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SUBJECT:  $UF_6$  Production from Surface Reactions of Uranium and Fluorine  
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**ABSTRACT**

The production of  $UF_6$  by reaction of a collimated stream of fluorine gas with a resistively heated uranium wire was studied at temperatures from 870 to 1020°C and pressures less than  $10^{-3}$  torr. At these temperatures below the uranium melting point, the formation of  $UF_3$  intermediate on the uranium surface resulted in low  $UF_6$  yields. The kinetic energy of the  $UF_6$  ion was on the order of thermal energies. The work function of uranium was measured to be  $4.20 \pm 0.14$  eV

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## 1. SUMMARY

The yield of  $UF_6^-$  from the reaction of fluorine gas with a resistively heated uranium wire ranged from 0.08 to 0.22% of the initial  $UF_6$  formed and was independent of temperature. This was in contrast to the 99+% yield predicted by thermodynamics for the formation of  $UF_6^-$  on a bare uranium surface. Uranium trifluoride formed on the uranium wire surface as an intermediate in the reaction to produce  $UF_6^-$ . Because  $UF_3$  has a high work function,  $UF_6$  formed on  $UF_3$  was unable to form negative ions. At temperatures less than  $2000^\circ K$ , all fluorination reactions should ultimately proceed to completion, forming  $UF_6^-$ . However, the presence of slowly reacting  $UF_3$  intermediate resulted in a system limited by reaction kinetics. Under the investigated conditions the reaction to produce  $UF_6^-$  was a strong function of pressure. The thermoionic work function of uranium metal was also measured to be  $4.20 \pm 0.14$  eV, which is in reasonable agreement with the literature.

## 2. INTRODUCTION AND BACKGROUND

The production of  $UF_6^-$  ions has potential applications in negative ion source technology and uranium isotope separation. Due to the large electron affinity of  $UF_6$  ( $\sim 4.9$  eV) and low work function of uranium metal ( $\sim 3.5$  eV), most  $UF_6$  molecules formed by the reaction of  $F_2$  and U would be expected to form  $UF_6^-$  ions. According to the following Saha-Langmuir equation (3), over 99% of  $UF_6$  would be expected to form as  $UF_6^-$ :

$$\frac{n^-}{n^0} = \frac{W^-}{W^0} \exp[(EA - e\phi)/kT] \quad (1)$$

where  $n^-$  and  $n^0$  are the number of ions and neutral molecules, respectively. The ratio of the degeneracy of the electronic states,  $W^-/W^0$ , is assumed to be of the order one. EA is the electron affinity of  $UF_6$ ,  $\phi$  is the work function of U metal,  $e$  is the charge of an electron, and  $k$  and  $T$  are the Boltzmann constant and absolute temperature.

Dittner and Datz (3) measured over 99% conversion to negative ions on passing  $UF_6$  over a carbon-coated platinum wire. Since the work function of uranium is lower than that of carbon-coated platinum, high ion yields would also be expected for  $UF_6$  passed over a heated uranium wire. This was verified qualitatively by Compton *et al.* (1). The  $UF_6^-$  was also observed to predominate when fluorine reacted with a hot uranium wire (2).

Therefore, the objective of this study was to determine the negative ion yield for the U,  $F_2$  reaction as a function of temperature.

### 3. APPARATUS AND PROCEDURE

A uranium wire was resistively heated and contacted with a collimated stream of fluorine gas. Temperature was measured through a glass port, using an optical pyrometer. For each run, a piece of 33-mil uranium wire was cleaned with emery paper and washed with acetone. The apparatus is shown schematically in Fig. 1. A positive potential was applied to the collector to attract the negative ions.

After the fluorine gas was introduced, the  $UF_6^-$  ion current was recorded as a function of time for each of the three temperatures. A previous study (1) indicated that virtually all of the negative species collected would be  $UF_6^-$  ions. The yield of  $UF_6^-$  (defined here as the percentage of initial  $UF_6$  converted to  $UF_6^-$ ) was determined by calculating the total number of negative ions collected and by measuring the weight loss of the wire during reaction. All weight loss was attributed to  $UF_6$  since its vapor pressure is several orders of magnitude higher than those of other uranium fluorides (5). However, during some runs, a thick coating of  $UF_3$  built up on the wire, resulting in a net weight gain. The amount of  $UF_6$  produced was then determined by weighing the wire after scraping off the coating and correcting for fluorine. A scanning electron microscope was used to examine the wires after the reaction to determine the physical nature of the surface coating.

