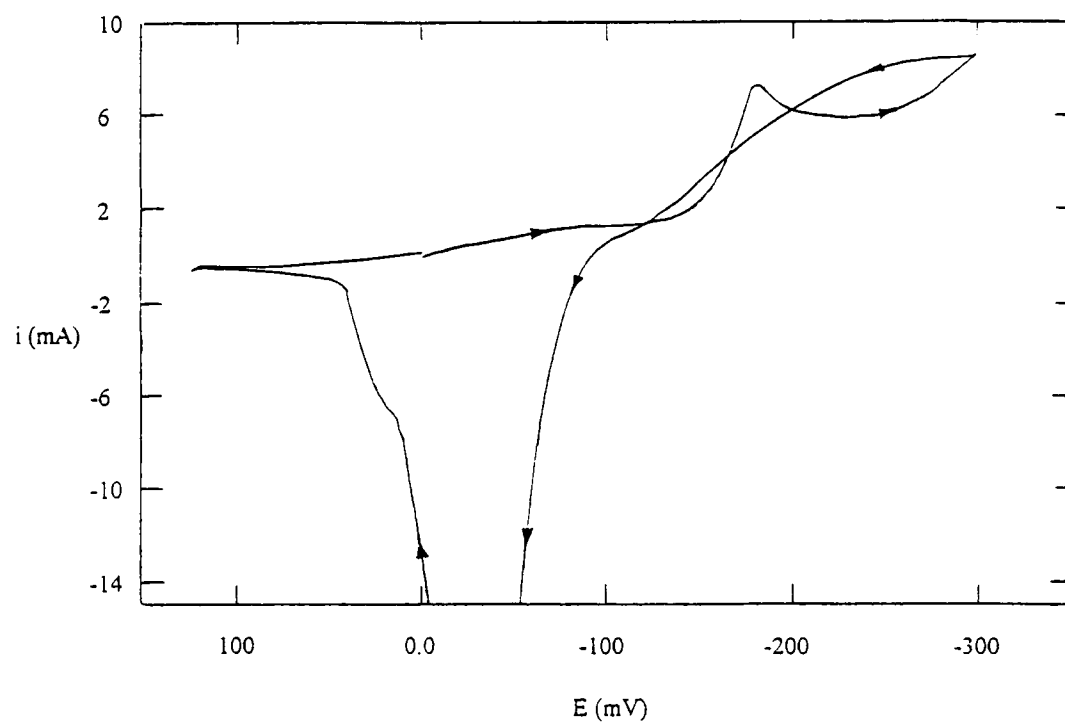


Figure 4.24. Cyclic voltammogram exhibiting "crossover" waves due to the deposition of a tungsten layer. K_3WF_8 (0.0469 M) in FLINAK, 600°C, 100 mV/s scan rate, $A_{\text{pt}} = 0.157 \text{ cm}^2$.

ESCA spectra on the electroplates revealed tungsten metal alone with the characteristic binding energies for pure tungsten metal at 31.0 and 33.15 eV. No peaks associated with platinum or any other metallic element were evident, indicating that the platinum electrode was covered with tungsten metal. An assumed density for the tungsten layers of 19.35 g/cm³ gave estimated deposit thicknesses in the 1 - 2 μ m range for the 60 second deposition times, depending on the number of coulombs of charge as calculated by integrating the area under the reduction wave.

Deposition from melts under the same conditions as above except containing equimolar amounts of oxide and tungsten species produced only black deposits, which washed off during the cleaning process. ESCA spectra in this case showed only platinum metal with characteristic binding energies at 70.9 and 74.3 eV. These experiments show that oxide is detrimental to the electroplating of tungsten in FLINAK, in agreement with the statement in the patent by Senderoff and Mellors (1) that tungsten was electroplated from a melt having no appreciable oxides. Very small amounts of oxide seem to be tolerated since electroplates were obtained when a small anodic wave associated with oxide was present. It is not known if the oxide was incorporated into the tungsten layer since it is difficult to eliminate the oxide peak background on an ESCA spectrum. Senderoff and Mellors reported no impurities were in their plates at more than trace levels, including oxide.

5.) Chronoamperograms. Chronoamperometry on the melt with no added oxide was performed. A very slight rise and fall in the current was seen,

after the initial current decay related to double-layer charging. This small current rise was interpreted as due to the formation of nucleation sites, which increased the electroactive area of the electrode, hence increasing the current until the nucleation step was completed. As expected (57), the peak current maximum associated with the nucleation process was reached more quickly and with increased current the more negative the applied potential step. This nucleation current was not seen on chronoamperograms where oxide was added in a 1:1 ratio with the tungsten species. A chronoamperogram can be seen in Figure 4.25 where the current continues to increase with time after the maximum nucleation current, making meaningful information difficult to extract.

3. Anodization of tungsten metal into FLINAK.

To show that tungsten can be anodized into FLINAK and to identify the tungsten oxidation region, a tungsten wire was cleaned by applying an AC current between the tungsten wire and a tungsten rod in a NaOH/NaNO₂ bath. This was followed by sonication of the tungsten wire in distilled water before drying in an oven at 125 °C. The tungsten wire electrode was then lowered halfway into the cell under a helium flow for approximately one minute. This hot helium served to further dry the electrode before insertion into the melt. The wire was allowed to reach equilibrium with the melt before a voltammogram was obtained. The voltage was then first swept toward positive potentials in order to anodize the tungsten into the FLINAK. An anodic current began to flow at about 0.2 to 0.3 V vs. the platinum quasi-reference electrode (Figure 4.26), then quickly

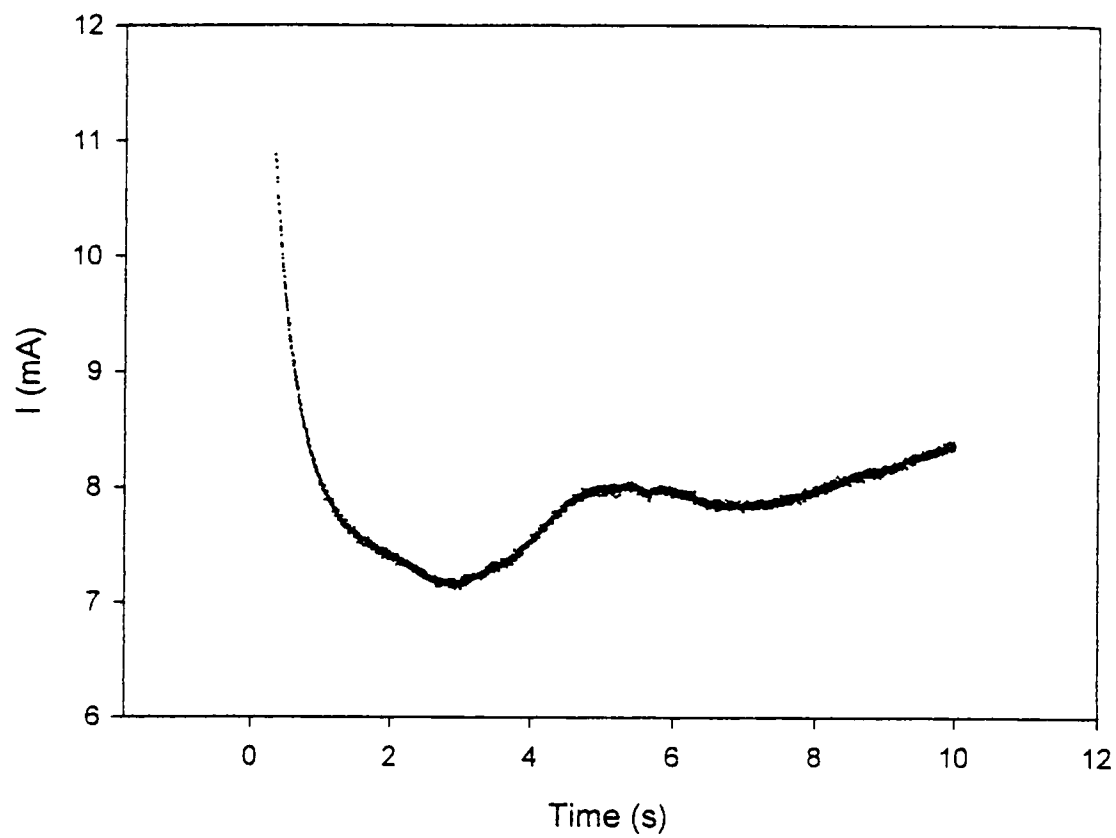


Figure 4.25. Chronoamperogram for $\text{K}_3\text{WF}_8/\text{K}_3\text{WF}_6$ in FLINAK showing the nucleation wave. Potential step = -0.8 V, platinum wire working electrode.

