MOLECULAR BEAM STUDY OF THE KINETICS OF THE FLUORINE-URANIUM DIOXIDE REACTION

Contents

ABSTRACT	ix
1. INTRODUCTION	1
1.1. Statement of the Problem	1
1.2. Fluorine	2
1.3. Uranium Dioxide	2
1.4. Previous Kinetic Investigations	3
1.4.1. Uranium oxides-fluorine	3
1.4.2. Metals-fluorine	5
1.5. Previous Molecular Beam Studies of Reactive Scattering .	5
2. MODULATED MOLECULAR BEAM MASS SPECTROMETRY	7
2.1. Introduction	7
2.2. Definitions	7
2.2.1. Molecular beam	7
2.2.2. Modulated beam	8
2.3. Unique Features of Beam Modulation	10
2.3.1. A case study: dissociative adsorption	10
2.3.2. Additional considerations	14
3. EXPERIMENTAL	17
3.1. Description of Apparatus	17
3.1.1. General Features	17
3.1.2. Vacuum System	17
3.1.2.1. Source Chamber	23

3.1.2.1.1.	Cryo-pump	23
3.1.2.1.2.	Fluorine cryo-pumping	24
3.1.2.1.3.	Pressure measurement	27
3.1.2.2.	Target chamber	27
3.1.2.2.1.	Description	27
3.1.2.2.2.	Beam-to-background ratio	28
3.1.2.3.	Detection chamber	29
3.1.3.	Gas Inlet System	30
3.1.3.1.	Description	30
3.1.3.2.	Passivation	32
3.1.3.3.	Fluorine specifications	32
3.1.4.	Beam Source	33
3.1.4.1.	Description	33
3.1.4.2.	Beam properties	33
3.1.5.	Beam Modulation and Reference Signal	39
3.1.5.1.	Beam Modulation	39
3.1.5.2.	Reference Signal	40
3.1.6.	Uranium Dioxide Target	41
3.1.6.1.	Target description	41
3.1.6.2.	Target mounting and heating	42
3.1.6.3.	Temperature measurement	42
3.1.6.4.	Target contamination	43
3.1.6.5.	Electron beam heater thermal expansion.	43

4. RESULTS	73
4.1. Data Acquisition	73
4.2. Fluorine Beam Strength as a Function of Temperature	74
4.3. Reaction Products Identification	76
4.3.1. Ions present at all temperatures	78
4.3.2. Ions present in the 900°-1600°K temperature range	79
4.3.3. Ions present above 1600°K	81
4.4. Data Presentation	81
4.4.1. Temperature dependence	83
4.4.2. Beam intensity dependence	83
4.4.3. Modulation frequency dependence	86
4.4.4. Target crystallographic orientation	86
4.5. Target Pre- and Post-examinations	86
4.5.1. Scanning electron microscope	89
4.5.2. X-ray diffraction	89
4.5.3. Microprobe analysis	89
4.5.4. Auger analysis	89
4.5.5. Profilometry	89
5. DISCUSSION	93
5.1. Quasi-Equilibrium Analysis	93
5.1.1. Thermodynamic data	98
5.1.2. Conclusions	103
5.2. Reactor Vector Temperature Dependence	103
5.3. Reaction Modeling	105
5.4. Reaction Vector Modulation Frequency Dependence	107

3.1.7. Detection System	44
3.1.7.1. Description	44
3.1.7.2. Electron Multiplier Gain Stability	45
3.1.7.3. Electronics	47
3.1.7.4. Resolution Settings	48
3.1.7.5. Calibration	48
3.1.7.5.1. Ionization cross-section of fluorine	50
3.1.7.5.2. Measured correspondence factor between F_2 and UF_6	51
3.1.7.5.3. Calculated correspondence factor between F_2 and UF_4	53
3.1.7.6. Data Handling	55
3.1.7.6.1. Phase lag measurements	55
3.1.7.6.2. Amplitude measurements	57
3.1.7.6.3. Application to the fluorine- uranium dioxide reaction	60
3.1.8. Mechanical Alignment	61
3.2. Phase-Sensitive Detection	62
3.2.1. Lock-in Detection	62
3.2.2. Pulse Counting	63
3.2.2.1. Description	63
3.2.2.2. Pulse amplification	63
3.2.2.3. RF pick-up	64
3.2.2.4. Illustration: the tantalum-fluorine reaction	66
3.2.3. Comparison	71

5.4.1. Multi-branch reaction mechanism	207
5.4.2. Bulk diffusion	108
5.4.3. Surface diffusion	109
5.4.4. Surface coverage effect	111
5.4.5. Conclusions	111
6. CONCLUSIONS	113
ACKNOWLEDGEMENTS	114
REFERENCES	115

MOLECULAR BEAM STUDY OF THE KINETICS OF THE
FLUORINE-URANIUM DIOXIDE REACTION

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ABSTRACT

The kinetics of uranium dioxide fluorination were studied using an experimental system in which a molecular beam of fluorine was directed at a heated uranium dioxide single crystal wafer maintained in high vacuum. Gaseous reaction products desorbed from the uranium dioxide were monitored by a quadrupole mass spectrometer with an off-axis electron multiplier. The fluorine beam was modulated; ac phase-lock detection and pulse counting were employed to enhance the signal-to-noise ratio. By the modulated molecular beam mass spectrometry technique, both the apparent reaction probability and the reaction phase lag were obtained; the phase lag is related to the duration of some reaction processes on the target surface. Reaction probabilities of 1×10^{-4} or greater could be detected.

The uranium dioxide targets were heated from the rear by electron bombardment to a maximum of 1800°K. The equivalent fluorine beam pressure at the target ranged between 1×10^{-7} and 1×10^{-4} torr. The beam modulation frequency could be varied from 1 to 900 Hz.

Fluorination of the uranium dioxide was found to produce uranium tetrafluoride in the 900°-1600°K temperature range, confirming the

results obtained from thermodynamic considerations (quasi-equilibrium analysis). The kinetics of the interactions were found to be strongly non-linear. With regard to fluorine an apparent order of reaction greater than one was found under low fluorine beam pressure and/or high temperature conditions. An apparent order of one was eventually obtained as the target temperature was decreased and/or the beam intensity was increased. Phase lags were found to be generally dependent upon the fluorine beam pressure.

Fluorination of the uranium dioxide was found to be affected by *some process acting as a flywheel* smoothing the phase response of the interaction as the modulation frequency was varied. Well established reaction and diffusion mechanisms identified in previous modulated beam investigations failed to fit the data and further work is warranted in this area.

1. INTRODUCTION

1.1. Statement of the Problem

The reaction of fluorine and various uranium compounds, including UO_2 , in order to obtain the hexafluoride, UF_6 , has been the subject of experimental investigation since the discovery of nuclear fission.

The uranium hexafluoride can be fed to enrichment plants in which $^{235}\text{UF}_6$ is separated from $^{238}\text{UF}_6$. Uranium hexafluoride is the only volatile uranium compound which is suitable for this purpose. More recently its use has been proposed in gas-core reactors and nuclear powered lasers.¹⁻²

The production of refined UF_6 from uranium ore concentrates was successfully applied on an industrial scale by Allied Chemical Corporation.³ It employed fluid-bed reactors for chemical conversion steps and fractional distillation techniques for final UF_6 purification. The success of this venture enhanced interest in the application to the reprocessing of reactor fuel materials.

Although reprocessing of spent nuclear fuels has been accomplished successfully by solvent extraction processes, other methods which do not depend upon the use of organic solvents and aqueous systems appear to have important potential advantages. One method which was under development is based on the ability to convert uranium and plutonium in the spent fuel to volatile hexafluorides which can be readily separated from the fission products and purified by established techniques.⁴

Effective engineering design requires an understanding of the mechanisms and rates of attack of the ceramic oxide pellets by the reacting gases. To this end, the fluorination of single crystals of uranium dioxide by molecular fluorine at temperatures up to 1800°K at low pressures (ca. 10^{-5} torr) has been investigated in this work.

1.2. Fluorine

Being the most electronegative of all elements, fluorine constitutes an attractive oxidizing agent in many applications.

Although it is the most reactive element and recognized as a very dangerous material it can be handled without undue hazards if proper precautions are taken.

Specific information about materials, equipment (availability, techniques), safety precautions as well as tables and graphs giving the physical and thermodynamic properties of fluorine can be found in reference (5).

1.3. Uranium Dioxide

As a result of the importance of UO_2 as a nuclear reactor fuel there now exists a large body of knowledge concerning the properties, technology and irradiation behavior of uranium dioxide.

For our purpose, the availability of UO_2 in single crystals has been a major advantage since the reactivity of a solid may be determined largely by its method of preparation. Indeed, previous investigations have shown that the rate of attack of UO_2 by F_2 is proportional to the sample surface area. Starting with a single crystal of known crystallographic orientation eliminates the need for extensive sample

characterizations, including porosity, specific surface area and grain size.

1.4. Previous Kinetic Investigations

1.4.1. Uranium oxides-fluorine

Early investigations were performed at the Argonne National Laboratory and were reported in a large number of reports and publications [see for example references (4) and (6-11)].

Their purpose was to demonstrate the feasibility of an industrial reprocessing plant based on the fluoride volatility process.

Their work resulted in the two-zone oxidation fluorination concept. Since high density, sintered UO_2 were found to be only slightly reactive towards fluorine, the process incorporates a step wherein the sintered fuel is activated prior to fluorination by oxidation with air or oxygen to form U_3O_8 fines. These are then fluorinated at 500°C .

Using a thermobalance, Iwasaki et al.¹²⁻¹⁴ and G. Vandenbussche¹⁵ were able to give a more fundamental kinetic representation of the reaction. Their rate studies covered the temperature range between 200° and 540°C .

Below 430°C , a thick layer of intermediate scale is formed on the unreacted core and the overall reaction consists of two steps. In the first step UO_2 is converted to UO_2F_2 and in the second step the UO_2F_2 is further changed to UF_6 :

The first step is very rapid in comparison with the second step, the latter corresponding to a uniform attack of the surface of the sample. The activation energies of the second step were determined to be 23 kcal/mole¹⁵ and between 29.3 and 33.1 kcal/mole.¹³ The reaction rates were approximately proportional to the partial pressure of fluorine.

Above 430°C the quantity of the intermediate UO_2F_2 was generally small. Although the formation of UO_2F_2 was confirmed as the only definite compound in the intermediate by x-ray analysis, the atomic ratio of fluorine to uranium was usually less than that of stoichiometric UO_2F_2 .

R. Idrissi et al.¹⁶ studied the formation of different intermediate phases in the reaction $\text{UO}_2 + \text{F}_2 \rightleftharpoons \text{UO}_2\text{F}_2$ by fluorination in situ of a (111) face of a UO_2 single crystal in a high energy electron diffractor (RHEED). The reaction corresponded to the following mechanism:

The experiments consisted in sending an excess of F_2 on the surface of the sample maintained at $400^\circ C$ followed by a prolonged thermal treatment at the same temperature. The different phases from UO_2F_2 to UO_2 were identified as they appeared.

1.4.2. Metals-fluorine

McKinley¹⁷ performed mass-spectrometric measurements of the reaction of polycrystalline nickel at temperatures between 900° and $1600^\circ K$ with fluorine at pressures between 10^{-7} and 10^{-4} torr. Gaseous NiF , NiF_2 and F were the major products and were formed rapidly on the surface at rates linear with fluorine pressure. NiF_2 formation and desorption were important between 900° and $1600^\circ K$ with a maximum rate at 1250° - $1300^\circ K$. The rate-limiting step in the formation of NiF_2 had an activation energy of 39 kcal/mole and was probably due to the dissociation of fluorine on the surface. NiF was present on the surface over the entire temperature range and desorbed above $1100^\circ C$.

D. E. Rosner¹⁸ investigated the high-temperature kinetics of the attack of molybdenum and tungsten surfaces by atomic fluorine. The atomic fluorine was generated by microwave discharge. It was shown that despite the well-known reactivity of molecular fluorine, prior dissociation produces a marked enhancement in the W- or Mo-removal probability at fluorine fluxes and surface temperatures corresponding to appreciable steady-state adatom populations. The enhancements were over one order of magnitude at temperatures below $1200^\circ K$.

1.5. Previous Molecular Beam Studies of Reactive Scattering

This work is a continuation of an on-going effort in modulated molecular beam heterogeneous reaction studies in our laboratory.

Previously, Krakowski and Olander¹⁹ studied the dissociation of hydrogen on tantalum; R. Jones, R. Acharya, A. Z. Ullman, M. Balooch and Olander²⁰⁻²¹ studied the reaction of graphite with oxygen, water and hydrogen.