The work function of the uranium metal was determined by heating the wire and monitoring electron emission as a function of temperature. The Richardson equation shown below was then used to calculate the thermionic work function  $\phi$  (7):

$$i = AB T^2 \exp\left(\frac{e\phi}{RT}\right) \quad (2)$$

where  $i$  is the measured current,  $A$  is the surface area, and  $B$  is a constant. Other symbols have their usual meaning. Therefore according to Eq. (2), plotting  $\ln(i/T^2)$  as a function of  $1/T$  should give a straight line with the slope  $e\phi/k$ .

During an 887°C run, the positive potential on the collector was decreased to zero to estimate the maximum kinetic energy of the  $UF_6^-$  ions. Measurement of the  $F_2$  pressure at the wire surface was not possible. Pressure in the system was monitored several feet downstream and was typically 1 to  $5 \times 10^{-5}$  torr.

### 4. RESULTS

The yield of  $UF_6^-$  ions was  $0.14\% \pm 0.11\%$  and was essentially independent of temperature (see Table 1). The  $UF_3$  layer formed most rapidly at the

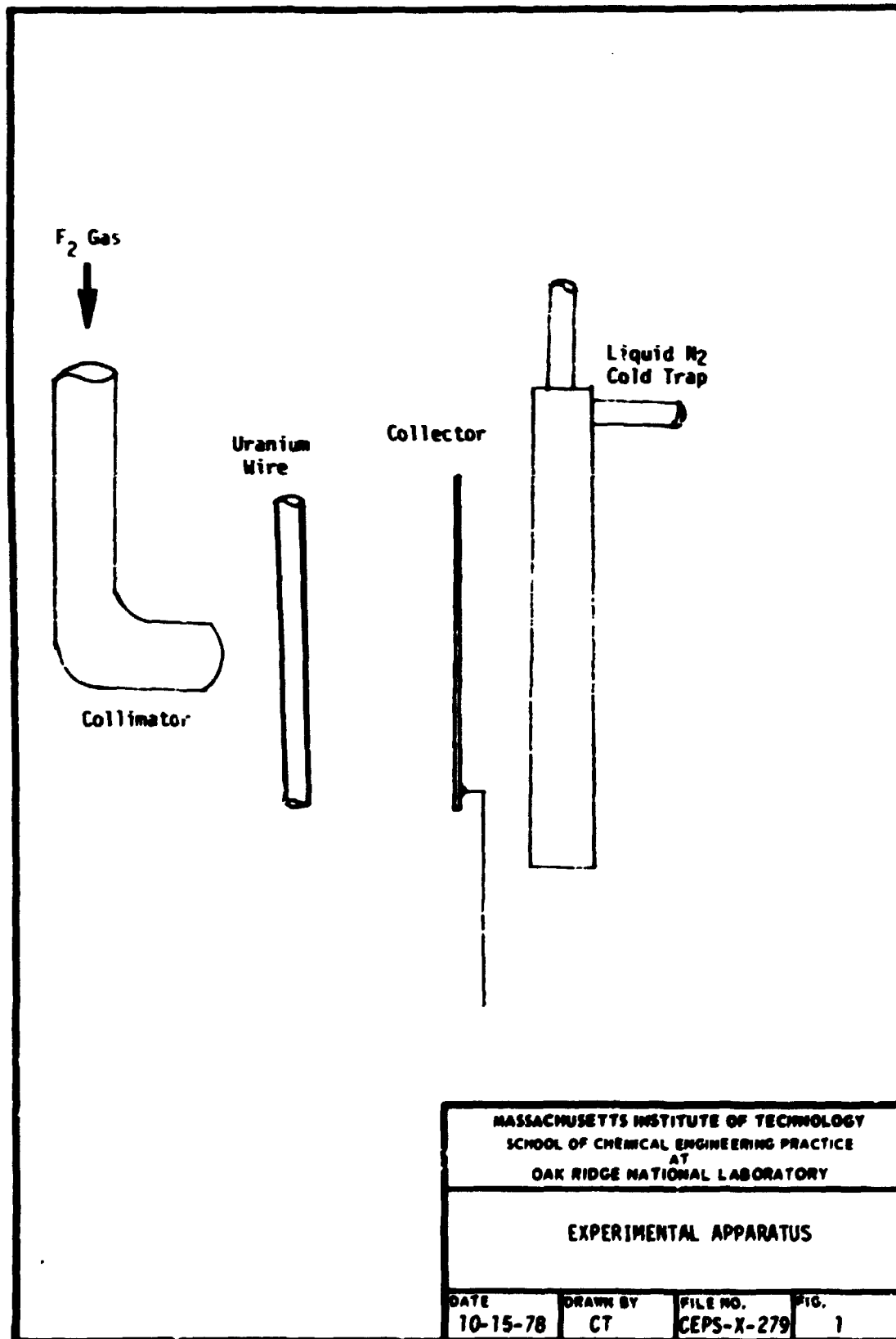


Table 1. Experimental Data

Run	1	2	3	4	5
Temperature (°C)	1020	960	896	887	870/1020
Reaction Time (hr)	2.7	1.6	3.6	1.2	0.75/4.5
Weight Change (mg)	-4.86	-12.2	+6.48	+13.4	-13.2
UF <sub>6</sub> Formed (mg)	4.86	12.2	15.9	1.39	13.2