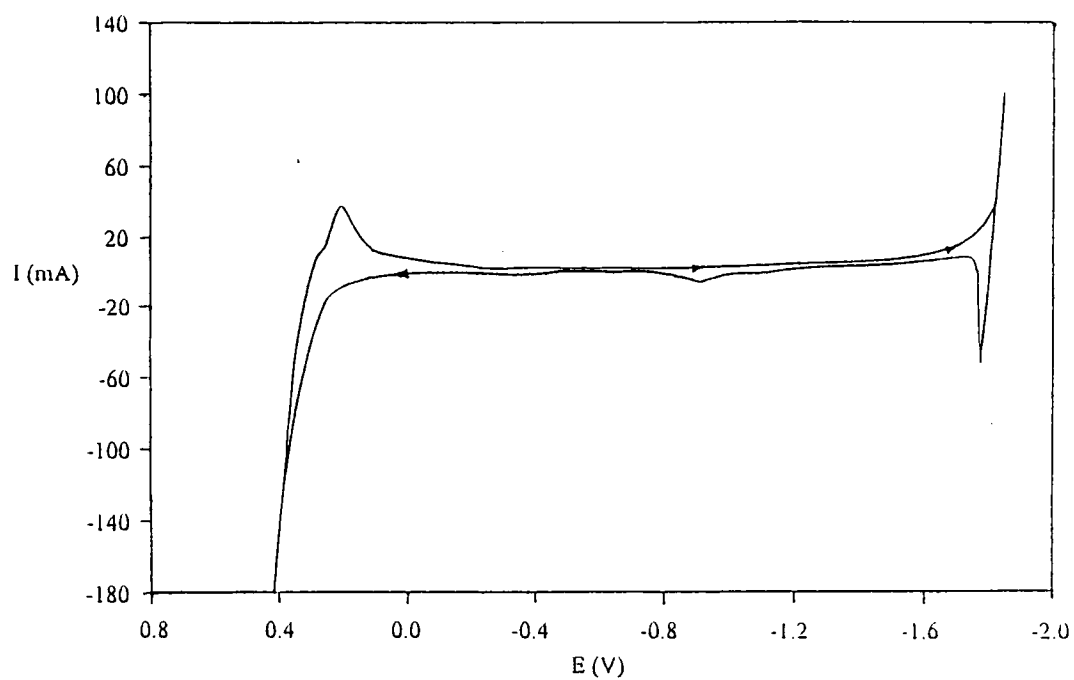


Figure 4.26. Cyclic voltammogram showing the oxidation of a tungsten wire in FLINAK. Scan rate = 100 mV/s.

reached the maximum current available with the instrument. The region of the tungsten oxidation was in the region of the stripping peaks from voltammograms seen for the K_3WF_8/K_3WF_6 mixture in FLINAK, indicating the stripping peaks were indeed due to stripping of a tungsten layer on the electrode surface.

CHAPTER V

SUMMARY AND CONCLUSIONS

A. Oxide Determinations for Fluoride Salts.

An apparatus for the determination of oxide in fluoride salts was modified by the use of an yttria-stabilized-zirconia oxygen pump in place of a manometric measuring device. It was shown that this apparatus can determine the oxide content of FLINAK, and presumably most other fluoride salts, to as low as 12 ppm. This apparatus assured a minimum level of oxide in the FLINAK before the salt was used in the chemical and electrochemical studies of tungsten in the melt. The best results in the chemical and electrochemical studies were obtained in FLINAK which had less than 12 ppm oxide and which had been sparged with helium gas for several days to remove residual HF.

B. Synthesis of Tungsten Fluoride Compounds.

Several known and previously unknown tungsten fluoride compounds were synthesized by a new high-temperature route. This new route involved the direct combination of 1) WF_6 and KF, or 2) WF_6 , W and MF (M = Na, K, Rb or Cs), at temperatures near or above the melting point of the alkali salt. Tungsten

metal was used in the latter mixtures as a reductant to obtain products whenever the tungsten oxidation state was less than six.

Mixtures in the first case above gave the eight-coordinate tungsten product K_2WF_8 . In similar mixtures, but at longer reaction times under KF limiting conditions, KWF_7 was obtained as a condensate on the cooler regions of the reaction cell. Both W (VI) compounds were identified by their Raman spectroscopic bands.

Mixtures of the second case, in which MF was the limiting reactant, yielded all four MWF_6 products. When stoichiometric amounts of MWF_6 and the corresponding MF salt were combined, two seven-coordinate W(V) compounds, K_2WF_7 and Rb_2WF_7 , and three eight-coordinate W(V) compounds, Na_3WF_8 , K_3WF_8 and Rb_3WF_8 , were obtained. The seven-coordinate compounds represent the first M_2WF_7 compounds of the group VI A transition metals. The compound K_3WF_8 has been synthesized previously by a different route, but the reported unit cell and color were different than the high-temperature synthesized material. Na_3WF_8 and Rb_3WF_8 represent previously unsynthesized compounds. The Raman bands of the Na_3WF_8 material matched well with those for Na_3TaF_8 . When W and MF ($M = Na, K$) were in excess in mixtures of the second case, and the reaction was allowed to continue for several days, the compounds M_3WF_6 and M_3WF_8 were found in roughly 50/50 proportions. K_3WF_6 was isolated from the mixture containing potassium as small crystals at the ends of KF dendrites above the melt. A crystal structure was obtained from these crystals which was

found to be analagous to K_3MoF_6 . This compound represents the first WF_6^{3-} species and the lowest valent, isolated tungsten fluoride.

A dimer of formula $[Cu(WF_6)_2(CH_3CN)_3]_2$ was formed when WF_6 was combined with CH_3CN in a nickel cell at $120^\circ C$. It was found that the mixture attacked the copper gasket, causing oxidation of the copper metal to Cu^{2+} , and reduction of the WF_6 to WF_6^- . The importance of this compound was the ν_2 Raman band frequency it revealed for the WF_6^- species, which was not present in the MWF_6 compounds.

C. Chemical Reduction of Tungsten in FLINAK.

Results were presented which demonstrated that previous reports (1,4-7) on the species present in FLINAK, from the reduction of WF_6 by W metal, were in error. Rather than dissolved WF_4 (5-7, 8) or a cluster species (4), there were two species present, WF_6^{3-} and WF_8^{3-} , following the introduction of WF_6 into molten FLINAK containing W metal as a reductant. It was also shown that the concentration of tungsten species necessary to obtain the best plates from a FLINAK bath, as reported in these studies, was in the range where WF_6^{3-} and WF_8^{3-} were found to be in approximately equal proportions. Interestingly, increasing the tungsten species concentration caused an increase in the formation of WF_8^{3-} over WF_6^{3-} . Since poor quality deposits were reported with increasing tungsten species concentration, this was interpreted as due to the increase in WF_8^{3-} concentration in relation to WF_6^{3-} .

The chemical reduction of W(VI) in FLINAK was proposed as the overall reaction: $5\text{W(VI)} + \text{W(0)} \rightarrow 6\text{W(V)}$, followed by the equilibrium process: $3\text{W(V)} + 2\text{W(0)} \rightleftharpoons 5\text{W(III)}$, where at low W(V) concentrations, W(V) and W(III) are in approximately equal proportions.

D. Electrochemical Reduction of Tungsten in FLINAK.

Residual HF dissolved in the FLINAK bath was found to adversely affect the electrochemistry of tungsten. Removal of the HF was accomplished by a helium gas sparge over several days, or by maintaining a vacuum over the melt overnight.

The voltammograms of K_2WF_8 revealed three reduction waves (R_0 , R_1 and R_2). The wave R_0 grew in as a shoulder with increasing concentration of tungsten species, and was thought to be either the reduction of a W(VI) species associated with loss of a fluoride ligand from WF_8^{2-} to produce WF_7^- , or the reduction of a W(VI) species to a species with an intermediate oxidation state such as W(III). Wave R_1 was associated with a $6e^-$ reduction of W(VI) to W(0), since the single oxidation wave in this case was peak shaped, indicating stripping of a deposited layer of tungsten. This tungsten layer was rapidly attacked by the remaining W(VI) species in the melt to produce tungsten species with oxidation states intermediate between W(0) and W(VI), leaving no detectable tungsten metal on the electrode as determined by an ESCA

spectrum. Wave R_2 was shown to be associated with reduction of a tungsten oxyfluoride, such as WOF_6^{2-} , by successive addition of oxide. This also caused the stripping wave to become less sharp or ideal, which was associated with deposition of tungsten with inclusion of oxide.

The voltammetry of KWF_6 and K_2WF_7 was found to be the same as the voltammetry of K_3WF_8 in FLINAK, indicating that a tungsten species with the same number of fluoride ligands was formed in each case under the excess fluoride conditions in the melt. This species was considered to be WF_8^{3-} , since Raman spectra of solidified melts revealed only the bands associated with K_3WF_8 .

Cyclic voltammograms of K_3WF_8 in FLINAK produced one wave, R_1 , at temperatures below 600°C . Above this temperature a shoulder, R_0 , began to grow in and became larger with increasing temperature. This was thought to be due to the dissociation of WF_8^{3-} to WF_7^{2-} and F^- , or possibly the reduction of W(V) to W(III). Below 700°C there was one main oxidation wave, Ox_3 , with two minor waves at more positive potentials. Above 700°C , Ox_3 decreased to the level of the minor waves and a fourth wave, Ox_4 , grew in at more positive potentials as R_0 increased. However, the number of oxidation waves and their peak potentials changed with increasing temperature, making any redox couple assignments difficult or meaningless.

Addition of oxide to the melt containing K_3WF_8 produced a wave, R_2 , at ~ -500 mV. The species reduced in this case was assumed to be from the displacement of two fluoride ligands in WF_8^{3-} with oxide to form WOF_6^{3-} .

Further characterization of wave R_1 revealed a shift of the peak toward more negative potentials with increasing concentration at $\sim 540^\circ\text{C}$, suggesting some quasi-reversible or irreversible character to the process. In addition, the peak potential separation between R_1 and the oxidation waves were greater than those expected for a reversible process. The separation between R_0 and Ox_4 was within range for a reversible process, but the exact peak potential for R_0 was difficult to determine since it existed as a shoulder on R_1 .