Moreover, applications of molecular beam techniques to reaction studies have been regularly reviewed.²²⁻²⁸

2. MODULATED MOLECULAR BEAM MASS SPECTROMETRY

2.1. Introduction

The principal unique advantages of introducing a gas sample into a mass spectrometer in the form of a modulated molecular beam, rather than as a gas added to the background were first demonstrated by S. N. Foner and R. L. Hudson²⁹ on the mass spectra of free radicals in flames.

Application of the same experimental philosophy to the study of gas-solid chemical reactions was first made by Smith and Fite^{30,31} with the nickel-chlorine study.

Since then, as pointed out recently by D. R. Olander³² "The literature ... is unique ... in having produced,..., nearly as many review papers as experimental reports."

Since a thorough description of the advantages, limitations and past investigations can be found in the previously mentioned references (22-28,32), this chapter attempts to present, as simply as possible, the fundamentals of a modulated beam experiment which have to be clearly comprehended in order to derive full profit from the reading of the published literature.

2.2. Definitions

2.2.1. Molecular beam

A molecular beam is a uni-directional, collision-free flow of individual molecules traveling through a region of high vacuum.

It is produced by allowing a gas or a vapor to flow through an orifice into a region where a high vacuum is maintained. By the use of collimators a fraction of the total gas flow is selected to form a uni-directional beam.

The advantages of working with a molecular beam are the following:

- a. the identity of the particles in free molecular flow is maintained between the source and the area of interaction (target);
- b. a highly directional beam maximizes interactions with the target and minimizes contributions to the background gas;
- c. a molecular beam is in suitable form for the modulation process.

2.2.2. Modulated beam experiment

A modulated beam is a beam which is periodically interrupted by a mechanical obstacle, generally a multi-bladed rotary disk (Fig. 1a). The blades simply scatter the beam, the scattered particles being added to the background gas.

A detector situated on the beam path would see a beam intensity as a square wave repeating itself with a given frequency (Fig. 1b).

The chopping frequency is determined by the number of blades on the disk and the speed of rotation and is selected by the operator.

The reason for modulation resides in the fact that the particles in the modulated beam interact with the target according to an ac mode whereas the particles from the residual gas interact according to a dc mode.

(a)

(b)

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Fig. 1. Beam Modulation.

2.3. Unique Features of Beam Modulation

2.3.1. A case study: dissociative adsorption

Let us consider a beam of molecules A_2 impinging on a surface S.

As a result of the interaction some of the molecules A_2 can be dissociated in atoms A.

A complete description of the possible mechanism includes:

- a. no interaction $A_2 + S \rightarrow A_2 + S$
- b. adsorption $A_2 + S \rightarrow (SA_2)_a$
- c. desorption of A_2 $(SA_2)_a \rightarrow A_2 + S$
- d. dissociation $(SA_2)_a + S \rightarrow 2(SA)_a$
- e. recombination $2(SA)_a \rightarrow (SA_2)_a + S$
- f. desorption of A $(SA)_a \rightarrow A + S$

where $(SA_2)_a$ and $(SA)_a$ represent the adsorbed states of A_2 and A respectively. Let us assume that:

- i) the desorption of A_2 and recombination steps are negligible;
- ii) the dissociation step is very fast compared to the desorption of A;
- iii) the adsorption step can be described by a factor η called the sticking probability which is the ratio between the number of molecules A_2 adsorbing on the surface to the total number of molecules A_2 impinging on the surface;
- iv) the desorption of A can be described by a rate constant k [sec^{-1}];
- v) the beam of molecules A_2 is modulated with a period T.

As a result of these assumptions we can describe the interaction

Let $n(t)$ be the surface concentration [molecules/cm²] of species $(SA)_a$ as a function of time, t , and I_0 the constant beam intensity [molecules/cm²-sec] when the beam is on.

A mass balance for $(SA)_a$ yields:

i) when the beam is on: $-\frac{T}{2} \leq t \leq 0$,

$$\frac{dn(t)}{dt} = 2\eta I_0 - kn(t) \quad [1]$$

ii) when the beam is off: $0 \leq t \leq \frac{T}{2}$,

$$\frac{dn(t)}{dt} = -kn(t) \quad [2]$$

Solving [1] and [2] for steady-state conditions, i.e.,

$$n_{on}(t = -\frac{T}{2}) = n_{off}(t = \frac{T}{2})$$

$$n_{on}(t = 0) = n_{off}(t = 0),$$

yields:

$$n(t) = \frac{2\eta I_0}{k} \left(1 - \frac{e^{-kt}}{e^{kT/2} + 1}\right) \quad \text{for} \quad -\frac{T}{2} \leq t \leq 0 \quad [3]$$

$$= \frac{2\eta I_0}{k} \frac{e^{-kt}}{1 + e^{-kT/2}} \quad \text{for} \quad 0 \leq t \leq \frac{T}{2} \quad [4]$$

If one monitors the interaction with a mass spectrometer, the output of the detector tuned to the species A, $\text{Sig}(A)$, is proportional to $kn(t)$

$$\text{Sig}(A) = \alpha_A kn(t)$$

where α_A is a constant of proportionality.

Similarly, the output of the mass spectrometer tuned to the species A_2 is:

$$\text{Sig}(A_2) = \alpha_{A_2} (1-\eta) I_0 \quad \text{for} \quad -\frac{T}{2} \leq t \leq 0 \quad [5]$$

$$= 0 \quad \text{for} \quad 0 \leq t \leq \frac{T}{2} \quad [6]$$

when $\eta \ll 1$,

$$\text{Sig}(A_2) = \alpha_{A_2} I_0 \quad \text{for} \quad -\frac{T}{2} \leq t \leq 0 \quad [7]$$

$$= 0 \quad \text{for} \quad 0 \leq t \leq \frac{T}{2} \quad [8]$$

Let us expand $\text{Sig}(A_2)$ and $\text{Sig}(A)$ in Fourier series:

$$\text{Sig}(A_2) = \alpha_{A_2} I_0 \left(\frac{1}{2} - \frac{2}{\pi} \sin \omega t - \frac{2}{3\pi} \sin 3\omega t - \frac{2}{5\pi} \sin 5\omega t - \dots \right) \quad [9]$$

$$\begin{aligned} \text{Sig}(A) = \alpha_A \eta I_0 \left(1 - \frac{4}{\pi} \frac{\sin(\omega t - \delta_1)}{\sqrt{1 + \omega^2/k^2}} - \frac{4}{3\pi} \frac{\sin(3\omega t - \delta_3)}{\sqrt{1 + 9\omega^2/k^2}} \right. \\ \left. - \frac{4}{5\pi} \frac{\sin(5\omega t - \delta_5)}{\sqrt{1 + 25\omega^2/k^2}} - \dots \right) \end{aligned} \quad [10]$$

where:

$$\omega = \frac{2\pi}{T} \quad [11]$$

is the angular frequency;

$$\delta_n = \tan^{-1} \left(\frac{n\omega}{k} \right) \quad n = 1, 3, 5, \dots \quad [12]$$

is the phase difference between $\text{Sig}(A)$ and $\text{Sig}(A_2)$ at the frequency $n\omega$.

The ratio of the amplitudes of the coefficients of $\text{Sig}(A)$ and $\text{Sig}(A_2)$ at a given n yields:

$$r_n = \frac{\alpha_A}{\alpha_{A_2}} \frac{2\eta}{\sqrt{1 + (n\omega)^2/k^2}} ; \quad [13]$$

whereas the ratio of the two time-independent terms gives

$$r_0 = \frac{\alpha_A}{\alpha_{A_2}} 2\eta \quad [14]$$

The unique advantage of modulation can be seen by comparing the information contained in the time-dependent terms yielding the r_n 's and δ_n 's to the information one would get in a dc experiment; the latter is restricted to the determination of r_0 only.

Having experimentally determined α_A/α_{A_2} ,

- i) a dc experiment would give r_0 from which one can get the value of η ;
- ii) a modulated beam experiment would give the r_n 's and δ_n 's from which the values of η and k are extractable.

The transformation of the reactant beam (A_2) into the product signal (A) is illustrated in Fig. 2: plots of

$$\frac{\text{Sig}(A_2)}{\alpha_{A_2}} \quad (\text{square wave})$$

and

$$\frac{\text{Sig}(A)}{2\eta\alpha_A} \quad (\text{skewed wave})$$

as a function of time are shown; the first and third harmonics (sine waves) of both signals are also shown for a particular value of k.

The times t_1 and t_3 are a measure of the phase differences δ_1 and δ_3 .

Compared to a dc beam experiment, a modulated beam experiment allows a deeper probing of the kinetics of the interaction under study.

2.3.2. Additional considerations

The modulation of the beam serves two other purposes.

First of all, the identification of the primary reaction products is more reliable. Let us consider the following sequence:

the first reaction corresponding to the primary process, the second one being a parasitic reaction occurring on the wall of the apparatus.

In a dc experiment both AB and A_2B would appear as reaction products whereas in a modulated beam experiment AB would have a strong ac component and A_2B would not.

The second purpose derives from signal-to-noise considerations. This subject has been treated fairly extensively in the literature

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Fig. 2. First and third harmonics of the reactant and reaction product signal.

[see for example references (33-35)].

From the standpoint of signal-to-noise considerations the most important features introduced by modulation are:

- a) ac amplifiers and ac signal processing techniques can be used, avoiding flicker noise;
- b) turning on and off the source of interaction is equivalent to repetitively "zero" the system, eliminating zero drift, which results in a large improvement on sensitivity or ultimate detectability.

3. EXPERIMENTAL

3.1. Description of Apparatus

3.1.1. General features

In this work the kinetics of uranium dioxide fluorination were studied using an experimental system in which a modulated molecular beam of fluorine is directed at a heated uranium dioxide single crystal wafer. Gaseous reaction products and the reflected reactant are monitored by a quadrupole mass spectrometer.

The beam transport portion is shown in Fig. 3. The system was designed:

- a) to be compact, to minimize beam spreading (i.e., $1/r^2$) losses;
- b) to handle fluorine whose aggressiveness towards most organic and inorganic materials is well-known;
- c) to allow horizontal mounting of the target.

Flanging and equipment photographs are shown in Figs. 4, 5, 6, 7.

3.1.2. Vacuum system

The system consists of three vacuum chambers differentially pumped:

- a) the source chamber in which a modulated beam of fluorine is generated;
- b) the target chamber in which the interactions between the fluorine and the uranium dioxide take place;
- c) the detection chamber containing a quadrupole mass spectrometer.

Fig. 3. Apparatus cross-section.

Fig. 4. Vacuum System Ports.

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Fig. 5. Equipment layout.

CBB 7510-8044

Fig. 6. Equipment layout -- vacuum pumps from left to right:
cryo-vacuum pump; diffusion pump (bottom);
titanium sublimation pump; ion pump.

CBB 751-3046

Fig. 7. Equipment layout operating area. Major components from left to right: oscilloscope; lock-in detection rack; mass spectrometer console; electron beam heater power supply, pulse counting system (CAT).

3.1.2.1. Source chamber

The beam source exhausts into the source chamber which is fabricated from a 6-inch diameter stainless steel tee. The source tube enters through a glass plate capping one arm of the tee (S1) and the beam is extracted through a collimating orifice in the center of the opposite arm. The stem of the tee leads to the vacuum pump (S2).

Within the source chamber are the source tube, the chopper motor and an optical switch to monitor the rotation of the blade. Cooling water for the motor is introduced through CAJON ultra-torr bore-through adapters (S5) and electrical connections to the motor and optical switch are made through an eight-pin feedthrough mounted on a 2-3/4" O.D. ConFlat flange (S4). Typical operating pressures of less than 1×10^{-4} torr are obtained in this Viton O-ring sealed chamber when a strong beam is generated. Under no-load conditions a pressure of 5×10^{-8} torr is generally obtained.

3.1.2.1.1. Cryo-pump

The EXCALIBUR Model # CVR-1006 Cryo-Vacuum Pump reduces system pressure by capture and retention of mass on refrigerated surfaces utilizing the mechanisms of cryo-pumping and cryosorption.

The interral pump design consists of elements refrigerated by liquid helium ($T_{eb} \approx 4.2^\circ K$), cold gaseous helium at approximately $20^\circ K$ and liquid nitrogen ($T_{eb} = 77.4^\circ K$). Cryo-pumping of all gases other than hydrogen, helium and neon is effected mostly on the refrigerated baffles and shield surfaces. The latter gases are vacuum pumped by a cryosorption mechanism on a bonded panel of Linde Molecular Sieve

which forms part of the liquid helium reservoir.