UF <sub>6</sub> <sup>-</sup> Yield (%)	0.17	0.22	0.12	0.08	0.12

lower temperatures examined and is believed to have caused the weight gain during reaction at 896°C.

Figures 2 and 3 show the ion current as a function of time. In Fig. 2, temperature and F<sub>2</sub> pressure were kept constant; yet ion current increased with time. In Fig. 3 the wire was first contacted with F<sub>2</sub> at 870°C for 45 min. Then the temperature was increased to 1020°C (t = 0). After 1.1 hr, the F<sub>2</sub> pressure was increased. Following the pressure increase, the ion current rose to a value greater than that shown in Fig. 2. Figure 4 shows that collector current increased significantly with increased background F<sub>2</sub> pressure. No ion current was detected when the collector potential was reduced to zero, which indicates that the kinetic energies of the ions were only on the order of thermal energy.

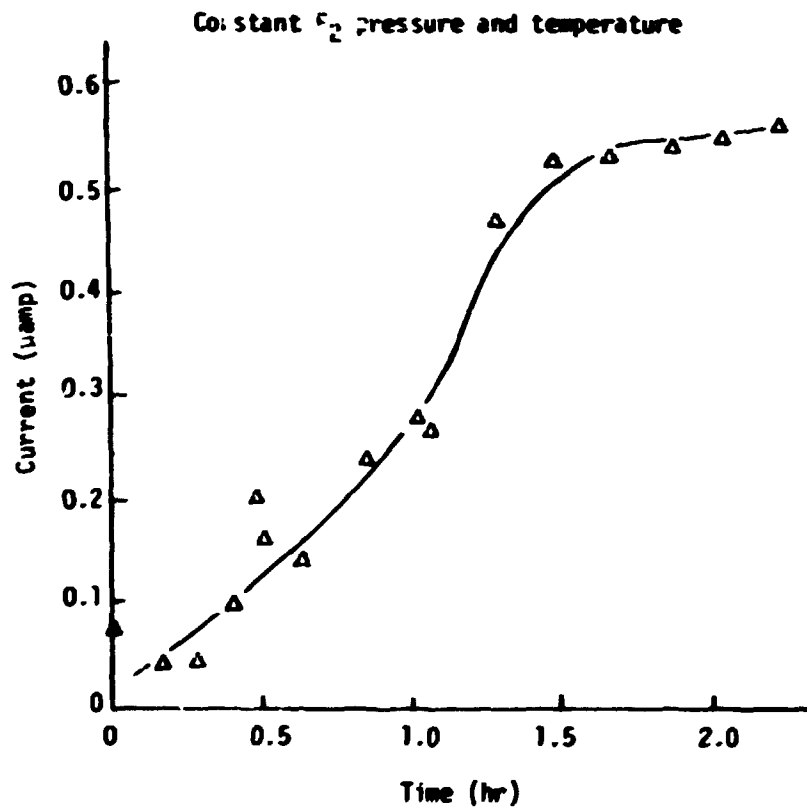
Figure 5 is an electron photomicrograph of a uranium wire after reaction at 896°C. The thickness of the surface coating is approximately 0.3 μm. Figure 6 shows the surface coating of the same wire at higher magnification. This photomicrograph reveals that the coating was porous. X-ray diffraction studies showed that the surface layers on wires contacted at 896°C and 1020°C consisted solely of UF<sub>3</sub>.