The diffusion coefficients for the species reduced at R_1 were calculated for a reversible and irreversible process. For a reversible process, at 700°C and assuming a five-electron transfer, the diffusion coefficient was $2.66 \times 10^{-6} \pm 0.15 \text{ cm}^2/\text{s}$. For an irreversible process, at 700°C and assuming a five-electron transfer with $\alpha n_a = 0.5$, the average diffusion coefficient was $4.01 \times 10^{-5} \pm 0.24 \text{ cm}^2/\text{s}$. The latter number was consistent with the diffusion coefficient determined by Polyakova and coworkers (16) for the TaF_7^{2-} species in FLINAK at 700°C .

A comparison of the experimental $|E_p - E_{p/2}|$ parameter with those calculated for a reversible and irreversible process, considering $n=1$ and $\alpha n_a=0.5$, indicated the process at R_1 was reversible above $\sim 675^\circ\text{C}$. When the wave at R_1 was compared to the wave expected for a reversible deposition process, the majority of the experimental wave coincided with the theoretical wave, except for some tailing thought to be associated with convective stirring, and some current at the foot of the wave (although this may be associated with the wave R_0).

Plots of i_p vs $\log v$ had slopes of 0.489 and 0.443, indicating some diffusion control. In this case, activation energies of 41.7 and 58.9 kJ/mole were calculated from a plot of $i_p T^{1/2}$ vs. T^{-1} . These high activation energies agreed fairly well with those obtained for the TaF_7^{2-} and $TaOF_5^{2-}$ species (16), which were reported as 39.1 and 43.9 kJ/mole, respectively. However, more than simple diffusion control was indicated when the αn_α values, calculated from the slopes of $-E_p$ vs. $\log v$ (which should be less than 1.0), were 1.17 and 1.47. This can be seen in Figure 4.17 where a transition from diffusion to activation control of the electrode process is indicated at sweep rates between 0.1 to 1 V/s.

Coulometry and "simulated" pulse voltammetry of wave R_1 (and R_2 in the case of pulse voltammetry) were both inconclusive in determining the number of electrons transferred. However, the pulse voltammetry was consistent with the interpretation of R_2 as an oxide species.

Deposition from a FLINAK bath at 750°C at -0.3 V produced a dark deposit, which after cleaning in 1:1 HCl, was shown by an ESCA spectrum to be tungsten metal on the surface of the electrode.

The electrochemistry of the K_3WF_8/K_3WF_6 mixed material produced two reduction peaks, R_1 and R_2 , and were assigned to R_1 and R_2 associated with K_3WF_8 alone. A small shoulder seen between these two waves was thought to be the reduction of the species produced from K_3WF_6 , such as WF_6^{3-} . A single oxidation wave in the form of a stripping peak was produced. A shoulder at less positive potentials was associated with the oxide species reduced at R_2 , since upon addition of Na_2O , this oxidation shoulder began to increase until the

stripping wave could no longer be seen at a 1:1 oxide/tungsten species ratio. In the case of no added oxide, when the potential was stepped to -800 mV for 60 seconds, tungsten metal alone was found deposited on the electrode, as indicated by an ESCA spectrum. When oxide was added in a 1:1 ratio, only black deposits were obtained, and no tungsten was seen on an ESCA spectrum.

The oxidation wave of a tungsten wire in FLINAK was in the same potential region for the stripping waves seen for all of the tungsten compounds added to FLINAK, showing that the stripping peaks were due to the oxidative removal of a tungsten layer.

E. Conclusion.

The electrochemistry of tungsten in FLINAK is very difficult to interpret, since the mechanism is very complex. For example, in the case of K_3WF_8 in FLINAK, which was studied in detail, electron transfer is most likely not the controlling step. Dissociation of the fluoride ligands may be involved as well, i.e., the rate of charge transfer may be determined by the rate at which the central ion can detach itself from the ligands prior to transfer across the double layer. This phenomenon and the results discussed above suggest the process must have some quasi-reversible character. Polykova and coworkers (16) found the tantalum deposition process to have both quasi-reversible and irreversible character, depending on the scan rate. The character of the tungsten reduction process was also seen to change with increasing scan rate and also with

increasing temperature, which suggests irreversible and quasi-reversible behavior. The correlation between the W(V) and Ta(V) species is also suggested by the agreement of the tungsten species diffusion coefficient with the tantalum species diffusion coefficient. The diffusion coefficients of various species in molten FLINAK are expected to be in the 10^{-4} to 10^{-5} cm²/s range (49).

The Ox₃ stripping peak associated with K₃WF₈ in FLINAK due to a deposited tungsten layer was the most ideal at a bath temperature around 650 to 700°C, and was essentially free from interference from other oxidation waves. This suggested stripping from a more uniform or possibly more crystalline tungsten surface layer than was deposited at other temperatures, and also suggested the 650 to 700°C range to be the optimum plating temperature from a FLINAK bath containing the W(V) species. However, the best plates were observed in a bath containing the K₃WF₈/K₃WF₆ mixture in roughly equal proportions, although a temperature study was not performed. Previous studies of the deposition of tungsten from alkali fluoride baths in which WF₆ was reduced *in situ* by tungsten metal were shown to contain this mixture of K₃WF₈/K₃WF₆, and the optimum plating temperature of these baths was reported to be 780 to 800°C (5-7).

F. Thoughts for Future Work.

Further work could be performed in the synthesis of larger quantities of the M₃WF₆ species, from which a Raman spectrum of the pure compound could

be acquired. One way to obtain pure K_3WF_6 or K_3WF_8 may be from the K_3WF_8/K_3WF_6 mixed material, which could be dissolved in a room temperature molten salt, or liquid HF, and recrystallized to achieve separation of the two compounds.

Since the RbF and CsF salts were contaminated with oxide, removal of the oxide by slow recrystallization or some other means, such as HF purification, may allow some of the rubidium and cesium M_3WF_8 and M_3WF_6 compounds to be synthesized in pure or crystalline form, or may even allow formation of an M_2WF_6 compound.

Since the identity of R_0 in each case above is not known with certainty (suggested as either the result of a loss of F^- , or the reduction of the tungsten species to an intermediate oxidation state), a method of determining the species/process would help in the understanding the tungsten reduction mechanism. Raman spectroscopy could be used to characterize the tungsten species in the FLINAK melt at higher temperatures, and would indicate the formation of a lower coordinated tungsten fluoride (i.e. loss of F^-). In this case, the individual compounds themselves would need to be characterized at higher temperatures, and the Raman bands compared to those obtained in FLINAK at higher temperatures.

One way the species may be examined at higher temperatures is to place the tungsten species in a molten chloride salt, which can be enclosed in silica glass, greatly simplifying the spectroscopic setup. One would have to assume

that replacement of the fluoride ligand with chloride would not be significant in such an environment. This has been demonstrated in the case for NbF_7^{2-} (58).

Another method would be the use of a bundled fiber optic probe coated with vapor deposited diamond, which would be immersed directly in the melt. The Raman beam in this case would be channeled through the central fiber, and the signal collected by a surrounding bundle of fibers. The diamond coat would be transparent in the spectroscopic region of interest and would resist corrosion by the fluoride salt.

For the electrochemical studies, a rotating disk electrode experiment could eliminate interference from thermal convective diffusion, as seen by the tailing in the voltammograms. The coulometric experiment could be improved by enclosing the counter electrode in a separate compartment from the working electrode, thus eliminating reaction between the reduced and oxidized forms of the tungsten species.

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APPENDIX

APPENDIX

Crystal data and structure refinement for K_2WF_7 .

Empirical formula	F_7K_2W
Formula weight	395.05
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 5.736(2)$ Å $\alpha = 90^\circ$ $b = 11.723(4)$ Å $\beta = 90.00(3)^\circ$ $c = 9.800(3)$ Å $\gamma = 90^\circ$
Volume, Z	$659.0(4)$ Å ³ , 4
Density (calculated)	3.982 Mg/m ³
Absorption coefficient	18.854 mm ⁻¹
$F(000)$	700
Crystal size	$0.40 \times 0.30 \times 0.30$ mm
θ range for data collection	2.71 to 22.54°
Limiting indices	$0 \leq h \leq 6, -12 \leq k \leq 12, -10 \leq l \leq 10$
Reflections collected	1878
Independent reflections	869 ($R_{int} = 0.0861$)
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	869 / 0 / 91
Goodness-of-fit on F^2	1.078
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0443, wR2 = 0.0986$
R indices (all data)	$R1 = 0.0672, wR2 = 0.1118$
Largest diff. peak and hole	1.707 and -1.662 eÅ ⁻³

Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for K_2WF_7 is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
W(1)	7501(1)	6291(1)	2456(1)	23(1)
K(1)	12491(8)	4398(4)	1357(5)	31(1)
K(2)	2503(9)	8316(5)	522(6)	43(1)
F(1)	9740(21)	6301(16)	1007(13)	62(5)
F(2)	5202(21)	6283(14)	1006(15)	55(4)
F(3)	9797(30)	5440(19)	3518(20)	93(6)
F(4)	5264(28)	5431(22)	3492(19)	109(8)
F(5)	7489(38)	4744(17)	1745(25)	114(7)
F(6)	5606(49)	7362(28)	3156(59)	305(31)
F(7)	9611(39)	7408(21)	3094(44)	213(20)

Anisotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for K_2WF_7
The anisotropic displacement factor exponent takes the form:
 $-2\pi^2 [(ha^*)^2 U_{11} + \dots + 2hka^*b^*U_{12}]$

	U11	U22	U33	U23	U13	U12
W(1)	20(1)	25(1)	24(1)	-6(1)	3(1)	1(1)
K(1)	29(2)	33(3)	30(3)	0(2)	4(2)	1(2)
K(2)	46(3)	41(3)	43(3)	-3(3)	0(2)	2(3)
F(1)	37(7)	120(16)	30(8)	22(9)	14(6)	8(9)
F(2)	39(7)	73(12)	52(9)	10(8)	-1(6)	-8(8)
F(3)	79(12)	113(17)	88(14)	11(13)	-17(10)	33(12)
F(4)	59(10)	188(24)	80(13)	69(16)	32(9)	2(13)
F(5)	115(15)	75(15)	153(21)	-19(15)	-19(14)	20(14)
F(6)	92(20)	160(29)	663(82)	-287(45)	40(30)	-18(19)
F(7)	65(15)	92(19)	482(59)	-141(29)	-32(22)	4(13)

Bond lengths [Å] and angles [°] for K_2WF_6 .