Since the pumping principle involves capture and retention of mass within the system, periodic regeneration or activation of pumping elements is necessary. This operation is achieved by warming the pumping surfaces and exhausting the captured mass with the roughing system. Specific instructions for regeneration as well as for all pump operations are given in the operating instructions manual.³⁶

3.1.2.1.2. Fluorine cryo-pumping

When generating a strong fluorine beam the gas load in the source chamber is about 5×10^{17} molecules/second or 1.5×10^{-2} liter-torr/sec. In order to keep the pressure below 10^{-4} torr, a minimum pumping speed, $S_{\min}$, is:

$$S_{\min} = \frac{1.5 \times 10^{-2}}{10^{-4}} = 150 \text{ liter/sec at } 10^{-4} \text{ torr.}$$

The Excalibur CVR-1006, with a rated pumping speed for nitrogen of 600 liter/sec at 10^{-7} torr, was chosen for its simplicity of operation. The inherent nature of these pumps with regard to available pumping speed, ultimate attainable pressure and system cleanliness makes this type specially attractive, at a competitive cost, to obtain a very high and clean vacuum.

Diffusion pumping could not be utilized because of rapid degradation of the pump oil. Some investigators have used soda lime spread on trays between the system and the diffusion pump; this may result in some contamination of the vacuum system with O_2 and H_2O from the fluorine-soda lime reaction; moreover degradation of the pump oil is

not completely eliminated.

From the thermodynamic functions for molecular fluorine given in reference (37), one can calculate the equilibrium vapor pressure above solid and liquid fluorine at low temperatures. The results are given in Table I.

Table I shows that in order to be able to pump fluorine it is necessary to cool the cryopanel at temperatures below 30°K.

Fluorine was found to be reactive probably with the bonded panel of Linde molecular sieve. When the pump was running out of liquid helium and the amount of fluorine in retention in the pump was large, a large burst of pressure in the chamber occurred. In order to avoid this undesirable effect, frequent regenerations were performed in order to keep the quantity of fluorine in storage at a minimum. This was achieved simply by letting the cryopanel warm up to liquid nitrogen temperature after 2-3 days of experimentation. This procedure, however, results in a larger than normal consumption of liquid helium necessary to cool the pump elements back to 4.2°K.

Evacuation of fluorine is performed by valving the pump off the system with a 6-inch gate valve and warming up the pump elements. The gas load is evacuated through a mechanical pump with a foreline trap, itself protected by a soda lime (mixture of calcium and sodium hydrates) trap where the fluorine reacts to give inert fluorides (CaF_2 and NaF), oxygen and water.

Table I. Vapor Pressure of Molecular Fluorine

	Temperature °K	Vapor Pressure Torr
Solid I		
	15	2.3×10^{-22}
	20	9.5×10^{-15}
	25	3.9×10^{-10}
	30	4.8×10^{-7}
	35	7.9×10^{-5}
	40	3.6×10^{-3}
	45.55	9.2×10^{-2}
Solid II		
	45.55	9.2×10^{-2}
	50	6.1×10^{-1}
	53.54	2.2
Liquid		
	53.54	2.2
	55	3.4
	60	12.8
	65	38.8
	70	98.2
	75	216
	80	425
	85.02	760

3.1.2.1.3. Pressure measurement

Pressure is measured by a RG-75 ionization gauge tube using a VEECO RG-84 controller.

The performance of the thoria-coated iridium filament of the tube is completely unsatisfactory in presence of fluorine at a pressure greater than 10^{-5} torr. A reaction between fluorine and the filament is responsible for a steady increase in the temperature of the filament to achieve a given emission current causing the filament to thin and break after a short time.

As a consequence, only spot checks of the source chamber pressure were performed.

3.1.2.2. Target chamber

3.1.2.2.1. Description

The target chamber is fabricated from a 6-inch diameter stainless steel tee. The beam enters through a 0.8 millimeter (1/32") diameter collimating orifice in the center of one arm of the tee, the opposing arm leads to the vacuum pump through a stainless steel 45°-elbow. The reaction products coming from the surface are sampled through a collimator situated at the center of the stem of the tee. Several tantalum foil radiation heat shields (thickness = 7.6×10^{-2} mm) are placed on the chamber walls between the different chambers to minimize the heat loads on the optical switch and chopper motor on one side and the mass spectrometer on the other side. A small view port with a sapphire window (T1) directly views the target surface for temperature measurement by an infrared pyrometer. Two other view ports, on the beam axis (T3) and on the mass filter axis (T7) are used for

system alignment. A larger view port (T2) is provided for inspection of target chamber contents. The target holder is mounted within the target chamber on top of an electron beam heater.

This chamber is evacuated by a CVC 6-inch oil diffusion pump with liquid nitrogen baffle and gate valve. A Welch # 1397 mechanical pump with molecular and soda lime traps is used to rough the system or back the diffusion pump.

Pressure is measured by a RG-75 ionization gauge tube using a VEECO RG-84 controller. This copper and Viton A gasket sealed chamber attains a base pressure of 3×10^{-9} torr and operates at about 1×10^{-7} torr under a strong beam load.

Since the fluorine pressure is very low the reaction with the silicone oil (DC 705) is not a factor. Similarly the performance of the gauge tube has been satisfactory.

3.1.2.2.2. Beam-to-background ratio

It is observed that the pressure in the target chamber is roughly three orders of magnitude smaller than the equivalent primary beam pressure at the target as defined in section 3.1.4.2. Therefore, an enviable beam-to-background ratio of 1,000 is obtained with this apparatus.

The major background species is likely to be the same species as the beam gas but the molecules which do not come directly from the beam source may be of an entirely different nature with respect to temperature, electronic state, modulation, etc... This is extremely important for a non-linear surface process for which the non-modulated dc background directly affects the reaction rate. Consequently, a

system parameter, the beam-to-background ratio must be considered. Since, in our work, the value of this parameter is 1000, the perturbation brought about by the dc background can be neglected.

3.1.2.3. Detection chamber

The detection chamber is fabricated from a 6-inch diameter stainless steel tee. A collimator of 1.6 millimeter (1/16") diameter, situated in the center of one arm of the tee, allows sampling of the products desorbed from the target surface. The opposing arm connects to the mass filter flange (D1) whereas the stem of the tee (D5) leads to a couple of vacuum pumps. Another flange (D3) mounted on a flexible bellows is connected to the electron multiplier flange. A small glass view port attached to the mass filter flange is provided for alignment purposes. Another glass view port (D2) is provided to check the geometry of the electron multiplier housing with regard to the mass filter. Within the detection chamber are the ionizer, quadrupole mass filter and electron multiplier.

This chamber is evacuated by a titanium sublimation pump and a 100 liter/sec ULTEK ion pump. Roughing is accomplished only through the 1.6 mm diameter collimating orifice in the wall between the detection and target chambers.

The pressure is monitored by a RG-75 ionization gauge tube using a VARIAN 971-0003 controller. This copper gasket sealed chamber attains a base pressure of 1×10^{-10} torr and operates at about 1×10^{-9} torr under a strong beam load.

Both the target and detection chambers receive a bake-out on every pump-down from atmosphere. Baking is done for one to two

days at 150°C using BRISKEAT silicon rubber embedded heating tapes.

3.1.3. Gas inlet system

3.1.3.1. Description

As shown in Fig. 8, molecular fluorine is taken from a gas cylinder and a MATHESON # 15F-679K fluorine regulator through nickel, monel and copper tubing to a GRANVILLE PHILLIPS variable leak valve.

The cylinder is enclosed in a barricade to protect the operator from any metal ignition which conceivably could occur in any part of a system containing fluorine under high pressure. The pressure reducing regulator system is equipped with two 940F metering valves to allow purging with nitrogen. Both 940F valves, regulator and cylinder main valve are handled remotely.

Since commercial fluorine may contain up to 0.2% hydrogen fluoride, it is imperative that it be removed by passing the fluorine through a MATHESON 68-108 sodium fluoride (NaF) trap. A liquid nitrogen cold trap removes the last hydrogen fluoride traces left and other impurities (CF_4 , F_2O ,...). Moreover, since at liquid nitrogen temperature, fluorine is a liquid with a vapor pressure of about 100 torr, the cold trap is a constant pressure gas source for the Granville Phillips valve whose leak rate is dependent upon the high pressure setting. An ACCO 460-K Helicoid compound monel gauge for fluorine use measures the pressure in the line above the leak valve. Its range varies from vacuum to 30 psig. A WALLACE TIERNAN 62-075 differential pressure gauge measures the pressure in the line below the leak valve. Its range varies from 0 to 10 inch of water (equivalent to 19.5 torr) by 0.1 inch (0.195 torr) increment. The proper use of this gauge requires

XBL 768-7275

Fig. 8. Gas Inlet System.

that the case be evacuated to zero absolute pressure.³⁸

The set-up can be evacuated by a WELCH # 1402 mechanical pump with molecular sieve (foreline) and soda lime traps.

Provision has been made for the introduction of uranium hexafluoride or any other gas to allow calibration of the system as shown in Fig. 8.

All valves outside the barricade in contact with fluorine gas are HOKE 4621N4M monel diaphragm sealed valves.

3.1.3.2. Passivation

The corrosion resistance of all the materials of construction depends upon the formation of a passive fluoride film. Therefore, before any equipment, lines or fittings are placed in service they must be thoroughly cleansed, purged with a stream of dry nitrogen and passivated. The passivating procedure consists of slowly displacing the dry nitrogen in the system by bleeding fluorine into the system.

A detailed passivation procedure as well as complete instructions regarding the hydrogen fluoride trap, barricade and pressure regulating system can be found in references (39-40).

3.1.3.3. Fluorine specifications

According to reference (40), fluorine has a minimum purity of 98.0%. The impurities comprise 1.25% maximum of oxygen, nitrogen and other inert gases and 0.75% maximum of carbon dioxide, hydrogen fluoride and other gases.

The purity of the fluorine beam was examined by measuring the modulated signals of the beam contaminants and comparing them to the fluorine signal. Calculations were performed following the procedure

outlined in section 3.1.7.5.

After passing the gas through the sodium fluoride trap and the liquid nitrogen trap, the amount of impurities present was approximately:

- nitrogen	0.4 %
- oxygen	0.05%

Although the oxygen content cannot be considered as negligible, it is not high enough to mask completely the eventual presence of a molecular oxygen reaction product signal of some importance.

3.1.4. Beam Source

3.1.4.1. Description

The source tube is a quartz multichannel source. It consists of an array of ~ 30 small 0.05 mm diameter capillaries formed in a 0.3 mm thick quartz membrane by electron beam milling.⁴¹ The membrane closes off a 3 cm length of 8 mm diameter quartz tube which is joined to a 30 cm length of 13 mm diameter quartz tubing. The source tube is connected to the fluorine line through quartz-pyrex and pyrex-stainless steel joints. The source tube is centered about the axis of the source chamber and is held by two sleeves whose positions are adjustable for alignment purposes.

3.1.4.2. Beam properties

The molecular beam forming qualities of this multichannel source have been investigated in reference (42).

The total leak rate, ℓ , is related to the source pressure, p_s [torr], by

$$\ell = \frac{p_s}{RT} C_s \text{ [molecules/sec]} \quad [15]$$

where R is the gas constant (1.015×10^{-22} liter-torr/molecule-°K),

T is the absolute temperature and C_s is the source conductance.

Helium measurements performed by R. Jones and V. Kruger of the source conductance have yielded $C_s = 1.37 \times 10^{-2}$ liter/sec.

As C_s is inversely proportional to the square root of the gas molecular weight:

$$\begin{aligned} C_s(F_2) &= \sqrt{\frac{4}{38}} C_s(He) \\ &= 0.445 \times 10^{-2} \text{ liter/sec} \end{aligned} \quad [16]$$

The total leak rate of fluorine as a function of source pressure is displayed in Fig. 9.

$$\begin{aligned} \ell &= \frac{p_s}{1.015 \times 10^{-22} \times 298} \times 0.445 \times 10^{-2} \text{ liter/sec} \\ &= 1.47 \times 10^{17} \times p_s \text{ liter/sec} \end{aligned} \quad [17]$$

where p_s is expressed in torr.