The work function of the uranium wire was calculated as 4.20 ± 0.14 eV using the Richardson equation [Eq. (2)], which is plotted in Fig. 7. This compares favorably with reported values of 3.27, 3.63, and 4.32 eV (9).

## 5. DISCUSSION OF RESULTS

The fluorination of uranium to form UF<sub>6</sub> has been suggested to proceed according to the following sequence (10):





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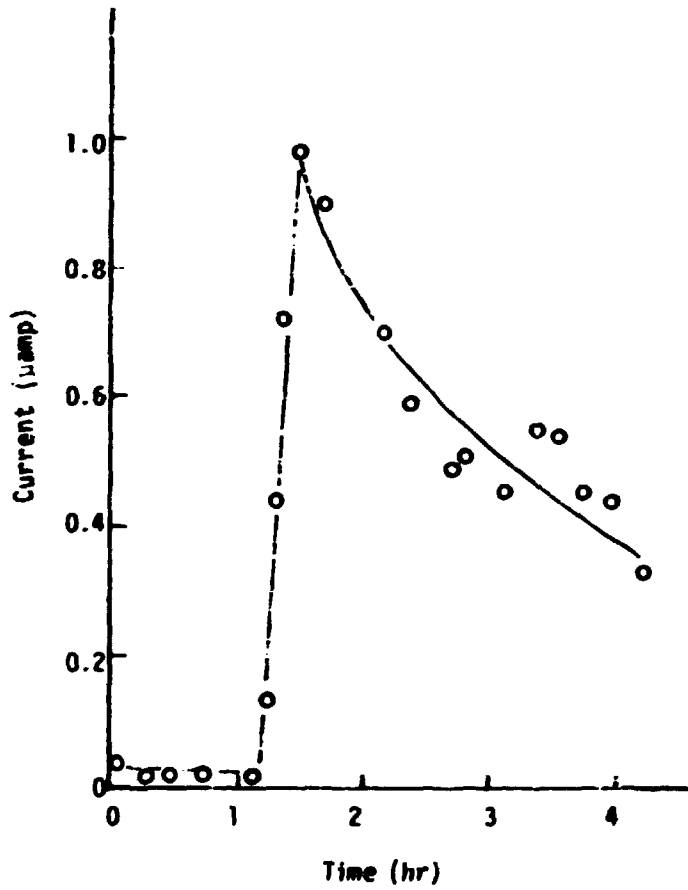
COLLECTOR ION CURRENT VS TIME (1020°C)

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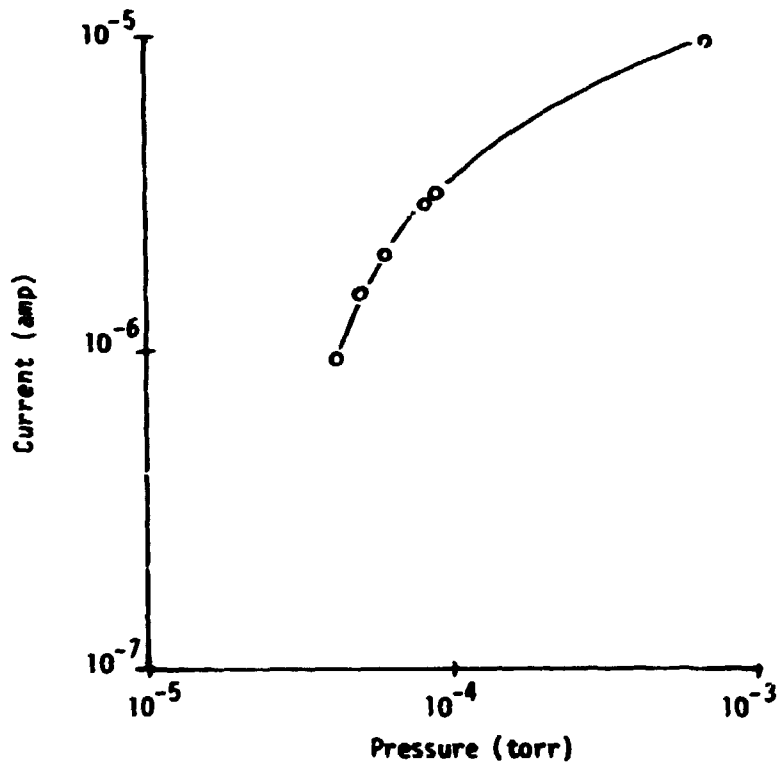
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FIG.  
2