✓W(1)-F(6)	1.80(2)	✓W(1)-F(7)	1.89(2)
W(1)-F(1)	1.914(12)	W(1)-F(4)	1.92(2)
W(1)-F(2)	1.939(14)	W(1)-F(5)	1.94(2)
W(1)-F(3)	1.95(2)	W(1)-K(1)	3.778(5)
W(1)-K(1)#1	3.787(5)	W(1)-K(1)#2	3.823(5)
W(1)-K(1)#3	3.824(5)	W(1)-K(2)#4	4.011(6)
K(1)-F(7)#5	2.68(2)	K(1)-F(6)#5	2.67(3)
K(1)-F(2)#6	2.723(15)	K(1)-F(1)	2.75(2)
K(1)-F(1)#2	2.77(2)	K(1)-F(2)#2	2.78(2)
K(1)-F(4)#6	2.89(2)	K(1)-F(3)	2.89(2)
K(1)-F(5)#6	2.92(2)	K(1)-F(5)	2.92(2)
K(1)-F(5)#2	3.20(3)	K(2)-F(2)	2.88(2)
K(2)-F(1)#1	2.88(2)	K(2)-F(3)#7	2.90(2)
K(2)-F(4)#8	2.94(2)	K(2)-F(4)#9	2.95(2)
K(2)-F(3)#9	2.97(2)	K(2)-F(6)#8	3.03(5)
K(2)-F(7)#7	3.02(4)	K(2)-F(5)#9	3.16(2)
K(2)-F(7)#1	3.20(4)	K(2)-F(6)	3.33(6)
K(2)-W(1)#9	4.011(6)	F(1)-K(1)#2	2.77(2)
F(1)-K(2)#6	2.88(2)	F(2)-K(1)#1	2.723(15)
F(2)-K(1)#2	2.78(2)	F(3)-K(2)#10	2.90(2)
F(3)-K(2)#4	2.97(2)	F(4)-K(1)#1	2.89(2)
F(4)-K(2)#11	2.94(2)	F(4)-K(2)#4	2.95(2)
F(5)-K(1)#1	2.92(2)	F(5)-K(2)#4	3.16(2)
F(5)-K(1)#2	3.20(3)	F(6)-K(1)#3	2.67(3)
F(6)-K(2)#11	3.03(5)	F(7)-K(1)#3	2.68(2)
F(7)-K(2)#10	3.02(4)	F(7)-K(2)#6	3.20(4)
F(6)-W(1)-F(7)	77.1(10)	F(6)-W(1)-F(1)	133.2(19)
F(7)-W(1)-F(1)	79.1(12)	F(6)-W(1)-F(4)	76.2(17)
F(7)-W(1)-F(4)	128.1(16)	F(1)-W(1)-F(4)	147.5(10)
F(6)-W(1)-F(2)	82.6(16)	F(7)-W(1)-F(2)	133.0(13)
F(1)-W(1)-F(2)	85.0(5)	F(4)-W(1)-F(2)	86.0(7)
F(6)-W(1)-F(5)	141.9(11)	F(7)-W(1)-F(5)	140.2(10)
F(1)-W(1)-F(5)	75.1(9)	F(4)-W(1)-F(5)	72.4(11)
F(2)-W(1)-F(5)	74.3(8)	F(6)-W(1)-F(3)	124.2(20)
F(7)-W(1)-F(3)	75.3(12)	F(1)-W(1)-F(3)	86.9(7)
F(4)-W(1)-F(3)	84.3(8)	F(2)-W(1)-F(3)	147.9(8)
F(5)-W(1)-F(3)	73.5(9)	F(6)-W(1)-K(1)	167.8(10)
F(7)-W(1)-K(1)	90.9(7)	F(1)-W(1)-K(1)	44.3(5)
F(4)-W(1)-K(1)	110.4(7)	F(2)-W(1)-K(1)	107.7(4)
F(5)-W(1)-K(1)	49.6(7)	F(3)-W(1)-K(1)	48.8(6)
F(6)-W(1)-K(1)#1	93.4(9)	F(7)-W(1)-K(1)#1	170.5(7)
F(1)-W(1)-K(1)#1	107.6(5)	F(4)-W(1)-K(1)#1	48.4(7)
F(2)-W(1)-K(1)#1	43.3(4)	F(5)-W(1)-K(1)#1	49.3(6)
F(3)-W(1)-K(1)#1	111.4(6)	K(1)-W(1)-K(1)#1	98.62(12)
F(6)-W(1)-K(1)#2	121.4(19)	F(7)-W(1)-K(1)#2	118.0(13)
F(1)-W(1)-K(1)#2	43.6(4)	F(4)-W(1)-K(1)#2	114.0(7)
F(2)-W(1)-K(1)#2	44.2(4)	F(5)-W(1)-K(1)#2	56.8(7)
F(3)-W(1)-K(1)#2	114.3(6)	K(1)-W(1)-K(1)#2	66.20(12)
K(1)#1-W(1)-K(1)#2	66.36(12)	F(6)-W(1)-K(1)#3	38.6(10)
F(7)-W(1)-K(1)#3	40.4(7)	F(1)-W(1)-K(1)#3	102.6(6)
F(4)-W(1)-K(1)#3	109.8(8)	F(2)-W(1)-K(1)#3	103.2(5)
F(5)-W(1)-K(1)#3	176.7(7)	F(3)-W(1)-K(1)#3	108.9(6)
K(1)-W(1)-K(1)#3	130.18(7)	K(1)#1-W(1)-K(1)#3	130.19(7)
K(1)#2-W(1)-K(1)#3	119.91(10)	F(6)-W(1)-K(2)#4	114.8(18)

Bond lengths and angles for K_2WF_7 (continued)...