Angular emission patterns have been measured⁴² and theory has been developed to predict the variation with source pressure of the peaking factor χ defined as,

$$\chi = \frac{\text{centerline intensity of channel source}}{\text{centerline intensity of orifice (cosine emission)}} \bigg|_{\ell} \quad [18]$$

where the subscript ℓ indicates that both be operated at the same total leak rate. It has been shown⁴² that χ depends upon the reduced pressure variable p_s/p_L^* where p_L^* is the source pressure for which the mean free path is equal to the channel length L ,

$$p_L^* = \frac{kT}{\sqrt{2} \pi \sigma^2 L} \quad [\text{torr}] \quad [19]$$

where k is Boltzmann's constant, T is the absolute temperature and σ is the molecular collision diameter. Since σ is different for each gas, p_L^* is different and at equal p_g , T and L , the ratio p_g/p_L^* differs and so does χ for each gas. An experimental determination of χ by V. Kruger and R. Jones using helium gas is displayed in Fig. 9.

The beam intensity may now be evaluated. For a given pressure the development leading to Fig. 9 gives the leak rate, ℓ .

The centerline intensity, $J(o)$, is given by:

$$J(o) = \frac{\chi \ell}{\pi} \quad \text{molecules/sec-steradian} \quad [20]$$

The geometry of beam collimation is shown in Fig. 10. Using the point source approximation, the flux at the target position, I_o , is:

$$I_o = \frac{\chi \ell}{\pi} \pi \left(\frac{r_{c_1}}{d_c} \right)^2 \frac{1}{\pi r_{c_1}^2} \left(\frac{d_c}{d_t} \right)^2 \cos 45^\circ \quad [\text{molecules/cm}^2\text{-sec}] \quad [21]$$

After simplification,

$$I_o = \frac{\chi \ell}{\pi} \left(\frac{1}{d_t} \right)^2 \cos 45^\circ \quad [\text{molecules/cm}^2\text{-sec}] \quad [22]$$

The collimation only defines the target area on which the beam strikes and does not affect the beam intensity. However the beam intensity at the target is not uniform. The problem has been treated by R. A. Olstad.⁴³ A comparison between the theoretical profile as given by reference (43) and the experimentally observed profile is made in section 4.5.5.

Figure 11 shows the variation of beam intensity on the target, I_o , with source pressure for different gases. The deviation from unit

Fig. 9. Leak rate and peaking factor as a function of source driving pressure.

XBL 767-7206

Fig. 10. Beam collimation geometry.

XBL 767-7195

Fig. 11. Beam intensity on the target, I_0 , as a function of source driving pressure.

slope is due to the non-linear variation of χ with pressure. Curve B corresponding to He gas has been calculated using the results shown in Fig. 9. Curves C, D and E corresponding to N_2 , F_2 and UF_6 respectively have been experimentally obtained by measuring and normalizing the scattered gas signal. The left hand coordinate of Fig. 11 gives the beam intensity for fluorine only.

Equivalent beam pressure has been used to relate beam experiments to more conventional investigations. It is the pressure for which a target, bathed in the gas at beam temperature, receives the same collision flux as from the beam i.e.

$$I_o = \frac{n\bar{v}}{4} = p_{eq} \frac{\bar{v}}{4kT}$$

or

$$p_{eq} = I_o \frac{\sqrt{MT}}{3.51 \times 10^{22}} \text{ [torr]}, \quad [23]$$

M is the molecular weight and T is the beam temperature.

The right hand coordinate of Fig. 11 gives the equivalent pressure for fluorine only.

No experimental determination of the velocity spectrum of the beam has been made and it is assumed that there is no significant deviation from a Maxwellian spectrum as discussed in reference (44).

3.1.5. Beam modulation and reference signal

3.1.5.1. Beam modulation

The gas effusing from the multichannel source is chopped by a multi-bladed rotating disk driven by a synchronous motor mounted in

a water-cooled copper block. A GLOBE SC 53A111-2, two-phase, six-pole motor is used with a 7-cm diameter symmetrically cut six-blade (or two-blade) chopper to provide a beam modulated at twice (or 2/3) the frequency of the power driving the motor. A modulation rate different from the motor frequency allows the rejection of spurious periodic signals arising from dc noise picked up by the detection system or vibrationally induced. The motor is driven by two variable frequency sine wave voltages displaced in phase by 90° .⁵⁵ Metering is provided to monitor the output voltages. With this arrangement the motor can be used from 90 to 24,000 rpm.

3.1.5.2. Reference signal

The reference signal synchronized to the beam chopping is obtained by using a HEI optical switch OS-561A-200; it consists of an infrared light emitting diode activating a phototransistor across a gap large enough to accommodate the thickness of the rotating blade. The rotation of the disk (stability and symmetry) is monitored by displaying the optical sensor output voltage on an oscilloscope.

Due to the particular mounting positions of the collimator and optical switch, chopping of the gas and light beams are generally not synchronized; this results in a constant phase difference between the actual reactant waveform and the reference waveform which is fed to the phase-sensitive detection system. This phase shift is referred to as a mechanical phase shift.

A disadvantage of the optical switch is its sensitivity to temperature. The collector dark current increases exponentially with

temperature. When the heat load from the target chamber is large, the collector dark current is high enough such that the sensor no longer turns off.

3.1.6. Uranium dioxide target

3.1.6.1. Target description

Uranium dioxide single crystal wafers of three different crystallographic orientations were supplied by Oak Ridge National Laboratory.⁴⁵ Their thickness varies between 0.65 and 1.0 mm.

The shape of the wafers are determined by their crystallographic orientation. Discs cut along a (111) plane are approximately circular with a diameter of 1.75 cm; discs cut along a (100) plane are ellipsoidal with a 1.75 cm small axis and a 4 cm large axis; discs cut along a (110) plane are rectangular with sides equal to 1.75 and 3 cm.

X-ray diffraction of the specimens confirmed their crystal orientation. However it also showed that the specimen plane could deviate by as much as 3° from the specified plane.

Each wafer is constituted of a large single crystal surrounded by smaller ones which are in turn surrounded by polycrystalline material. The single crystal at the center occupies an area several times the size of the area illuminated by the fluorine beam.

Surface roughness of the samples are checked by profilometry. Surface irregularities are within one micron of the mean surface plane.

No attempt has been made to polish the samples further due to their extreme brittleness.

3.1.6.2. Target mounting and heating

The target is mounted on a tantalum support which is heated by electron bombardment. The electron beam heater has been described in reference (46) and is fixed to the end of a linear motion feedthrough.

Due to the poor physical contact between the tantalum support and the target coupled with the low thermal conductivity of UO_2 , the support has to be heated excessively in order to raise the target upper face to the desired temperature. As the latter increases the heat loss by radiation is responsible for an appreciable temperature increase of the thermal shields, apparatus walls and optical switch whose proper functioning ceases at high temperature (as discussed in 3.1.5.2.). Under these conditions a maximum temperature of the UO_2 disk upper face of 1800°K is attainable.

3.1.6.3. Temperature measurement

Target temperature is measured by an IRCON 300 C infrared pyrometer.

The target face is viewed at normal incidence through a sapphire window having 92% transmission at the 2.0 and 2.6 micron wavelength of the infrared pyrometer. The emittance of the uranium dioxide is taken as 0.75 independent of the crystallographic face or the temperature. A critical review of the literature⁴⁷⁻⁴⁹ tends to indicate that this value may be low. However, if the actual emittance of the UO_2 samples is larger than 0.75, the difference between the real temperature of the sample, T_{real} , and the apparent temperature read by the pyrometer for an emittance of 0.75, $T_{0.75}$, stays small. The

observed variation of the apparent temperature with the emittance as set on the pyrometer was

$$T_{app} \propto \frac{1}{\epsilon_{app}^{0.25}}$$

as expected from theory. Therefore,

$$\epsilon_{real}^{0.25} T_{real} = (0.75)^{0.25} T_{0.75}$$

or

$$T_{real} = \left(\frac{0.75}{\epsilon_{real}} \right)^{0.25} T_{0.75} \quad [24]$$

In assuming $\epsilon = 0.75$, T_{real} would be overestimated by a maximum of 7% (corresponding to $\epsilon_{real} = 1$).

3.1.6.4. Target contamination

As it has been discussed in section 3.1.2.2.2, the beam-to-background ratio is about 1000. Assuming an average true reaction probability of 0.1, the rate of surface etching due to the formation of volatile reaction products would be two orders of magnitude larger than the rate of surface contamination, assuming that the background consists entirely of contaminant species having a sticking probability equal to one.

3.1.6.5. Electron beam heater thermal expansion

The length of the electron beam heater structure increases as the heat input increases. This effect has to be corrected by moving the heater down by means of the linear motion feedthrough until the beam signal peaks again. The maximum correction to be applied is 0.65 mm.

3.1.7. Detection system

3.1.7.1. Description

Quadrupole mass spectrometers are used to provide compact mass selective detectors.

The relative positioning of the ionizer, quadrupole mass filter and electron multiplier is shown in Fig. 3:

- i) the spectrometer is equipped with an EAI dual filament ionizer described in reference (50);
- ii) the mass filter consists of an EAI five-inch quadrupole filter rod assembly;
- iii) the detector, a Galileo Channeltron Electron Multiplier (CEM) Model # 4700, is positioned at 90° with reference to the mass filter axis.

This particular configuration, compared to the direct positioning of the electron multiplier behind the quadrupole filter, has been introduced by EXTRANUCLEAR Inc.⁵¹ It reduces noise due to photons and metastable neutrals produced in the ionizer, which, if allowed to strike the first dynode of the multiplier, would produce large untunable noise throughout the entire mass spectrum. This effect can be easily checked by the presence or absence of noise between peaks in a mass spectrum display. Ions emerging from the mass filter are guided to the input face of the electron multiplier by electric fields, while photons and neutral molecules pass harmlessly by. This configuration also preserves the detector lead oxide coating⁵² against the corroding action of fluorine. In our set-up, a better mechanical stability is also obtained because the electron multiplier flange supports most of

the mass filter weight; it also provides a convenient way to align the spectrometer by moving the bellows-mounted detector flange. Ion deflection is optimized by peaking the signal of interest when varying the ion energy and the positive potential applied to a deflector plate situated above the electron multiplier and behind the mass filter. The deflector plate is shown in Fig. 3 and the effects of varying its potential and the ion energy with all other settings fixed, are illustrated in Fig. 12a and 12b.

The off axis positioning is accompanied by a loss of signal. It was not possible to determine this factor experimentally. Comparison tests have been conducted by EXTRANUCLEAR on their spectrometers with multipliers on axis and off axis.⁵¹ They have shown that the loss in signal at any mass in the off axis mode is not greater than 20%, but the signal-to-noise ratio in many cases is increased by a factor of 1000 or more.

3.1.7.2. Electron multiplier gain stability

As it has already been observed by W. H. Beattie,⁵³ the gain of the electron multiplier decreases steadily with exposure to the heavy metal fluorides such as UF_3^+ , TaF_4^+ , ... The primary process causing loss of sensitivity is adsorption of compounds on the surface of the glass-coated electron multiplier. Partial restoration of the gain is obtained by baking the detection chamber. This annoying effect requires that frequent comparison of the reaction product signal and the reference signal (fluorine) be made in order to account properly for it.

The gain of a new high-current CEM # 4700 multiplier is typically 3×10^6 @ 3000 V. Towards the end of our investigation the gain was

XBL 767-7197

Fig. 12. Signal relative intensity as a function of
a. deflector plate voltage
b. ion energy

down to about 1×10^5 @ 3000 V.

3.1.7.3. Electronics

The mass spectrometer head is powered by an EAI Quad 250B electronics package except for the ionizer controller which is described in reference (20).

The mass range covered by the spectrometer is determined by the frequency of the RF voltage fed to the quadrupole rods.

The frequencies of oscillation and corresponding mass ranges are as follows:

<u>Switch Position</u>	<u>Mass Range</u>	<u>Frequency</u>
Low	1-100 amu	5.0 MHz
Medium	10-250 amu	3.3 MHz
High	100-800 amu	1.6 MHz

Slight changes of the frequency in the high mass range result in an appreciable shift of the mass being monitored. Let us consider the following example: a frequency of oscillation of 1.8 MHz determines a mass range of 50 to 500 amu compared to 1.6 MHz which gives a 100-800 amu mass range. An experimenter monitoring a peak in the middle of the mass range would look at mass 275 for 1.8 MHz and at mass 450 for 1.6 MHz. A change of 0.2 MHz, therefore, results in a shift of 175 amu or approximately 1 amu per kHz. A RF frequency with a better than 0.1% stability is required to stay on the same mass peak. This requirement can be met only with a more sophisticated design than the one used in the EAI RF-DC generator. To overcome this lack of stability, it was necessary to work at low resolution in the high mass range such as

small shifts due to the RF did not affect the system reliability.