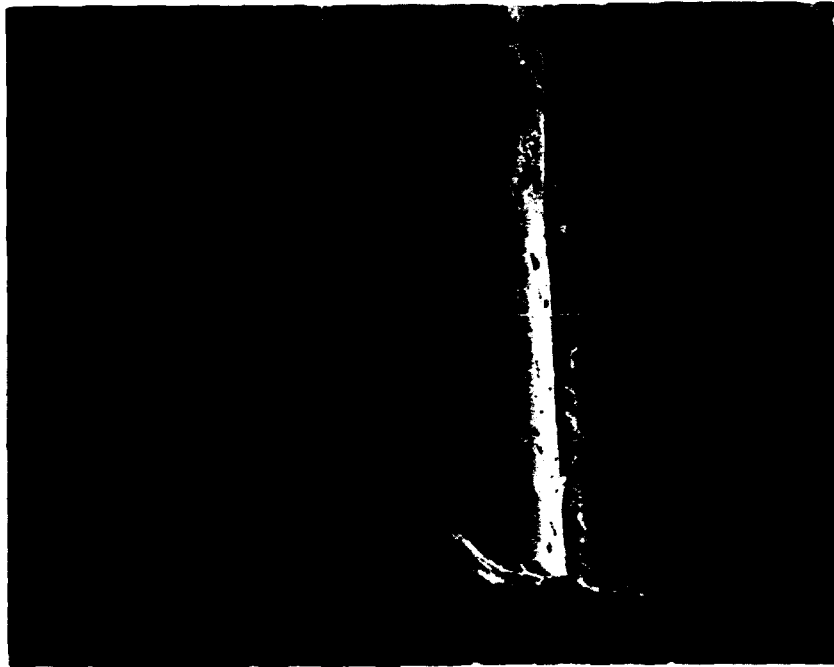
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COLLECTOR ION CURRENT VS TIME (870, 1020°C)			
DATE	DRAWN BY	FILE NO.	FIG.
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COLLECTOR ION CURRENT VS PRESSURE

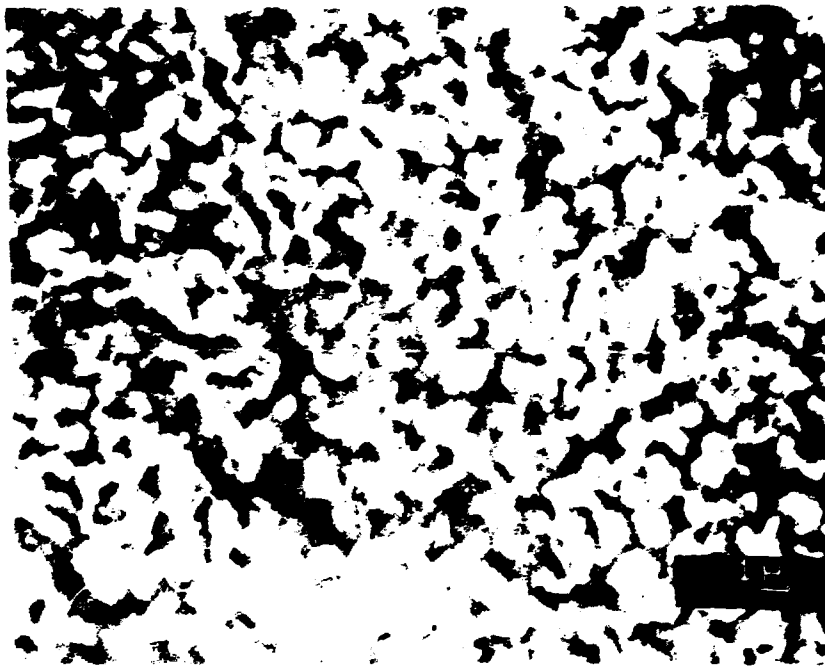
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10-15-78	CT	CEPS-X-279	4