F(7)-W(1)-K(2)#4	116.1(12)	F(1)-W(1)-K(2)#4	111.9(5)
F(4)-W(1)-K(2)#4	44.2(6)	F(2)-W(1)-K(2)#4	110.9(5)
F(5)-W(1)-K(2)#4	50.6(7)	F(3)-W(1)-K(2)#4	45.0(6)
K(1)-W(1)-K(2)#4	68.33(11)	K(1)#1-W(1)-K(2)#4	68.32(11)
K(1)#2-W(1)-K(2)#4	107.40(11)	K(1)#3-W(1)-K(2)#4	132.69(11)
F(7)#5-K(1)-F(6)#5	50.9(7)	F(7)#5-K(1)-F(2)#6	171.2(6)
F(6)#5-K(1)-F(2)#6	121.0(7)	F(7)#5-K(1)-F(1)	118.2(6)
F(6)#5-K(1)-F(1)	169.0(7)	F(2)#6-K(1)-F(1)	69.8(4)
F(7)#5-K(1)-F(1)#2	72.7(9)	F(6)#5-K(1)-F(1)#2	94.2(13)
F(2)#6-K(1)-F(1)#2	113.5(5)	F(1)-K(1)-F(1)#2	82.6(6)
F(7)#5-K(1)-F(2)#2	97.5(10)	F(6)#5-K(1)-F(2)#2	72.4(12)
F(2)#6-K(1)-F(2)#2	81.7(5)	F(1)-K(1)-F(2)#2	113.6(4)
F(1)#2-K(1)-F(2)#2	55.9(4)	F(7)#5-K(1)-F(4)#6	117.8(9)
F(6)#5-K(1)-F(4)#6	91.2(13)	F(2)#6-K(1)-F(4)#6	55.8(5)
F(1)-K(1)-F(4)#6	93.8(6)	F(1)#2-K(1)-F(4)#6	169.2(5)
F(2)#2-K(1)-F(4)#6	117.4(4)	F(7)#5-K(1)-F(3)	88.9(10)
F(6)#5-K(1)-F(3)	117.7(12)	F(2)#6-K(1)-F(3)	93.2(6)
F(1)-K(1)-F(3)	56.1(5)	F(1)#2-K(1)-F(3)	119.4(5)
F(2)#2-K(1)-F(3)	169.8(5)	F(4)#6-K(1)-F(3)	65.7(5)
F(7)#5-K(1)-F(5)#6	122.4(6)	F(6)#5-K(1)-F(5)#6	72.5(8)
F(2)#6-K(1)-F(5)#6	49.0(5)	F(1)-K(1)-F(5)#6	117.8(5)
F(1)#2-K(1)-F(5)#6	127.1(6)	F(2)#2-K(1)-F(5)#6	71.4(5)
F(4)#6-K(1)-F(5)#6	46.2(6)	F(3)-K(1)-F(5)#6	111.8(6)
F(7)#5-K(1)-F(5)	69.7(7)	F(6)#5-K(1)-F(5)	120.2(7)
F(2)#6-K(1)-F(5)	117.7(5)	F(1)-K(1)-F(5)	48.8(5)
F(1)#2-K(1)-F(5)	72.3(5)	F(2)#2-K(1)-F(5)	127.9(6)
F(4)#6-K(1)-F(5)	112.8(6)	F(3)-K(1)-F(5)	47.3(6)
F(5)#6-K(1)-F(5)	158.1(8)	F(7)#5-K(1)-F(5)#2	117.7(10)
F(6)#5-K(1)-F(5)#2	116.7(13)	F(2)#6-K(1)-F(5)#2	67.9(5)
F(1)-K(1)-F(5)#2	68.3(5)	F(1)#2-K(1)-F(5)#2	45.6(5)
F(2)#2-K(1)-F(5)#2	45.5(5)	F(4)#6-K(1)-F(5)#2	123.6(5)
F(3)-K(1)-F(5)#2	124.4(5)	F(5)#6-K(1)-F(5)#2	94.4(6)
F(5)-K(1)-F(5)#2	94.8(6)	F(7)#5-K(1)-W(1)	96.5(6)
F(6)#5-K(1)-W(1)	141.7(9)	F(2)#6-K(1)-W(1)	89.6(3)
F(1)-K(1)-W(1)	29.0(3)	F(1)#2-K(1)-W(1)	93.6(3)
F(2)#2-K(1)-W(1)	140.0(3)	F(4)#6-K(1)-W(1)	88.0(4)
F(3)-K(1)-W(1)	30.5(3)	F(5)#6-K(1)-W(1)	128.7(4)
F(5)-K(1)-W(1)	30.4(4)	F(5)#2-K(1)-W(1)	95.1(4)
F(2)-K(2)-F(1)#1	65.8(4)	F(2)-K(2)-F(3)#7	144.6(5)
F(1)#1-K(2)-F(3)#7	103.3(5)	F(2)-K(2)-F(4)#8	103.6(5)
F(1)#1-K(2)-F(4)#8	144.8(5)	F(3)#7-K(2)-F(4)#8	65.0(5)
F(2)-K(2)-F(4)#9	114.1(5)	F(1)#1-K(2)-F(4)#9	150.7(5)
F(3)#7-K(2)-F(4)#9	91.8(7)	F(4)#8-K(2)-F(4)#9	64.4(6)
F(2)-K(2)-F(3)#9	151.6(5)	F(1)#1-K(2)-F(3)#9	113.0(5)
F(3)#7-K(2)-F(3)#9	63.6(6)	F(4)#8-K(2)-F(3)#9	92.0(6)
F(4)#9-K(2)-F(3)#9	52.1(5)	F(2)-K(2)-F(6)#8	66.0(6)
F(1)#1-K(2)-F(6)#8	103.5(7)	F(3)#7-K(2)-F(6)#8	85.9(8)
F(4)#8-K(2)-F(6)#8	45.2(6)	F(4)#9-K(2)-F(6)#8	102.5(8)
F(3)#9-K(2)-F(6)#8	136.3(6)	F(2)-K(2)-F(7)#7	101.1(6)
F(1)#1-K(2)-F(7)#7	66.3(5)	F(3)#7-K(2)-F(7)#7	46.6(6)
F(4)#8-K(2)-F(7)#7	84.4(7)	F(4)#9-K(2)-F(7)#7	137.0(7)
F(3)#9-K(2)-F(7)#7	104.0(6)	F(6)#8-K(2)-F(7)#7	69.3(10)
F(2)-K(2)-F(5)#9	107.4(5)	F(1)#1-K(2)-F(5)#9	107.2(5)
F(3)#7-K(2)-F(5)#9	108.0(6)	F(4)#8-K(2)-F(5)#9	108.0(6)
F(4)#9-K(2)-F(5)#9	43.7(5)	F(3)#9-K(2)-F(5)#9	44.6(5)
F(6)#8-K(2)-F(5)#9	141.9(9)	F(7)#7-K(2)-F(5)#9	144.8(7)
F(2)-K(2)-F(7)#1	82.7(5)	F(1)#1-K(2)-F(7)#1	46.6(5)
F(3)#7-K(2)-F(7)#1	115.1(7)	F(4)#8-K(2)-F(7)#1	168.4(6)
F(4)#9-K(2)-F(7)#1	104.3(6)	F(3)#9-K(2)-F(7)#1	78.4(6)

Bond lengths and angles for K_2WF_7 (continued)...

F(6)#8-K(2)-F(7)#1	145.1(7)	F(7)#7-K(2)-F(7)#1	104.0(6)
F(5)#9-K(2)-F(7)#1	60.6(6)	F(2)-K(2)-F(6)	46.2(5)
F(1)#1-K(2)-F(6)	83.7(6)	F(3)#7-K(2)-F(6)	168.9(6)
F(4)#8-K(2)-F(6)	113.9(8)	F(4)#9-K(2)-F(6)	78.3(6)
F(3)#9-K(2)-F(6)	105.9(6)	F(6)#8-K(2)-F(6)	101.0(7)
F(7)#7-K(2)-F(6)	144.1(7)	F(5)#9-K(2)-F(6)	61.3(6)
F(7)#1-K(2)-F(6)	63.6(8)	F(2)-K(2)-W(1)#9	129.7(3)
F(1)#1-K(2)-W(1)#9	129.1(3)	F(3)#7-K(2)-W(1)#9	84.1(4)
F(4)#8-K(2)-W(1)#9	84.3(4)	F(4)#9-K(2)-W(1)#9	27.0(3)
F(3)#9-K(2)-W(1)#9	27.7(3)	F(6)#8-K(2)-W(1)#9	127.4(7)
F(7)#7-K(2)-W(1)#9	129.3(5)	F(5)#9-K(2)-W(1)#9	28.4(4)
F(7)#1-K(2)-W(1)#9	84.3(4)	F(6)-K(2)-W(1)#9	84.8(4)
W(1)-F(1)-K(1)	106.7(6)	W(1)-F(1)-K(1)#2	108.0(5)
K(1)-F(1)-K(1)#2	97.4(6)	W(1)-F(1)-K(2)#6	119.7(8)
K(1)-F(1)-K(2)#6	111.7(4)	K(1)#2-F(1)-K(2)#6	111.0(5)
W(1)-F(2)-K(1)#1	107.4(6)	W(1)-F(2)-K(1)#2	106.7(5)
K(1)#1-F(2)-K(1)#2	98.3(5)	W(1)-F(2)-K(2)	118.8(7)
K(1)#1-F(2)-K(2)	112.7(4)	K(1)#2-F(2)-K(2)	110.8(5)
W(1)-F(3)-K(2)#10	117.8(9)	W(1)-F(3)-K(1)	100.7(8)
K(2)#10-F(3)-K(1)	115.0(6)	W(1)-F(3)-K(2)#4	107.3(8)
K(2)#10-F(3)-K(2)#4	116.4(6)	K(1)-F(3)-K(2)#4	96.6(6)
W(1)-F(4)-K(1)#1	101.8(8)	W(1)-F(4)-K(2)#11	117.1(11)
K(1)#1-F(4)-K(2)#11	113.8(5)	W(1)-F(4)-K(2)#4	108.9(7)
K(1)#1-F(4)-K(2)#4	97.1(8)	K(2)#11-F(4)-K(2)#4	115.6(6)
W(1)-F(5)-K(1)#1	100.4(8)	W(1)-F(5)-K(1)	99.9(8)
K(1)#1-F(5)-K(1)	158.1(8)	W(1)-F(5)-K(2)#4	101.0(9)
K(1)#1-F(5)-K(2)#4	92.2(7)	K(1)-F(5)-K(2)#4	92.0(6)
W(1)-F(5)-K(1)#2	92.7(8)	K(1)#1-F(5)-K(1)#2	85.6(6)
K(1)-F(5)-K(1)#2	85.2(6)	K(2)#4-F(5)-K(1)#2	166.3(7)
W(1)-F(6)-K(1)#3	116.5(14)	W(1)-F(6)-K(2)#11	117.6(22)
K(1)#3-F(6)-K(2)#11	109.8(13)	W(1)-F(6)-K(2)	105.2(22)
K(1)#3-F(6)-K(2)	93.3(15)	K(2)#11-F(6)-K(2)	111.6(9)
W(1)-F(7)-K(1)#3	112.4(10)	W(1)-F(7)-K(2)#10	114.7(15)
K(1)#3-F(7)-K(2)#10	109.5(11)	W(1)-F(7)-K(2)#6	107.6(16)
K(1)#3-F(7)-K(2)#6	95.8(11)	K(2)#10-F(7)-K(2)#6	115.4(7)

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 -x+2,-y+1,-z #3 -x+2,y+1/2,-z+1/2
 #4 -x+1,y-1/2,-z+1/2 #5 -x+2,y-1/2,-z+1/2 #6 x+1,y,z
 #7 x-1,-y+3/2,z-1/2 #8 x,-y+3/2,z-1/2 #9 -x+1,y+1/2,-z+1/2
 #10 x+1,-y+3/2,z+1/2 #11 x,-y+3/2,z+1/2

Crystal data and structure refinement for K_3WF_6

Empirical formula	F_6K_3W
Formula weight	415.15
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Cubic
Space group	$Fm\bar{3}m$
Unit cell dimensions	$a = 8.9160(10)$ Å $\alpha = 90^\circ$ $b = 8.9160(10)$ Å $\beta = 90^\circ$ $c = 8.9160(10)$ Å $\gamma = 90^\circ$
Volume, Z	$708.78(14)$ Å ³ , 4
Density (calculated)	3.890 Mg/m ³
Absorption coefficient	18.093 mm ⁻¹
F(000)	740
Crystal size	$0.32 \times 0.24 \times 0.22$ mm
θ range for data collection	3.96 to 22.35°
Limiting indices	$-1 \leq h \leq 9$, $-1 \leq k \leq 9$, $-1 \leq l \leq 9$
Reflections collected	219
Independent reflections	40 ($R_{int} = 0.0856$)
Absorption correction	Semi empirical from Ψ scans
Max. and min. transmission	1.000 and 0.699
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	40 / 0 / 7
Goodness-of-fit on F^2	1.275
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0465$, $wR2 = 0.1381$
R indices (all data)	$R1 = 0.0465$, $wR2 = 0.1381$
Largest diff. peak and hole	1.130 and -0.726 eÅ ⁻³

Anisotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for K_3WF_6
 The anisotropic displacement factor exponent takes the form:
 $-2\pi^2 [(ha^*)^2 U_{11} + \dots + 2hka^*b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
W(1)	48(2)	48(2)	48(2)	0	0	0
K(1)	83(7)	83(7)	83(7)	0	0	0
K(2)	74(8)	74(8)	74(8)	0	0	0
F(1)	33(20)	357(46)	357(46)	0	0	0

Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for K_3WF_6 , $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
W(1)	0	0	0	48(2)
K(1)	2500	2500	2500	83(7)
K(2)	5000	5000	5000	74(8)
F(1)	2029(43)	0	0	249(29)

Table 3. Bond lengths [Å] and angles [°] for K₃WF₆.