3.1.7.4. Resolution settings

Resolution is defined as $M/\Delta M$ where M is the mass number and ΔM is the width of the mass peak in amu measured at half peak height.

Molecules with a low molecular weight (F_2 , N_2 , O_2 ,...) are detected in the low mass range with a resolution, R , equal to two times their mass number (equivalent to stating that two equal gaussian peaks differing by one amu are separated by a valley whose depth is 90% of the height of one peak).

Reaction products are detected in the high mass range with a resolution, R , equal to their mass number divided by nine (equivalent to stating that two equal gaussian peaks differing by eighteen amu are separated by a valley whose depth is 90% of the height of one peak). Working at low resolution gives a high sensitivity and small shifts of the RF frequency constitute small perturbations only. Obviously, in this latter case, the different species to be monitored must at least be eighteen amu apart. Having to work in two different mass ranges it is essential to have a sensitivity correspondence factor between the two mass ranges.

3.1.7.5. Calibration

For the simple case of diffuse scattering of a gas i , from the target surface, the signal due to the scattered gas i at some mass M , for a spectrometer with a molecule density sensitive ionizer, is:

$$S_{i,M} = \frac{\sigma_i f_{i,M} \gamma_i \beta_{M,O,i}}{v_i} \quad [25]$$

where:

- σ_i is the total ionization cross-section of species i for a given ionization potential;
- $f_{i,M}$ is the ratio of the intensity of peak of mass M to the sum of intensities of all peaks appearing in the mass spectrum of species i ;
- γ_i is a geometric constant accounting for the collimation geometry and scattered beam angular distribution (all distributions are assumed cosine in this work);
- β_M is an instrumental constant accounting for the overall spectrometer efficiency at mass M ;
- $I_{o,i}$ is the beam intensity at the target surface;
- v_i is the mean speed of a molecule of species i ; v_i is related to the temperature at which species i is emitted from the target, T_i , and to the mass m_i of the species i by

$$v_i = \sqrt{\frac{8kT_i}{\pi m_i}} \quad [26]$$

If species i is supplied by the molecular beam source (section 3.1.4.2) and all of the incident molecules are reflected diffusely, $I_{o,i}$ is proportional to the leak rate, ℓ , from the source tube; ℓ is proportional to the pressure in the source tube, p_s , and to the conductance, C_s , itself inversely proportional to the square root of the molecular weight of the effusing gas. For this case, $S_{i,M}$ can be written as:

$$S_{i,M} = \frac{\sigma_i f_{i,M} \gamma_i \beta_M p_{s,i}}{\sqrt{T_i}}, \quad [27]$$

which is independent of m_i .

Generally, γ_i and β_M are not known and σ_i is known only for a few simple species.

3.1.7.5.1. Ionization cross-section of fluorine

By comparing the signal magnitudes of a nitrogen and a fluorine beam we can obtain an approximate value for the ionization cross-section of fluorine if we assume

$$\gamma_{N_2} \beta_{28} = \gamma_{F_2} \beta_{38}$$

If the experimental conditions are such that:

$$p_{s,F_2} \approx p_{s,N_2},$$

and

$$T_{F_2} = T_{N_2},$$

then,

$$\frac{\sigma_{F_2}}{\sigma_{N_2}} = \frac{S_{F_2} f_{N_2,28}}{S_{N_2} f_{F_2,38}}. \quad [28]$$

For an ionization potential of 100 eV,

$$f_{N_2,28} = \frac{1}{1.075} \quad \text{and} \quad f_{F_2,38} = \frac{1}{1.5};$$

therefore,

$$\frac{\sigma_{F_2}}{\sigma_{N_2}} = 1.4 \frac{S_{F_2}}{S_{N_2}} \quad [29]$$

Experimentally, for $p_s \approx 0.45$ torr and $T = 300^\circ K$,

$$S_{N_2} = 59.5 \text{ mV} \quad \text{and} \quad S_{F_2} = 12.75 \text{ mV.}$$

Therefore,

$$\frac{\sigma_{F_2}}{\sigma_{N_2}} = 0.3, \quad [30]$$

which compares reasonably well with the value of 0.4 obtained from reference (53).

The result reported in Eq. [30] has been used to calculate the amount of nitrogen and oxygen impurities in the beam (3.1.3.3).

3.1.7.5.2. Measured correspondence factor between F_2 and UF_6

Similarly we can compare the signal magnitudes of a fluorine and an uranium hexafluoride beam.

The UF_6 mass spectrum is displayed in Fig. 13. The parent peak UF_6^+ is very small and the major peak is UF_5^+ which has a mass equal to 333 amu.

Experimentally, for $p_s = 0.45$ torr and $T = 300^\circ K$, $S_{F_2} = 12.7$ mV (measured in the low mass range) and $S_{UF_6} = 48.5$ mV (measured in the high mass range).

With the measured values of

$$f_{F_2, 38} = \frac{1}{1.5} \quad \text{and} \quad f_{UF_6, 333} = \frac{1}{2} ,$$

Fig. 13. Mass spectrum of UF_6 (ionization potential = 70 eV).

assuming $\gamma_{F_2} = \gamma_{UF_6}$,

$$\frac{\sigma_{UF_6}}{\sigma_{F_2}} \frac{\beta_{333}}{\beta_{38}} = \frac{s_{UF_6}}{s_{F_2}} \frac{f_{F_2,38}}{f_{UF_6,333}} = 5.45 \quad [31]$$

To find the correspondence factor C_{UF_6/F_2} at equal beam intensity on the target surface, we can write from Eq. [25]:

$$C_{UF_6/F_2} = \left(\frac{s_{UF_6}}{s_{F_2}} \right)_{I_0} = \frac{\sigma_{UF_6}}{\sigma_{F_2}} \frac{f_{UF_6,333}}{f_{F_2,38}} \frac{\gamma_{UF_6}}{\gamma_{F_2}} \frac{\beta_{333}}{\beta_{38}} \frac{v_{F_2}}{v_{UF_6}} \quad [32]$$

Assuming $\gamma_{UF_6} = \gamma_{F_2}$ and introducing Eqs. [26] and [31],

$$C_{UF_6/F_2} = 12.5 \sqrt{\frac{T_{F_2}}{T_{UF_6}}} \quad [33]$$

where the experimental values of $f_{F_2,38}$ and $f_{UF_6,333}$ have been used.

Equal beam intensities result in a UF_5^+ signal which is 12.5 times larger than the F_2^+ signal provided that both species are emitted from the target at the same temperature.

3.1.7.5.3. Calculated correspondence factor between F_2 and UF_4

It is shown in section 4.3 that uranium tetrafluoride, UF_4 , is the major reaction product over a wide temperature range.

If we assume that reaction product desorption is diffuse (as is the primary beam scattered from a room temperature target), then equivalent fractions of scattered reactant or emitted product flux enter the solid angle subtended by the mass spectrometer ionizer and:

$$\gamma_{F_2} = \gamma_{UF_6} = \gamma_{UF_4} \quad [34]$$

A correspondence factor, C_{UF_4/F_2} , between the sensitivities of detection of UF_4 in the high mass range and F_2 in the low mass range can be calculated by a procedure similar to 3.1.7.5.2.

The UF_4 cracking pattern is given in section 4.3.2; the major peak corresponds to the UF_3^+ ion with

$$f_{UF_4,295} = \frac{1}{1.6}$$

Therefore from Eqs. [25] and [26],

$$C_{UF_4/UF_6} = \left(\frac{S_{UF_4}}{S_{UF_6}} \right)_{I_0} = \left(\frac{\sigma_{UF_4}^{\beta_{295}}}{\sigma_{UF_6}^{\beta_{333}}} \right) \frac{f_{UF_4,295}}{f_{UF_6,333}} \sqrt{\frac{m_{UF_4} T_{UF_6}}{m_{UF_6} T_{UF_4}}} \quad [35]$$

Assuming $\sigma_{UF_4}^{\beta_{295}} \approx \sigma_{UF_6}^{\beta_{333}}$,

$$C_{UF_4/UF_6} = 1.18 \sqrt{\frac{T_{UF_6}}{T_{UF_4}}} \quad [36]$$

Combining Eqs. [33] and [36] yields:

$$C_{UF_4/F_2} = C_{UF_4/UF_6} \times C_{UF_6/F_2} = 15 \sqrt{\frac{T_{F_2}}{T_{UF_4}}} \quad [37]$$

If we assume that the fluorine beam is scattered from a room temperature target whereas UF_4 is desorbed from a target whose temperature is T_g then,

$$C_{UF_4/F_2} = 15 \sqrt{\frac{300}{T_g}} \quad [38]$$

When $T_g \approx 300^\circ K$, a given UF_4 flux leaving the target gives a UF_3^+ signal which is 15 times the F_2^+ signal given by the same flux of F_2 leaving the target in the same geometrical conditions.

3.1.7.6. Data handling

A set of data is composed of reaction product amplitudes and phase angles (phase lags) relative to the modulated reactant beam.

3.1.7.6.1. Phase lag measurements

The measured phase lag for any species is the sum of phase lags from different steps.

Initially the chopped beam has a mechanical phase shift, ϕ_{mech} , independent of frequency due to the relative position of the beam axis and optical switch (see 3.1.5.2).

The beam is delayed in transit from the chopper to the target yielding a source-to-target transit phase lag, ϕ_{d1} .

Interaction with the target introduces the reaction phase lag, ϕ

Transit of desorbed product or scattered reactant from the target to the mass spectrometer adds a second transit phase lag, ϕ_{d2} .

Transit of the ionized molecules in the mass spectrometer detector adds a third phase lag, ϕ_{d3} .

Finally the transformation of the mass spectrometer output current to a voltage signal at the lock-in amplifier adds a complex impedance phase lag, ϕ_z .

The nature of the different phase corrections to be applied have been discussed by Jones.²⁰

The measured phase angles for scattered reactant (R) and desorbed product (P) are given by:

$$\phi_{\text{meas}}^P = \phi_{\text{mech}} + \phi_{d_1}^R + \phi + \phi_{d_2}^P + \phi_{d_3}^P + \phi_Z ; \quad [39]$$

$$\phi_{\text{meas}}^R = \phi_{\text{mech}} + \phi_{d_1}^R + \phi_{d_2}^R + \phi_{d_3}^R + \phi_Z . \quad [40]$$

The measured reaction product phase angle relative to the reactant phase angle at the same modulation frequency is:

$$\begin{aligned} \phi_{\text{meas}} &= \phi_{\text{meas}}^P - \phi_{\text{meas}}^R \\ &= \phi + \left(\phi_{d_2}^P - \phi_{d_2}^R \right) + \left(\phi_{d_3}^P - \phi_{d_3}^R \right) \end{aligned} \quad [41]$$

$$\phi_{\text{meas}} = \phi + \Delta\phi_{d_2} + \Delta\phi_{d_3} ; \quad [42]$$

where

$$\Delta\phi_{d_2} = \phi_{d_2}^P - \phi_{d_2}^R ; \quad [43]$$

$$\Delta\phi_{d_3} = \phi_{d_3}^P - \phi_{d_3}^R . \quad [44]$$

Scattered reactant and reaction product signals are both fed by the primary reactant beam; therefore, the reactant transit phase angle from the chopper to the target, $\phi_{d_1}^R$, is the same for both species. The complex impedance phase lag, ϕ_Z , affects each species equally for measurements at a common frequency.

3.1.7.6.2. Amplitude measurements

Systematic perturbations also affect the measured signal amplitudes. The measured amplitudes of scattered reactant and desorbed product may be related by demodulation factors ($A \leq 1$) to the true amplitudes.

The mass spectrometer signal, $s_R(t)$, due to the scattered reactant as a function of time, t , is:

$$s_R(t) = \frac{\sigma_R^f f_{R,M_R} \gamma_R \beta_R I_0 g(t)}{v_R} A_{d1}^R A_{d2}^R A_Z \quad [45]$$

where the beam with a strength I_0 at the surface has been modulated by a function $g(t)$. A_{d1}^R and A_{d2}^R are the demodulation factors associated with the chopper-target and target-ionizer transit times;⁶² no amplitude attenuation results from the transit time of the ions in the mass spectrometer; A_Z is the complex impedance amplitude attenuation factor which depends upon the frequency only. Equation [45] is similar to Eq. [25] except that it includes a time-dependent beam intensity and correction factors resulting from the modulated nature of the beam.