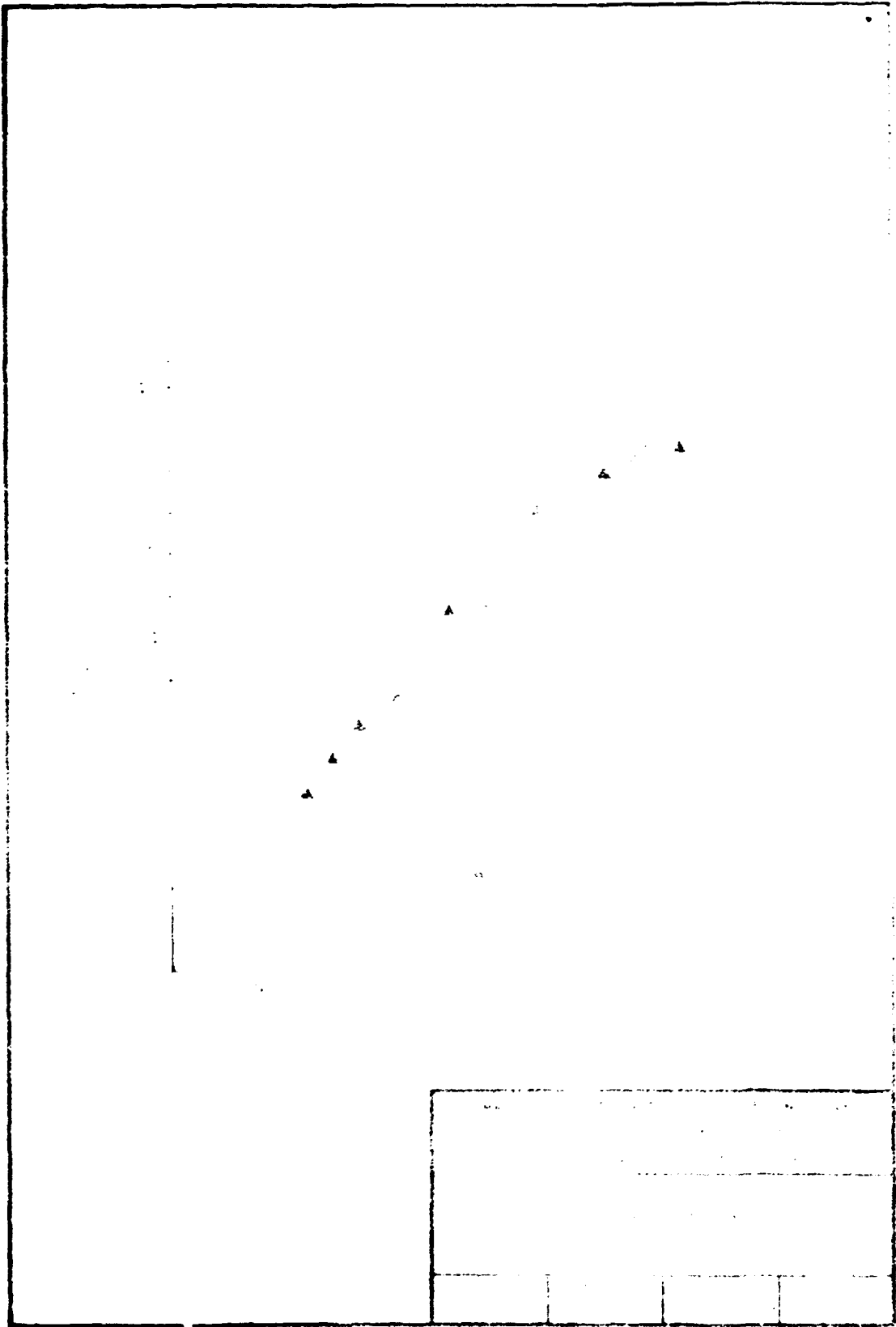
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SURFACE AND COATING ON WIRE  
(60X Magnification)