W(1)-F(1)#1	1.81(4)	W(1)-F(1)#2	1.81(4)
W(1)-F(1)	1.81(4)	W(1)-F(1)#3	1.81(4)
W(1)-F(1)#4	1.81(4)	W(1)-F(1)#5	1.81(4)
W(1)-K(1)	3.8607(4)	W(1)-K(1)#5	3.8607(4)
W(1)-K(1)#6	3.8607(4)	W(1)-K(1)#7	3.8607(4)
W(1)-K(1)#8	3.8607(4)	W(1)-K(1)#9	3.8607(4)
K(1)-F(1)#1	3.180(5)	K(1)-F(1)#2	3.180(5)
K(1)-F(1)	3.180(5)	K(1)-F(1)#10	3.180(5)
K(1)-F(1)#11	3.180(5)	K(1)-F(1)#12	3.180(5)
K(1)-F(1)#13	3.180(5)	K(1)-F(1)#14	3.180(5)
K(1)-F(1)#15	3.180(5)	K(1)-F(1)#16	3.180(5)
K(1)-F(1)#7	3.180(5)	K(1)-F(1)#8	3.180(5)
K(2)-F(1)#17	2.65(4)	K(2)-F(1)#18	2.65(4)
K(2)-F(1)#19	2.65(4)	K(2)-F(1)#10	2.65(4)
K(2)-F(1)#11	2.65(4)	K(2)-F(1)#12	2.65(4)
K(2)-K(1)#20	3.8607(4)	K(2)-K(1)#21	3.8607(4)
K(2)-K(1)#19	3.8607(4)	K(2)-K(1)#22	3.8607(4)
K(2)-K(1)#23	3.8607(4)	F(1)-K(2)#9	2.65(4)
F(1)-K(1)#9	3.180(5)	F(1)-K(1)#8	3.180(5)
F(1)-K(1)#7	3.180(5)		
F(1)#1-W(1)-F(1)#2	90.0	F(1)#1-W(1)-F(1)	90.0
F(1)#2-W(1)-F(1)	90.0	F(1)#1-W(1)-F(1)#3	180.000(1)
F(1)#2-W(1)-F(1)#3	90.0	F(1)-W(1)-F(1)#3	90.0
F(1)#1-W(1)-F(1)#4	90.0	F(1)#2-W(1)-F(1)#4	180.0
F(1)-W(1)-F(1)#4	90.0	F(1)#3-W(1)-F(1)#4	90.0
F(1)#1-W(1)-F(1)#5	90.0	F(1)#2-W(1)-F(1)#5	90.0
F(1)-W(1)-F(1)#5	180.0	F(1)#3-W(1)-F(1)#5	90.0
F(1)#4-W(1)-F(1)#5	90.0	F(1)#1-W(1)-K(1)	54.7
F(1)#2-W(1)-K(1)	54.7	F(1)-W(1)-K(1)	54.7
F(1)#3-W(1)-K(1)	125.3	F(1)#4-W(1)-K(1)	125.3
F(1)#5-W(1)-K(1)	125.3	F(1)#1-W(1)-K(1)#5	125.3
F(1)#2-W(1)-K(1)#5	125.3	F(1)-W(1)-K(1)#5	125.3
F(1)#3-W(1)-K(1)#5	54.7	F(1)#4-W(1)-K(1)#5	54.7
F(1)#5-W(1)-K(1)#5	54.7	K(1)-W(1)-K(1)#5	180.0
F(1)#1-W(1)-K(1)#6	125.3	F(1)#2-W(1)-K(1)#6	54.7
F(1)-W(1)-K(1)#6	125.3	F(1)#3-W(1)-K(1)#6	54.7
F(1)#4-W(1)-K(1)#6	125.3	F(1)#5-W(1)-K(1)#6	54.7
K(1)-W(1)-K(1)#6	109.5	K(1)#5-W(1)-K(1)#6	70.5
F(1)#1-W(1)-K(1)#7	125.3	F(1)#2-W(1)-K(1)#7	54.7
F(1)-W(1)-K(1)#7	54.7	F(1)#3-W(1)-K(1)#7	54.7
F(1)#4-W(1)-K(1)#7	125.3	F(1)#5-W(1)-K(1)#7	125.3
K(1)-W(1)-K(1)#7	70.5	K(1)#5-W(1)-K(1)#7	109.5
K(1)#6-W(1)-K(1)#7	70.5	F(1)#1-W(1)-K(1)#8	54.7
F(1)#2-W(1)-K(1)#8	125.3	F(1)-W(1)-K(1)#8	54.7
F(1)#3-W(1)-K(1)#8	125.3	F(1)#4-W(1)-K(1)#8	54.7
F(1)#5-W(1)-K(1)#8	125.3	K(1)-W(1)-K(1)#8	70.5
K(1)#5-W(1)-K(1)#8	109.5	K(1)#6-W(1)-K(1)#8	180.0
K(1)#7-W(1)-K(1)#8	109.5	F(1)#1-W(1)-K(1)#9	125.3
F(1)#2-W(1)-K(1)#9	125.3	F(1)-W(1)-K(1)#9	54.736(1)
F(1)#3-W(1)-K(1)#9	54.7	F(1)#4-W(1)-K(1)#9	54.7
F(1)#5-W(1)-K(1)#9	125.3	K(1)-W(1)-K(1)#9	109.5
K(1)#5-W(1)-K(1)#9	70.5	K(1)#6-W(1)-K(1)#9	109.5
K(1)#7-W(1)-K(1)#9	70.5	K(1)#8-W(1)-K(1)#9	70.5
F(1)#1-K(1)-F(1)#2	47.4(12)	F(1)#1-K(1)-F(1)	47.4(12)

Bond lengths and angles for $[\text{Cu}(\text{WF})_6(\text{CH}_3\text{CN})_3]_2$ (continued)...