Setting $g(t) = \frac{1}{2} [1 + g_1 e^{j\omega t}]$, the lock-in detector (section 3.2.1) sees this signal $s_R(t)$ as:²⁰

$$S_R e^{j\omega t} = \frac{\sigma_R f_{R,M_R} \gamma_R \beta_{M_R} I_0}{v_R} A_{d1}^R A_{d2}^R A_Z \frac{1}{2} g_1 e^{j\omega t} \quad [46]$$

where g_1 is the first Fourier coefficient of $g(t)$ and ω is the modulation frequency. The lock-in detector output is a signal of amplitude S_R at zero phase (no reaction delay):

$$s_R = \frac{\sigma_R f_{R,M_R} \gamma_R \beta_{M_R}}{v_R} A_{d_1}^R A_{d_2}^R A_Z \frac{1}{2} I_0 g_1 \quad [47]$$

The mass spectrometer signal, $s_P(t)$, due to the desorbed reaction product similarly is:

$$s_P(t) = \frac{\sigma_P f_{P,M_P} \gamma_P \beta_{M_P}}{v_P} R(t) A_{d_1}^R A_{d_2}^P A_Z \quad [48]$$

where $R(t)$ is the time-dependent reaction product desorption rate from the target.

The lock-in detector sees this signal $s_P(t)$ as

$$S_P e^{j\omega t} = \frac{\sigma_P f_{P,M_P} \gamma_P \beta_{M_P}}{v_P} A_{d_1}^R A_{d_2}^P A_Z R_1 e^{j(\omega t - \phi_{\text{meas}})} \quad [49]$$

where R_1 is the first Fourier coefficient of $R(t)$ and the measured reaction phase lag, ϕ_{meas} , from Eq. [42], is specifically noted. The lock-in detector measures a signal magnitude, S_P^* , at a phase setting ϕ_{meas} , which is

$$S_P^* = \frac{\sigma_P f_{P,M_P} \gamma_P \beta_{M_P}}{v_P} A_{d_1}^R A_{d_2}^P A_Z R_1 \quad [50]$$

The ratio of the measured reaction product signal to the measured reactant signal is:

$$\frac{S_P^*}{S_R} = \left(\frac{\sigma_P f_{P,M_P} \gamma_P}{\sigma_R f_{R,M_R} \gamma_R} \right) \left(\frac{\beta_{M_P}}{\beta_{M_R}} \right) \left(\frac{A_{d_2}^P}{A_{d_2}^R} \right) \left(\frac{v_R}{v_P} \right) \frac{R_1}{\frac{1}{2} I_0 g_1} \quad [51]$$

Since

$$\frac{v_R}{v_P} = \sqrt{\frac{T_R m_P}{T_P m_R}} \quad [52]$$

$$\frac{S_P^*}{S_R} = \left(\frac{\sigma_P^{f_P, M_P} \gamma_P}{\sigma_R^{f_R, M_R} \gamma_R} \right) \sqrt{\frac{T_R m_P}{T_P m_R}} \left(\frac{\beta_{M_P}}{\beta_{M_R}} \right) \left(\frac{A_{d_2}^P}{A_{d_2}^R} \right) \frac{R_1}{\frac{1}{2} I_0 g_1} \quad [53]$$

$$\frac{S_P^*}{S_R} = \left(\frac{\sigma_P^{f_P, M_P} \gamma_P}{\sigma_R^{f_R, M_R} \gamma_R} \right) \sqrt{\frac{T_R m_P}{T_P m_R}} \left(\frac{\beta_{M_P}}{\beta_{M_R}} \right) \left(\frac{A_{d_2}^P}{A_{d_2}^R} \right) \epsilon \quad [54]$$

where $\epsilon = \frac{R_1}{\frac{1}{2} I_0 g_1}$ is the apparent reaction probability.

If as in 3.1.7.5.3, we assume that equivalent fractions of scattered reactant or emitted product flux enter the solid angle subtended by the mass spectrometer ionizer, $\gamma_P = \gamma_R$. Moreover, all corrections require that proper temperature assignments be made:

i) reaction products are assumed to desorb after equilibration with the target surface and are assigned the target temperature, T_s , for the path from the target to the detector: $T_P = T_s$;

ii) a reactant beam of temperature T_B impinging on a target at temperature T_s ($T_s \neq T_B$) is scattered with a temperature T^* which is determined by T_B , T_s and the thermal accommodation coefficient which is not generally known. Therefore the reaction measurements are conveniently referred to the scattered reactant signal at some reference temperature, T_{Ref} , chosen in function of the experiment:

$$T_R = T_{Ref}$$

Therefore Eq. [54] becomes:

$$\frac{S_P^*}{S_R} = \left(\frac{\sigma_P f_{P,M_P} \beta_{M_P}}{\sigma_R f_{R,M_R} \beta_{M_R}} \sqrt{\frac{T_{Ref} m_P}{T_s m_R}} \right) \left(\frac{A_{d_2}^P}{A_{d_2}^R} \right) \epsilon \quad [55]$$

or

$$\epsilon = \left(\frac{\sigma_R f_{R,M_R} \beta_{M_R}}{\sigma_P f_{P,M_P} \beta_{M_P}} \sqrt{\frac{T_s m_R}{T_{Ref} m_P}} \right) \left(\frac{A_{d_2}^R}{A_{d_2}^P} \right) \quad [56]$$

3.1.7.6.3. Application to the fluorine-uranium dioxide reaction

The reaction product vector is composed of the reaction phase lag, ϕ , and the apparent reaction probability, ϵ .

Since uranium tetrafluoride is the major reaction product over a wide range of temperatures, Eq. [42] and [56] become

$$\phi = \phi_{meas} - \Delta\phi_{d_2} - \Delta\phi_{d_3} \quad [57]$$

where

$$\Delta\phi_{d_2} = \phi_{d_2}^{UF_4} - \phi_{d_2}^{F_2} \quad [58]$$

$$\Delta\phi_{d_3} = \phi_{d_3}^{UF_4} - \phi_{d_3}^{F_2} \quad [59]$$

$$\epsilon = \frac{(S_P^*)_{meas}}{(S_R)_{meas}} \left(\frac{\sigma_{F_2} f_{F_2,38} \beta_{38}}{\sigma_{UF_4} f_{UF_4,295} \beta_{295}} \sqrt{\frac{38T_s}{314T_{Ref}}} \right) \left(\frac{A_{d_2}^R}{A_{d_2}^P} \right) \quad [60]$$

The ratio

$$\frac{\sigma_{F_2} f_{F_2,38} \beta_{38}}{\sigma_{UF_4} f_{UF_4,295} \beta_{295}} \sqrt{\frac{38T_s}{314T_{Ref}}}$$

is the inverse of the correspondence factor between F_2 and UF_4 , C_{UF_4/F_2} , and has been determined for $T_{Ref} = 300^\circ K$ in section 3.1.7.5.3.

Introducing the result of Eq. [38] into [60] yields:

$$\epsilon = \frac{(S_P^*)_{meas}}{(S_R)_{meas}} \frac{\sqrt{T_S/300}}{15} \left(\frac{A_{d_2}^R}{A_{d_2}^P} \right) \quad [61]$$

When one performs all measurements at a phase angle such as the scattered reactant signal has a zero phase, then the measured lock-in detector output, $(S_P)_{meas}$ is:

$$(S_P)_{meas} = (S_P^*)_{meas} e^{-i\phi_{meas}}$$

and Eq. [61] can be written:

$$\epsilon e^{-i\phi_{meas}} = \frac{(S_P^*)_{meas}}{(S_R)_{meas}} \frac{\sqrt{T_S/300}}{15} \left(\frac{A_{d_2}^R}{A_{d_2}^P} \right) e^{-i\phi_{meas}} \quad [62]$$

3.1.8. Mechanical alignment

The molecular beam is to intersect the line of flight through the spectrometer at the center of the target face (Fig. 3).

During fabrication, after the collimator between the target and mass spectrometer chambers had been drilled, a gas laser beam was shown through the hole along the desired line of flight through the spectrometer mass filter. A drill was prepared for the second collimator with the spindle parallel to the desired line of flight through the source tube. The drill position was then translated to where it was

centered in the laser beam and the collimator hole in the wall between the target and source chambers was drilled.

Later, aligning the source tube mounts was done according to the procedure described in reference (54).

The mass spectrometer head is adjusted by jack screws on the bellows-mounted electron multiplier flange taking advantage of two view ports situated along the mass filter axis.

The target is aligned by adjusting the electron beam heater linear motion feedthrough with a beam on to peak the signal.

3.2. Phase-Sensitive Detection

The different means of signal processing have been discussed by Richard H. Jones.²⁰

3.2.1. Lock-in detection²⁰

Phase-lock processing by means of a PRINCETON APPLIED RESEARCH HR-8 with a # 127 two-phase accessory was chosen for most of the data taking in this experiment.

The modulated signal current from the spectrometer head is dropped across a 562 k Ω resistance soldered between the two terminals of a type D preamplifier and represents a voltage which is processed in analog form by the lock-in amplifier.

The lock-in amplifier reference channel is operated in the "selective external" mode by the square wave derived from the optical switch.

Signals are recorded on a HOUSTON INSTRUMENT Omniscribe recorder.

3.2.2. Pulse counting

3.2.2.1. Description

A computer of average transients "CAT" (Technical Measurements Corp. CN-1024/202) has been used to recover the modulated signals from the dc background noise. The CAT is connected through a pulse amplifier⁵⁵ to the electron multiplier output and set to repetitively scan the output signal with the onset of each scan synchronized to the beam modulation. The time for one scan can be subdivided into time intervals or "channels". As the channels are repetitively scanned, they accumulate a record of the signal plus noise. After a sufficient number of scans, the noise component in all channels will approach a common value and the periodic information will eventually be seen to rise out of the noise.

The information in storage in the different channels can be transferred on paper tape. A Fourier analysis is then performed to extract the amplitudes and phases of the different harmonics.

3.2.2.2. Pulse amplification

Digital (pulse counting) techniques are ideal in principle because equal weighting is given each ion pulse and pulse height discrimination can be used to filter certain noise levels.

To take full advantage of the method, the spectrometer would have to be equipped with an electron multiplier working in the saturation mode (high gain device: 1×10^8 @ 2800 V) i.e. generating pulses of equal height and ideally larger than noise pulses such that discrimination is possible. Our system is equipped with a high current CEM # 4700

(gain of 3×10^6 @ 3000 V) which is normally used in conjunction with analog electronics; this device generates pulses with a height distribution. Therefore, clean separation of the noise and signal pulse height distributions is required for an improvement of the signal-to-noise ratio, compared to lock-in detection, without an unacceptable loss of detection sensitivity.

The operating principle of the pulse amplifier used in our set-up is the following: each pulse of height, h , from the electron multiplier is amplified to a height $H = Gh$ where G is the amplification gain. If H is smaller than a preset reference value, H_{ref} , the pulse is not counted; if H is equal or larger than H_{ref} , the pulse is counted as one count in the appropriate channel of the CAT. Discrimination is made possible by varying the gain G .

As shown in Fig. 14, the highest count rates to be handled by the pulse counting system with less than a two-percent loss are about 10^5 pulses/second.

3.2.2.3. RF pick-up

A previous attempt²⁰ to use a pulse counting system has been unsuccessful largely due to a pick-up of the RF quadrupole power.

With all spectrometer settings turned on except for the filament emission current being set to zero, the number of noise pulses was less than one per second, confirming the effectiveness of the isolation and shielding obtained by mounting the electron multiplier in a perpendicular configuration with regard to the quadrupole filter.

-65-

XBL 767-7203

Fig. 14. Pulse counting system efficiency as a function of electron multiplier detection rate.

3.2.2.4. Illustration: the tantalum-fluorine reaction

Tantalum and fluorine have been found to react vigorously with each other even at moderate temperatures (600-1000°K) to give tantalum pentafluoride, TaF_5 . Since TaF_5 gives a mass spectrum, shown in Fig. 15, in the vicinity of the uranium fluoride species, it can conveniently be used for calibration or reference purposes.

Figure 16 shows the waveforms of the F_2^+ and TaF_4^+ species corresponding to the following conditions:

- temperature $\sim 700^\circ K$
- beam intensity $\sim 1 \times 10^{15}$ molecules/cm²-sec
- modulation frequency: 10 Hz
- counting times: F_2^+ 5 min.
 TaF_4^+ 30 min.

The results of the Fourier analysis performed on the two waveforms are listed in Tables II and III in which:

- i) harmonic "0" corresponds to the time-independent coefficient;
- ii) sigma represents the standard deviation.