DATE	DRAWN BY	FILE NO.	FIG.
10-15-78	CT	CEPS-X-279	5



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Reactions (3), (4), and (5) are all thermodynamically favored to go to completion (See Appendix 9.2). However, the buildup of  $\text{UF}_3$  on uranium metal during reaction indicates that  $\text{UF}_6$  production is limited by the kinetics of reaction (4) rather than by thermodynamics. Increasing temperature increased this rate, but the melting point of uranium ( $1132^\circ\text{C}$ ) was the maximum allowable temperature.

Direct contact between the uranium metal and  $\text{UF}_6$  is necessary for  $\text{UF}_6^-$  formation. But as already noted, the metal surface was coated with  $\text{UF}_3$ ; thus the reaction to form  $\text{UF}_6$  occurred on the  $\text{UF}_3$  rather than on the uranium metal. It is also possible that some  $\text{UF}_6$  may diffuse through the porous  $\text{UF}_3$  to the uranium surface to produce  $\text{UF}_6^-$ .

These mechanisms explain the variation of  $\text{UF}_6^-$  production with time. As indicated by Fig. 2, the thickness of the  $\text{UF}_3$  layer increased until steady state was reached between  $\text{UF}_3$  production and reaction to  $\text{UF}_6$ . The  $\text{UF}_3$  layer would be thinner at high temperatures because of higher reaction rates. Figure 3 indicates the presence of a thick layer of  $\text{UF}_3$ . When the temperature was increased, the ion current initially increased due to a thinning of the  $\text{UF}_3$  layer, but then decreased. An analogous but more pronounced effect was observed with the increase in pressure at 1.1 hr.

## 6. CONCLUSIONS

1. The yield of  $\text{UF}_6^-$  ions from the reaction of fluorine with a hot uranium wire ranged from 0.08 to 0.22% of the initial  $\text{UF}_6$  formed and was independent of temperature.
2. At the temperatures investigated,  $\text{UF}_3$  formed on the uranium surface as an intermediate and inhibited the formation of  $\text{UF}_6^-$ .
3. The formation of  $\text{UF}_6$  and  $\text{UF}_6^-$  was limited by the kinetics of  $\text{UF}_3$  fluorination reaction and was a strong function of fluorine pressure.
4. The kinetic energy of the product  $\text{UF}_6^-$  was estimated to be on the order of thermal energies.
5. At the temperature and pressure ranges studied, the system is not as efficient an ion source as the direct surface ionization of  $\text{UF}_6$  gas on hot uranium.

## 7. RECOMMENDATION

The reaction kinetics of uranium fluorination should be studied at higher pressures and temperatures using uranium alloys or molten uranium to eliminate  $UF_3$  formation on the uranium surface.

## 8. ACKNOWLEDGMENTS

The authors thank R.N. Compton and W.R. Garrett for their guidance and help. We also thank P.W. Reinhardt and A. Carter for their help, R.D. Birkhoff for use of the electron microscope, and R. Sherwin for the x-ray diffraction studies.

## 9. APPENDIX

## 9.1 Location of Original Data

Laboratory data were recorded in Databook A-8144-G on file at the MIT School of Chemical Engineering Practice, Bldg. 3001, ORNL.

## 9.2 Thermodynamic Data for Uranium Compounds (4, 6, 8)

<u>Reaction</u>	<u><math>\Delta G</math> (cal/mol) (298K &lt; T &lt; 1309K)</u>
1. $U + \frac{3}{2} F_2 \rightarrow UF_3$	$-343,000 + 52.7 T$
2. $U + 2F_2 \rightarrow UF_4$	$-448,500 + 67.4 T$
3. $U + 3F_2 \rightarrow UF_6$	$-510,800 + 64.6 T$

From these data, equilibrium constants were calculated:

<u>Reaction</u>	<u><math>K_2</math> (1300 K)</u>
1	$1.4 \times 10^{46}$
2	$4.7 \times 10^{60}$
3	$5.8 \times 10^{71}$

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