F(1)#2-K(1)-F(1)	47.4(12)	F(1)#1-K(1)-F(1)#10	164.8(14)
F(1)#2-K(1)-F(1)#10	119.42(10)	F(1)-K(1)-F(1)#10	119.42(10)
F(1)#1-K(1)-F(1)#11	119.42(10)	F(1)#2-K(1)-F(1)#11	164.8(14)
F(1)-K(1)-F(1)#11	119.42(10)	F(1)#10-K(1)-F(1)#11	72.2(11)
F(1)#1-K(1)-F(1)#12	119.42(10)	F(1)#2-K(1)-F(1)#12	119.42(10)
F(1)-K(1)-F(1)#12	164.8(14)	F(1)#10-K(1)-F(1)#12	72.2(11)
F(1)#11-K(1)-F(1)#12	72.2(11)	F(1)#1-K(1)-F(1)#13	91.0(2)
F(1)#2-K(1)-F(1)#13	119.42(10)	F(1)-K(1)-F(1)#13	72.2(11)
F(1)#10-K(1)-F(1)#13	91.0(2)	F(1)#11-K(1)-F(1)#13	47.4(12)
F(1)#12-K(1)-F(1)#13	119.42(10)	F(1)#1-K(1)-F(1)#14	91.0(2)
F(1)#2-K(1)-F(1)#14	72.2(11)	F(1)-K(1)-F(1)#14	119.42(10)
F(1)#10-K(1)-F(1)#14	91.0(2)	F(1)#11-K(1)-F(1)#14	119.42(11)
F(1)#12-K(1)-F(1)#14	47.4(12)	F(1)#13-K(1)-F(1)#14	164.8(14)
F(1)#1-K(1)-F(1)#15	119.42(10)	F(1)#2-K(1)-F(1)#15	91.0(2)
F(1)-K(1)-F(1)#15	72.2(11)	F(1)#10-K(1)-F(1)#15	47.4(12)
F(1)#11-K(1)-F(1)#15	91.0(2)	F(1)#12-K(1)-F(1)#15	119.42(10)
F(1)#13-K(1)-F(1)#15	72.2(11)	F(1)#14-K(1)-F(1)#15	119.42(11)
F(1)#1-K(1)-F(1)#16	72.2(11)	F(1)#2-K(1)-F(1)#16	91.0(2)
F(1)-K(1)-F(1)#16	119.42(10)	F(1)#10-K(1)-F(1)#16	119.42(11)
F(1)#11-K(1)-F(1)#16	91.0(2)	F(1)#12-K(1)-F(1)#16	47.4(12)
F(1)#13-K(1)-F(1)#16	119.42(10)	F(1)#14-K(1)-F(1)#16	47.4(12)
F(1)#15-K(1)-F(1)#16	164.8(14)	F(1)#1-K(1)-F(1)#7	119.42(10)
F(1)#2-K(1)-F(1)#7	72.2(11)	F(1)-K(1)-F(1)#7	91.0(2)
F(1)#10-K(1)-F(1)#7	47.4(12)	F(1)#11-K(1)-F(1)#7	119.42(11)
F(1)#12-K(1)-F(1)#7	91.0(2)	F(1)#13-K(1)-F(1)#7	119.42(11)
F(1)#14-K(1)-F(1)#7	72.2(11)	F(1)#15-K(1)-F(1)#7	47.4(12)
F(1)#16-K(1)-F(1)#7	119.42(10)	F(1)#1-K(1)-F(1)#8	72.2(11)
F(1)#2-K(1)-F(1)#8	119.42(10)	F(1)-K(1)-F(1)#8	91.0(2)
F(1)#10-K(1)-F(1)#8	119.42(11)	F(1)#11-K(1)-F(1)#8	47.4(12)
F(1)#12-K(1)-F(1)#8	91.0(2)	F(1)#13-K(1)-F(1)#8	47.4(12)
F(1)#14-K(1)-F(1)#8	119.42(10)	F(1)#15-K(1)-F(1)#8	119.42(11)
F(1)#16-K(1)-F(1)#8	72.2(11)	F(1)#7-K(1)-F(1)#8	164.8(14)
F(1)#17-K(2)-F(1)#18	90.000(3)	F(1)#17-K(2)-F(1)#19	90.000(6)
F(1)#18-K(2)-F(1)#19	90.000(7)	F(1)#17-K(2)-F(1)#10	180.000(2)
F(1)#18-K(2)-F(1)#10	90.0	F(1)#19-K(2)-F(1)#10	90.000(2)
F(1)#17-K(2)-F(1)#11	90.0	F(1)#18-K(2)-F(1)#11	180.000(2)
F(1)#19-K(2)-F(1)#11	90.000(2)	F(1)#10-K(2)-F(1)#11	90.000(3)
F(1)#17-K(2)-F(1)#12	90.0	F(1)#18-K(2)-F(1)#12	90.000(1)
F(1)#19-K(2)-F(1)#12	180.000(2)	F(1)#10-K(2)-F(1)#12	90.000(6)
F(1)#11-K(2)-F(1)#12	90.000(7)	F(1)#17-K(2)-K(1)	125.264(4)
F(1)#18-K(2)-K(1)	125.264(2)	F(1)#19-K(2)-K(1)	125.3
F(1)#10-K(2)-K(1)	54.736(3)	F(1)#11-K(2)-K(1)	54.736(2)
F(1)#12-K(2)-K(1)	54.736(2)	F(1)#17-K(2)-K(1)#20	54.736(4)
F(1)#18-K(2)-K(1)#20	54.736(2)	F(1)#19-K(2)-K(1)#20	54.7
F(1)#10-K(2)-K(1)#20	125.264(2)	F(1)#11-K(2)-K(1)#20	125.264(2)
F(1)#12-K(2)-K(1)#20	125.264(2)	K(1)-K(2)-K(1)#20	180.0
F(1)#17-K(2)-K(1)#21	125.3	F(1)#18-K(2)-K(1)#21	54.736(2)
F(1)#19-K(2)-K(1)#21	125.264(1)	F(1)#10-K(2)-K(1)#21	54.736(1)
F(1)#11-K(2)-K(1)#21	125.264(2)	F(1)#12-K(2)-K(1)#21	54.7
K(1)-K(2)-K(1)#21	70.5	K(1)#20-K(2)-K(1)#21	109.5
F(1)#17-K(2)-K(1)#19	125.264(1)	F(1)#18-K(2)-K(1)#19	125.264(3)
F(1)#19-K(2)-K(1)#19	54.7	F(1)#10-K(2)-K(1)#19	54.7
F(1)#11-K(2)-K(1)#19	54.736(1)	F(1)#12-K(2)-K(1)#19	125.264(2)
K(1)-K(2)-K(1)#19	70.5	K(1)#20-K(2)-K(1)#19	109.5
K(1)#21-K(2)-K(1)#19	109.5	F(1)#17-K(2)-K(1)#22	54.7
F(1)#18-K(2)-K(1)#22	125.264(2)	F(1)#19-K(2)-K(1)#22	54.736(1)
F(1)#10-K(2)-K(1)#22	125.264(1)	F(1)#11-K(2)-K(1)#22	54.736(2)
F(1)#12-K(2)-K(1)#22	125.3	K(1)-K(2)-K(1)#22	109.5
K(1)#20-K(2)-K(1)#22	70.5	K(1)#21-K(2)-K(1)#22	180.0

Bond lengths and angles for K_3WF_6 (continued)...

K(1)#19-K(2)-K(1)#22	70.5	F(1)#17-K(2)-K(1)#23	54.736(3)
F(1)#18-K(2)-K(1)#23	125.264(2)	F(1)#19-K(2)-K(1)#23	125.3
F(1)#10-K(2)-K(1)#23	125.264(3)	F(1)#11-K(2)-K(1)#23	54.736(2)
F(1)#12-K(2)-K(1)#23	54.736(1)	K(1)-K(2)-K(1)#23	70.5
K(1)#20-K(2)-K(1)#23	109.5	K(1)#21-K(2)-K(1)#23	109.5
K(1)#19-K(2)-K(1)#23	109.5	K(1)#22-K(2)-K(1)#23	70.5
W(1)-F(1)-K(2)#9	180.0	W(1)-F(1)-K(1)	97.6(7)
K(2)#9-F(1)-K(1)	82.4(7)	W(1)-F(1)-K(1)#9	97.6(7)
K(2)#9-F(1)-K(1)#9	82.4(7)	K(1)-F(1)-K(1)#9	164.8(14)
W(1)-F(1)-K(1)#8	97.6(7)	K(2)#9-F(1)-K(1)#8	82.4(7)
K(1)-F(1)-K(1)#8	89.0(2)	K(1)#9-F(1)-K(1)#8	89.0(2)
W(1)-F(1)-K(1)#7	97.6(7)	K(2)#9-F(1)-K(1)#7	82.4(7)
K(1)-F(1)-K(1)#7	89.0(2)	K(1)#9-F(1)-K(1)#7	89.0(2)
K(1)#8-F(1)-K(1)#7	164.8(14)		

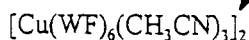
Symmetry transformations used to generate equivalent atoms:

#1 y,z,x	#2 z,x,y	#3 -y,-z,-x	#4 -z,-x,-y
#5 -x,-y,-z	#6 x-1/2,y,z-1/2	#7 -x+1/2,-y+1/2,-z	
#8 -x+1/2,-y,-z+1/2	#9 x,y-1/2,z-1/2	#10 y+1/2,z+1/2,x	
#11 z+1/2,x,y+1/2	#12 x,y+1/2,z+1/2	#13 -y+1/2,-z,-x+1/2	
#14 -y,-z+1/2,-x+1/2	#15 -z+1/2,-x+1/2,-y	#16 -z,-x+1/2,-y+1/2	
#17 -y+1/2,-z+1/2,-x+1	#18 -z+1/2,-x+1,-y+1/2		
#19 -x+1,-y+1/2,-z+1/2	#20 -x+1,-y+1,-z+1	#21 -x+1/2,-y+1,-z+1/2	
#22 x+1/2,y,z+1/2	#23 -x+1/2,-y+1/2,-z+1		

Crystal data and structure refinement for $[\text{Cu}(\text{WF})_6(\text{CH}_3\text{CN})_3]_2$

Empirical formula	$\text{C}_6\text{H}_9\text{CuF}_{12}\text{N}_3\text{W}_2$
Formula weight	782.40
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$\text{P2}_1/\text{c}$
Unit cell dimensions	$a = 12.189(4)$ Å $\alpha = 90^\circ$ $b = 14.054(5)$ Å $\beta = 114.23(3)^\circ$ $c = 11.033(4)$ Å $\gamma = 90^\circ$
Volume, Z	$1723.5(10)$ Å ³ , 4
Density (calculated)	3.015 Mg/m ³
Absorption coefficient	14.652 mm ⁻¹
F(000)	1404
Crystal size	$0.80 \times 0.75 \times 0.20$ mm
θ range for data collection	1.83 to 27.56°
Limiting indices	$-15 \leq h \leq 14$, $-18 \leq k \leq 0$, $0 \leq l \leq 14$
Reflections collected	4175
Independent reflections	3969 ($R_{\text{int}} = 0.0876$)
Completeness to $\theta = 27.56^\circ$	99.5 %
Absorption correction	None
Max. and min. transmission	0.1576 and 0.0300
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3969 / 0 / 216
Goodness-of-fit on F^2	1.121
Final R indices [$>2\sigma(I)$]	$R_1 = 0.0485$, $wR_2 = 0.1365$
R indices (all data)	$R_1 = 0.0627$, $wR_2 = 0.1737$
Extinction coefficient	$0.0047(4)$
Largest diff. peak and hole	3.351 and -4.401 eÅ ⁻³

Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for $[\text{Cu}(\text{WF})_6(\text{CH}_3\text{CN})_3]_2$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.