Table II illustrates the square waveform of the F_2^+ signal:

- i) the third, fifth, seventh,...harmonic amplitudes are approximately 1/3, 1/5, 1/7,... of the first harmonic amplitude (refer to section 2.3.1);
- ii) the amplitudes of the even harmonics are very small.

Table III shows that the information contained in the higher harmonics becomes rapidly without statistical value.

XBL 767-7200

Fig. 15. Mass spectrum of TaF_5 (ionization potential = 70 eV)

XBL 767-7198

Fig. 16. F_2^+ and TaF_4^+ waveforms.

Table II. Fourier Analysis of the F_2^+ Signal.

Harmonic	Amplitude		Phase Lag	
	Mean Value	Sigma	Mean Value	Sigma
0	.772E+04	.76E+01	--.--	--.--
1	.866E+04	.11E+02	.17	.07
2	.517E+02	.11E+02	-86.31	11.96
3	.287E+04	.11E+02	.02	.21
4	.276E+02	.11E+02	76.22	22.36
5	.168E+04	.11E+02	-.27	.36
6	.171E+02	.11E+02	-70.69	36.13
7	.118E+04	.11E+02	-.62	.52
8	.810E+01	.11E+02	-25.84	75.89
9	.875E+03	.11E+02	-.76	.70
10	.136E+02	.11E+02	87.11	39.61
11	.707E+03	.11E+02	-.76	.87
12	.163E+02	.11E+02	-74.48	37.84
13	.552E+03	.11E+02	-1.89	1.11
14	.715E+01	.11E+02	29.75	85.99
15	.446E+03	.11E+02	-.39	1.38

Table III. Fourier Analysis of the TaF_4^+ Signal.

Harmonic	Amplitude		Phase Lag	
	Mean Value	Sigma	Mean Value	Sigma
0	.429E+05	.18E+02	--,--	--,--
1	.513E+04	.25E+02	62.37	.28
2	.163E+03	.25E+02	46.44	8.91
3	.747E+03	.25E+02	67.06	1.95
4	.539E+02	.25E+02	69.11	27.00
5	.312E+03	.25E+02	70.66	4.65
6	.334E+02	.25E+02	71.12	43.51
7	.142E+03	.25E+02	63.78	10.23
8	.242E+02	.25E+02	-7.04	59.71
9	.103E+03	.25E+02	59.46	14.07
10	.311E+02	.25E+02	-54.61	46.76
11	.124E+03	.25E+02	82.87	11.76
12	.122E+02	.25E+02	-82.90	119.52
13	.788E+02	.25E+02	60.94	18.44
14	.446E+02	.25E+02	59.44	32.54
15	.932E+02	.25E+02	73.68	11.61

In order to make sure that the pulse counting and the lock-in detection techniques give the same results, a comparison was made between the two methods in the same experimental conditions. The results are shown to be in good agreement (Fig. 17).

3.2.3. Comparison

In considering the relative merits of pulse counting and lock-in detection the following factors emerge:

a) the use of lock-in detection has the advantage of enabling the experimenter to know if steady-state conditions have been reached since the lock-in output is readily readable whereas a pulse counting technique requires processing of the accumulated information; this advantage may disappear if the pulse counting system is interfaced with a computer which processes the information after each run;

b) only the amplitude and phase of the fundamental component of the signal can be obtained by lock-in detection whereas a single pulse counting experiment can give the amplitude and phase at a number of frequencies; however the use of a square wave excitation function results in the fact that the amplitudes of the Fourier components of the exciting signal decrease with increasing frequency at a rate proportional to the frequency. The result is that the signal-to-noise ratio of the high harmonics decreases rapidly to the point where no significant information is extractable;

c) since our detection system is optimized for analog processing, lock-in detection has been chosen for most of the data collection. Pulse counting has been occasionally used at low modulation frequencies (below 10 Hz) where the use of the PAR HR-8 becomes less practical.

XBL 767-7199

Fig. 17. Phase lags as a function of beam intensity by lock-in detection and pulse counting.

4. RESULTS

4.1. Data Acquisition

The primary experimental variables are the beam intensity I_0 (determined by the source pressure), the target temperature T_s , and the modulation frequency ω .

The goal of the experimental program is to generate a set of reaction probability vectors in the three dimensional space (I_0 , T_s , ω). A set of data is composed of reaction product amplitudes and phase angles and one or more reference measurements of reactant scattered from a room temperature target.

Three blocks of data are obtained by holding each of two parameters constant and varying the third one. This approach provides an overabundance of data but is absolutely necessary to obtain reliable information. Any two blocks of experimental data would, in principle, determine the third block of data, but since each setting of a parameter (particularly the target temperature T_s) is not conveniently duplicated, considerable interpolation of data from two blocks would be necessary to determine the third one.

With the present system, the target is maintained in a vacuum of ca. 10^{-8} torr. The maximum attainable temperature is limited to 1800° - 2000° K. The maximum beam pressure at the target has a maximum value of ca. 10^{-4} torr (intensity $\sim 3.0 \times 10^{16}$ molecules/cm²-sec) limited by the source chamber pumping speed. Beam pressure may be reduced three orders of magnitude before encountering serious background

contamination either in the target chamber or in the source chamber. Modulation frequency using the two-blade rotating disk may be varied from 1 to 300 Hz. For a six-blade chopper, the range is 3 to 900 Hz.

The raw data [ϕ_{meas} , $(S_{\text{UF}_4}^*)_{\text{meas}}$, $(S_{\text{F}_2})_{\text{meas}}$] are corrected to remove the effect of the density sensitive ionizer, unequal detection sensitivities in the different mass ranges and to remove the amplitude attenuation and phase lag due to molecular transit according to the discussion in section 3.1.7.6.

$$\phi = \phi_{\text{meas}} - \Delta\phi_{d_2} - \Delta\phi_{d_3}$$

and

$$e = \frac{(S_{\text{UF}_4}^*)_{\text{meas}}}{(S_{\text{F}_2})_{\text{meas}}} \frac{\sqrt{T_s/300}}{15} \left(\frac{A_{d_2}^{F_2}}{A_{d_2}^{UF_4}} \right)$$

4.2. Fluorine Beam Strength as a Function of Temperature

Taking the reflected fluorine beam with the target at room temperature as a reference, the relative intensity of the fluorine beam as a function of $(300/T_s)^{1/2}$ is plotted in Fig. 18, curve A. The shape of curve A at temperatures slightly above room temperature is based on experimental observation.

For no reaction and complete thermal accommodation, the reflected fluorine signal, S_{T_s} , at any target temperature T_s would be:

$$S_{T_s} = S_{300} \sqrt{\frac{300}{T_s}}, \quad [63]$$

XBL 767-7202

Fig. 18. Relative fluorine beam strength as a function of $\sqrt{\frac{300}{T_s}}$. Curve A is experimentally obtained. Curve B is calculated assuming no reaction and complete fluorine accommodation.

neglecting the amplitude transit attenuation factors which are very close to one at all temperatures. S_{300} is the reflected fluorine signal for a UO_2 target at room temperature. Equation [63] is represented by the straight line B on Fig. 18.

Curve A shows that after an initial drop, the reflected fluorine signal decreases slightly with increasing temperature. Between 400° and 600°K, the fluorine thermal accommodation coefficient decreases from ~ 0.4 to ~ 0.15.

The reflected fluorine signal decreases markedly above 800°-900°K, corresponding to the detection of volatile reaction products from the target. This observation suggests that the sticking (and reaction) probability of F_2 on UO_2 is larger than ~ 0.1. The decrease in reflected reactant signal does not show any sign of tapering off at high temperatures which leads to the conclusion that the consumption of fluorine would eventually be complete at very high temperatures (i.e. sticking probability approaching unity). It is worth noting that no radical change in the fluorine molecule cracking pattern is observed as the target temperature is increased.

4.3. Reaction Products Identification

With a modulated fluorine beam impinging on a UO_2 target, scanning the different mass ranges with a high resolution setting reveals the presence of the ions shown in Table IV. The highest detectable mass is about 700. Species with a molecular weight higher than 700 would have to contain at least three atoms of uranium and are not likely to be present.

Table IV. Different Ions Detected under Modulated F_2 Beam Impingement Conditions.

Temperature Range	Mass/Charge	Ion	Species identification	
			Positive	Possible
All temperatures	38	F_2^+	F_2	F
	32	O_2^+	O_2	
	28	N_2^+	N_2	
	20	HF^+	HF	
	19	F^+	F_2	
900°-1600°K	Same as above plus:		Same as above plus:	
	314	UF_4^+	UF_4	
	295	UF_3^+		
	276	UF_2^+		
	257	UF^+		
	238	U^+		
Above 1600°K	Same as above plus:		Same as above plus:	
	292	UOF_2^+		UOF_2 with $x = 2$ or 3
	289	UO_2F^+		UO_2F_y with $y = 1$ or 2
	273	UOF^+		
	270	UO_2^+	UO_2	
	254	UO^+		

4.3.1. Ions present at all temperatures

The ions F_2^+ and F^+ are present at all temperatures. Their presence is due to the fluorine reactant beam. However, at high temperatures, F^+ can also arise from fluorine atom desorption from the surface. Unfortunately, as already pointed out by McKinley,¹⁷ there is a persistent, erratic F^+ background from fluorides formed in and around the mass spectrometer ionizer, the magnitude of which is 200 to 1000 times higher than the signal to be measured. Due to the unfavorable signal-to-noise ratio, long time constants are required for operating the lock-in amplifier. This, in turn, is not recommended due to the rapid degradation of the electron multiplier gain when looking at mass 19. Therefore, we did not attempt to monitor F^+ .

The ions O_2^+ and N_2^+ are due to impurities in the fluorine beam (section 3.1.3.3). Since O_2^+ appears with zero phase lag and a fairly constant intensity relative to the signal of fluorine scattered from a room temperature target, molecular oxygen is not a reaction product in our experimental conditions. Similarly monitoring of mass 16 indicates that atomic oxygen is not a product of the reaction.

The modulated HF^+ signal results from wall collisions in the mass spectrometer ionizer. The presence of HF in mass spectrometer experiments utilizing fluorine was previously experienced by others.^{17,56} The signal corresponding to HF^+ has a modulated component with a phase different from the fluorine reactant phase and its amplitude goes down with time indicating that the ionizer walls are progressively cleansed of hydrogen-containing contaminants (H_2O , organic materials, ...).

The presence of a modulated HF^+ signal was of concern since UO_2 is known to react with HF to yield uranium tetrafluoride, UF_4 . It was therefore essential to understand the nature of the HF^+ signal. The positive identification of the origin of this spurious signal is based on:

i) HF introduced in the beam was detected with no phase lag compared to the fluorine signal contrarily to the spurious HF^+ signal;

ii) the phase lag and amplitude of the spurious HF^+ signal do not depend upon the target temperature;

iii) the amplitude of the HF^+ signal is proportional to the fluorine signal.

Therefore HF comes from a reaction occurring on the ionizer walls between the adsorbed hydrogen-containing contaminants and the modulated fluorine beam.

4.3.2. Ions present in the 900°-1600°K temperature range

All ions present in the 900°-1600°K temperature range derive from a single species identified as uranium tetrafluoride, UF_4 . The relative abundance of the different ions at 1250° and 1500°K are compared to the cracking pattern of UF_4 . The latter was obtained in a separate experiment by heating one gram of UF_4 powder contained in a small Knudsen cell sitting on the electron beam heater in the target chamber. The results are summarized in Table V.

Also shown in Table V are the different phase lags corresponding to a modulation frequency of 20 Hz. The constancy of the phase lags (at a given temperature) for the different ions points out to a common

Table V. Comparison of the relative abundance of the uranium fluoride ions with the tetrafluoride cracking pattern.

Ion	1250°K		1500°K		Measured UF ₄ cracking pattern
	Relative abundance	ϕ	Relative abundance	ϕ	
UF ₄ ⁺	7%	57.0°	6%	43.9°	6%
UF ₃ ⁺	100%	57.2°	100%	43.2°	100%
UF ₂ ⁺	18%	56.7°	16%	43.8°	16.5%
UF ⁺	23%	56.2°	23%	43.3°	23%
U ⁺	18%	56.7°	18%	43.7°	10%

origin. Moreover, except for U^+ , the relative ion abundances match the UF_4 cracking pattern. The apparent discrepancy for the U^+ ion is explainable by the large variation of the U^+ abundance as a function of the spectrometer settings (particularly the ionization potential) which were different for the UF_4 volatilization experiment compared to the reactive scattering experiments.