	x	y	z	U(eq)
W(1)	9650(1)	1951(1)	4598(1)	24(1)
W(2)	14514(1)	-379(1)	6987(1)	28(1)
Cu(1)	11685(2)	319(1)	7498(2)	25(1)
F(1)	8896(7)	715(6)	3958(8)	26(2)
F(2)	10985(8)	1287(6)	5978(8)	32(2)
F(3)	8859(10)	1958(7)	5699(10)	43(2)
F(4)	10483(9)	1798(7)	3551(10)	37(2)
F(5)	10417(10)	3112(6)	5253(11)	45(2)
F(6)	8391(9)	2579(8)	3267(11)	47(3)
F(7)	13218(8)	374(6)	7128(9)	28(2)
F(8)	13821(10)	-1511(7)	7252(12)	46(3)
F(9)	15251(10)	774(8)	6872(15)	58(3)
F(10)	15747(11)	-1117(8)	6814(15)	61(3)
F(11)	13594(13)	-409(11)	5187(11)	66(4)
F(12)	15351(11)	-315(8)	8810(12)	57(3)
N(1)	10111(13)	267(9)	7703(13)	31(3)
N(2)	12475(12)	-703(9)	8830(11)	30(3)
N(3)	12401(11)	1387(9)	8790(12)	30(3)
C(1)	9261(12)	190(9)	7863(14)	25(3)
C(2)	8170(20)	100(15)	8070(20)	56(5)
C(3)	13081(15)	-1297(11)	9449(15)	33(3)
C(4)	13848(19)	-2046(15)	10230(20)	57(6)
C(5)	12795(17)	1982(11)	9536(16)	36(3)
C(6)	13320(20)	2734(14)	10510(20)	55(5)

Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Cu}(\text{WF})_6(\text{CH}_3\text{CN})_3]_2$

	x	y	z	U(eq)
H(2A)	8270	414	8883	80
H(2B)	7997	-561	8127	80
H(2C)	7513	388	7342	80
H(4A)	13835	-2566	9658	80
H(4B)	13568	-2261	10877	80
H(4C)	14656	-1811	10671	80
H(6A)	14094	2529	11153	80
H(6B)	12805	2875	10940	80
H(6C)	13427	3294	10064	80

Anisotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for $[\text{Cu}(\text{WF})_6(\text{CH}_3\text{CN})_3]_2$

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2 [(ha^*)^2 U_{11} + \dots + 2hka^*b^* U_{12}]$$

	U11	U22	U33	U23	U13	U12
W(1)	28(1)	20(1)	21(1)	1(1)	7(1)	-1(1)
W(2)	27(1)	28(1)	31(1)	-1(1)	13(1)	1(1)
Cu(1)	27(1)	27(1)	20(1)	-1(1)	9(1)	1(1)
F(1)	16(4)	30(4)	30(4)	-4(3)	7(3)	-4(3)
F(2)	29(4)	34(5)	27(4)	7(3)	5(3)	0(3)
F(3)	56(6)	47(6)	41(5)	-5(4)	37(5)	2(4)
F(4)	39(5)	43(5)	40(5)	2(4)	27(4)	-1(4)
F(5)	54(6)	21(4)	55(6)	-5(4)	19(5)	-4(4)
F(6)	40(6)	43(6)	48(6)	21(5)	7(5)	8(4)
F(7)	29(4)	28(4)	37(5)	1(3)	23(4)	5(3)
F(8)	60(7)	33(5)	71(7)	-15(5)	52(6)	-10(4)
F(9)	39(6)	42(6)	119(11)	17(6)	58(7)	8(4)
F(10)	50(6)	43(6)	111(11)	-4(6)	55(7)	9(5)
F(11)	72(9)	97(11)	34(6)	-4(6)	28(6)	1(7)
F(12)	45(6)	58(7)	45(6)	-2(5)	-7(5)	8(5)
N(1)	41(7)	34(6)	27(6)	4(5)	21(6)	9(5)
N(2)	43(7)	31(6)	16(5)	1(5)	12(5)	-4(5)
N(3)	25(6)	36(7)	26(6)	-8(5)	9(5)	0(5)
C(2)	84(16)	48(11)	43(10)	-4(8)	32(11)	-11(10)
C(3)	37(8)	35(8)	27(7)	10(6)	13(6)	-1(6)
C(4)	48(11)	58(12)	66(13)	33(10)	25(10)	22(9)
C(5)	49(10)	26(7)	31(8)	-6(6)	16(7)	3(6)
C(6)	61(12)	40(10)	46(11)	-27(8)	3(9)	0(9)

Bond lengths [Å] and angles [°] for $[\text{Cu}(\text{WF})_6(\text{CH}_3\text{CN})_3]_2$

W(1)-F(3)	1.835(9)	W(1)-F(4)	1.837(9)
W(1)-F(6)	1.855(9)	W(1)-F(5)	1.872(9)
W(1)-F(2)	1.950(8)	W(1)-F(1)	1.956(8)
W(2)-F(11)	1.837(12)	W(2)-F(12)	1.847(11)
W(2)-F(8)	1.879(10)	W(2)-F(9)	1.881(10)
W(2)-F(10)	1.900(10)	W(2)-F(7)	1.959(8)
Cu(1)-N(2)	1.996(13)	Cu(1)-N(3)	2.006(12)
Cu(1)-N(1)	2.022(14)	Cu(1)-F(2)	2.055(8)
Cu(1)-F(1)#1	2.064(8)	Cu(1)-F(7)	2.072(8)
F(1)-Cu(1)#1	2.064(8)	N(1)-C(1)	1.13(2)
N(2)-C(3)	1.14(2)	N(3)-C(5)	1.13(2)
C(1)-C(2)	1.45(3)	C(3)-C(4)	1.44(2)
C(5)-C(6)	1.45(2)		
F(3)-W(1)-F(4)	173.4(4)	F(3)-W(1)-F(6)	91.9(5)
F(4)-W(1)-F(6)	92.8(5)	F(3)-W(1)-F(5)	93.1(5)
F(4)-W(1)-F(5)	91.5(5)	F(6)-W(1)-F(5)	90.6(5)
F(3)-W(1)-F(2)	89.0(4)	F(4)-W(1)-F(2)	86.3(4)
F(6)-W(1)-F(2)	179.1(5)	F(5)-W(1)-F(2)	89.5(4)
F(3)-W(1)-F(1)	87.0(4)	F(4)-W(1)-F(1)	88.2(4)
F(6)-W(1)-F(1)	91.3(4)	F(5)-W(1)-F(1)	178.1(4)
F(2)-W(1)-F(1)	88.6(4)	F(11)-W(2)-F(12)	176.2(6)
F(11)-W(2)-F(8)	92.0(6)	F(12)-W(2)-F(8)	87.3(5)
F(11)-W(2)-F(9)	92.5(7)	F(12)-W(2)-F(9)	88.1(6)
F(8)-W(2)-F(9)	175.3(6)	F(11)-W(2)-F(10)	92.1(6)
F(12)-W(2)-F(10)	91.7(6)	F(8)-W(2)-F(10)	88.7(5)
F(9)-W(2)-F(10)	92.5(5)	F(11)-W(2)-F(7)	86.8(5)
F(12)-W(2)-F(7)	89.4(5)	F(8)-W(2)-F(7)	91.0(4)
F(9)-W(2)-F(7)	87.9(4)	F(10)-W(2)-F(7)	178.8(5)
N(2)-Cu(1)-N(3)	94.5(5)	N(2)-Cu(1)-N(1)	94.9(5)
N(3)-Cu(1)-N(1)	96.0(5)	N(2)-Cu(1)-F(2)	172.2(5)
N(3)-Cu(1)-F(2)	89.9(5)	N(1)-Cu(1)-F(2)	91.1(4)
N(2)-Cu(1)-F(1)#1	88.5(4)	N(3)-Cu(1)-F(1)#1	171.9(4)
N(1)-Cu(1)-F(1)#1	91.3(4)	F(2)-Cu(1)-F(1)#1	86.3(4)
N(2)-Cu(1)-F(7)	88.3(5)	N(3)-Cu(1)-F(7)	87.0(4)
N(1)-Cu(1)-F(7)	175.5(5)	F(2)-Cu(1)-F(7)	85.4(4)
F(1)#1-Cu(1)-F(7)	85.5(3)	W(1)-F(1)-Cu(1)#1	150.1(5)
W(1)-F(2)-Cu(1)	152.7(5)	W(2)-F(7)-Cu(1)	144.8(4)
C(1)-N(1)-Cu(1)	175.7(12)	C(3)-N(2)-Cu(1)	165.4(13)
C(5)-N(3)-Cu(1)	178.5(14)	N(1)-C(1)-C(2)	179.5(17)
N(2)-C(3)-C(4)	180(2)	N(3)-C(5)-C(6)	179(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2, -y, -z+1

VITA

Sven Erik Eklund was born in Livonia County, Michigan on March 30, 1965. His parents settled in Byron, MI when he was aged nine and he lived there until he graduated from Byron Area High School in 1983. The following December he entered the USAF where he was trained as an interior electrician and spent a little over two years stationed at Seymour Johnson AFB in Goldsboro, NC, and then nearly two years at Kadena AB in Okinawa, Japan. After an honorable discharge from the USAF in March 1988, he worked for Diamond Chrome Plating in Howell, MI before entering college in the fall at Bob Jones University in Greenville, SC. At BJU he started as a Bible major, switched to an art major with a music minor, then finally graduated with a major in science education at the secondary level with a chemistry emphasis in December, 1992. He was then invited by Gleb Mamantov to start graduate school in the Department of Chemistry at The University of Tennessee in January, 1993. He earned a Ph.D. in chemistry in December of 1999, doing his graduate work in the area of molten salt electrochemistry. He will be teaching general chemistry at Tennessee State University in the Spring of 2000.