4.3.3. Ions present above 1600°K

As the target temperature is increased, UOF_2^+ , UO_2F^+ , UOF^+ , UO_2^+ and O^+ are detected. UO_2^+ and some UO^+ come from the vaporization of UO_2 as their appearance around 1700°K is independent of the presence of a fluorine beam. The identification of the parent species of UO_2F^+ , UOF_2^+ and UOF^+ is not possible and it is assumed that they come from such species as UOF_3 or UOF_2 or UO_2F whose existences have been postulated. 57-61

Figure 19 is a recording of the signals detected at various masses between 238(U^+) and 314(UF_4^+). When the spectrum is expanded, the jagged appearance of the peak tops indicate that:

1) UF_3^+ , UF_2O^+ , UF_2^+ , UFO^+ , UF^+ , U^+ have a strong modulated component;

ii) UO_2F^+ , UO_2^+ and UO^+ only have a weak, if any, modulated component.

4.4. Data Presentation

For reasons stated in 3.1.7.3, it has not been possible to collect data with good mass resolution in the spectrometer high mass range. Therefore most of the experiments have been performed in the 900°-1600°K

TEMPERATURE: $\sim 1900^\circ\text{K}$

BEAM INTENSITY: 1.5×10^{16} MOLECULES/ CM^2 -SEC

MODULATION FREQUENCY: 2 Hz

XBL 767-7194

Fig. 19. Mass spectrum between 238 and 314.

temperature range where the only detectable reaction product is uranium tetrafluoride.

Variations of apparent reaction probabilities and phase lags for UF_4 with respect to the temperature of the target, modulation frequency and beam intensity are shown in Figs. 20, 21, 22, and 23. In these plots, the modulation is given in Hz, f , which is related to the same quantity expressed in radians/sec, ω , by:

$$f = \frac{\omega}{2\pi}.$$

4.4.1. Temperature dependence (Fig. 20)

As the target temperature is increased, the apparent reaction probability goes through a maximum whose position depends upon the beam intensity. Simultaneous monitoring of the signals at masses 295 (corresponding to UF_3^+) and 276 (corresponding to UF_2^+) shows a progressive modification in the ratio of these two quantities at temperatures above 1600°K; this corresponds to the appearance of oxyfluoride species ($UOF_2^+, \dots$). The true UF_4 signal is therefore best represented, above 1600°K, by the dashed line as shown on the upper curve of Fig. 20.

Reaction phase lags decrease with increasing temperatures until they reach a plateau.

4.4.2. Beam intensity dependence (Fig. 21)

Variations of the apparent reaction probability with beam intensity show that the kinetic order tends to one at low temperatures and high beam intensities. Higher order kinetics show up when the temperature is increased and/or the beam intensity is decreased.

Fig. 20. Temperature dependence of the reaction probability and phase lag for uranium tetrafluoride.

XBL 768-7303

XBL 768-7304

Fig. 21. Variation of uranium tetrafluoride reaction probability and phase lag with beam intensity.

Since the phase lags are dependent upon the beam intensity the surface mechanisms responsible for the production of UF_4 are clearly non-linear even when the apparent kinetic order is one. The dependence of the phase lag with beam intensity can be described by:

$$\tan \phi \propto I_0^{-x}$$

where

$$0 \leq x \leq 0.25$$

4.4.3. Modulation frequency dependence (Figs. 22 and 23)

The variation of the apparent reaction probability with modulation frequency can be described over a wide temperature range (Fig. 22) by

$$\varepsilon \propto \omega^{-y}$$

where

$$0.5 \leq y \leq 0.75$$

The variation of the reaction phase lag with modulation frequency can be described by:

$$\tan \phi \propto \omega^z$$

where

$$z \approx 0.25 - 0.30$$

4.4.4. Target crystallographic orientation

Changing the crystallographic orientation of the target has not produced any discernible effect on the reaction product characteristics.

4.5. Target Pre- and Post-Examinations

The measurements described hereafter have been performed in ambient atmosphere and/or have required that the specimen to be examined be taken out of the vacuum chamber and exposed to air for a long period of time.

XBL 768-7305

Fig. 22. Variation of uranium tetrafluoride reaction probability with modulation frequency.

Fig. 23. Variation of uranium tetrafluoride reaction phase lag with modulation frequency.

XBL 768-7306

4.5.1. Scanning electron microscope

Figure 24 shows scanning electron micrographs of a (111) oriented specimen before and after exposure to fluorine. The initial surface roughness shown in Fig. 24a disappears rapidly as the reaction takes place leading to a surface appearance shown in Fig. 24b.; in the latter micrograph, large sections of the (111) face bordered by a "hill-type" structure can be seen. It is to be noted that the chemical etching due to the fluorine beam does not lead to a smooth (111) face. Observation has shown that the "plane-hill" structure is persistent even after long reaction times.

4.5.2. X-ray diffraction

Examination of a few targets by X-ray diffraction did not show any diffraction lines other than those of UO_2 .

4.5.3. Microprobe analysis

Scanning electron micrographs of targets which had been heated at temperatures above 1700°K led to the indications of large surface contamination by tantalum.

4.5.4. Auger analysis

An Auger scan of a target reacted at a maximum temperature of 1500°K did not show any Ta contamination. The analysis did not reveal the presence of fluorine either although the specimen had been exposed to a fluorine beam until it was taken out of the system.

4.5.5. Profilometry

A profilometer trace of the reaction spot along a section perpendicular to the beam direction is shown in Fig. 25.

(a)

50 μ

(b)

XBB 7510-7913A

Fig. 24. Scanning electron micrographs of a (111) specimen:
(a) before exposure to fluorine, and (b) after
exposure to fluorine.

Fig. 25. Comparison of reaction spot profiles.

XBL 768-7 307

The measured profile is then compared to the profile one would obtain if the target material being removed were proportional to the beam intensity. The latter can be calculated by applying the procedure outlined in reference (43) to the system geometry given in Fig. 10. The smooth line above the profilometer trace in Fig. 25 is thus the radial distribution of the intensity in the primary beam. It has an umbra ~ 0.8 mm in diameter and a penumbra extending from the umbra out to a diameter of ~ 3.5 mm.

5. DISCUSSION

5.1. Quasi-Equilibrium Analysis

Without assuming a detailed kinetic model, expressions for the rate of a gas-solid reaction may be formulated on the assumption that quasi-equilibrium conditions exist at gas-solid interfaces. The following discussion follows that of Stickney and Barry.⁶³

Let us consider the following set of equations:

where the K_P 's represent the equilibrium constants at constant pressure. The notation O_{soln} represents oxygen dissolved in UO_2 . The formation of UO_2F_2 is not included; this results from considering the phase diagrams of the Uranium-Oxygen-Fluorine system at various temperatures; they show that UO_2F_2 is formed only in presence of a large oxygen partial pressure (3.6×10^{-2} torr @ $700^\circ C$).⁶⁶ Equation [65] takes place in presence of a large core of unreacted UO_2 . Since no

molecular or atomic oxygen is detected as a reaction product, we assume that the UO_2 acts as an oxygen sink; this is translated in Eq. [66] in which O_2 can be dissolved in UO_2 whose mass is very large compared to the reacting mass of oxygen; therefore the stoichiometry of UO_2 is taken as a constant. Combining Eqs. [65] and [66], we obtain:

The evaluation of K_{P_2} requires the knowledge of the Gibbs energy changes corresponding to Eq. [66]. The chemical potential of O_2 dissolved in UO_2 is equal to the chemical potential of O_2 in the gas phase in equilibrium with UO_2 . Therefore the Gibbs energy change for Eq. [69] is the sum of the Gibbs energy change corresponding to Eqs. [65] and [66]:

$$\Delta G_2^0 = \Delta G_{65}^0 + \Delta G_{66}^0 \quad [70]$$

with $\Delta G_{66}^0 = \Delta \bar{G}_{\text{O}_2}$, which depends upon the uranium dioxide stoichiometry. From the law of mass action, we can write:

$$K_{P_1} = \frac{P_{\text{F}}^2}{P_{\text{F}_2}} = e^{-\frac{\Delta G_1^0}{RT}} \quad [71]$$

$$K_{P_2} = \frac{P_{\text{UF}_4}}{P_{\text{F}_2}^2} = e^{-\frac{\Delta G_2^0}{RT}} \quad [72]$$

$$K_{P_3} = \frac{P_{UF_5}}{P_{UF_4} \cdot P_F} = e^{-\frac{\Delta G_3^0}{RT}} \quad [73]$$

$$K_{P_4} = \frac{P_{UF_6}}{P_{UF_4} \cdot P_F^2} = e^{-\frac{\Delta G_4^0}{RT}} \quad [74]$$

where the ΔG^0 's represent the standard free energies of the reactions described by Eq. [64], [67], [68] and [69]. The gaseous species are assumed to be perfect gases and the activity of UO_2 is taken equal to one. The activity of oxygen dissolved in the UO_2 is accounted for by inclusion of the oxygen potential in Eq. [70].

Expressing P_{F_2} , P_{UF_4} , P_{UF_5} and P_{UF_6} as a function of P_F , K_{P_1} , K_{P_2} , K_{P_3} , K_{P_4} yields:

$$P_{F_2} = \frac{P_F^2}{K_{P_1}} \quad [75]$$

$$P_{UF_4} = \frac{K_{P_2}}{K_{P_1}^2} P_F^4 \quad [76]$$

$$P_{UF_5} = \frac{K_{P_2} \cdot K_{P_3}}{K_{P_1}^2} P_F^5 \quad [77]$$

$$P_{UF_6} = \frac{K_{P_2} \cdot K_{P_4}}{K_{P_1}^2} P_F^6 \quad [78]$$

Now the impingement rate Z_1 of species 1 of mass m_1 having a partial pressure p_1 in a system at temperature T is given by kinetic theory as:

$$Z_1 = \frac{p_1}{\sqrt{2\pi m_1 kT}} \quad [79]$$

A distinguishable fraction η_1 of species 1 are assumed to equilibrate with the surface (adsorb). The remaining fraction $(1-\eta_1)$ rebounds elastically.

Therefore, a surface mass balance on the element fluorine gives:

$$2\eta_{F_2} Z_{F_2} = R_F + 2R_{F_2} + 4R_{UF_4} + 5R_{UF_5} + 6R_{UF_6} \quad [80]$$

where $2\eta_{F_2} Z_{F_2}$ is the rate of adsorption of fluorine atoms fed by a molecular impingement rate Z_{F_2} and the R_i 's are the emission rates of the different possible products. The equilibrium partial pressures are assumed to be related to the desorption rates R_i 's by:

$$R_i = \eta_i Z_i = \frac{\eta_i p_i}{\sqrt{2\pi m_i kT}} \quad [81]$$

Due to the lack of specific information, the η_i 's of the products are assumed equal to one.

Therefore,

$$R_F = \frac{p_F}{\sqrt{2\pi m_F kT}} \quad [82]$$

$$R_{F2} = \frac{P_{F2}}{\sqrt{2\pi m_{F2}} kT} \quad [83]$$

Substituting [75] and [82] in [83] yields:

$$R_{F2} = \frac{1}{K_{P1}} (2\pi kT)^{1/2} \frac{m_F}{m_{F2}^{1/2}} R_F^2 \quad [84]$$

Similarly,

$$R_{UF4} = \frac{K_{P2}}{K_{P1}^2} (2\pi kT)^{3/2} \frac{m_F^2}{m_{UF4}^{1/2}} R_F^4 \quad [85]$$

$$R_{UF5} = \frac{K_{P2} \cdot K_{P3}}{K_{P1}^2} (2\pi kT)^2 \frac{m_F^{5/2}}{m_{UF5}^{1/2}} R_F^5 \quad [86]$$

$$R_{UF6} = \frac{K_{P2} \cdot K_{P4}}{K_{P1}^2} (2\pi kT)^{5/2} \frac{m_F^3}{m_{UF6}^{1/2}} R_F^6 \quad [87]$$

Introducing [84-87] in [80] gives:

$$\begin{aligned} 2Z_{F2} = & R_F + \frac{2}{K_{P1}} (2\pi kT)^{1/2} \frac{m_F}{m_{F2}^{1/2}} R_F^2 \\ & + \frac{4K_{P2}}{K_{P1}^2} (2\pi kT)^{3/2} \frac{m_F^2}{m_{UF4}^{1/2}} R_F^4 + \frac{5K_{P2} K_{P3}}{K_{P1}^2} (2\pi kT)^2 \frac{m_F^{5/2}}{m_{UF5}^{1/2}} R_F^5 \end{aligned}$$

$$+ \frac{6K_{p_2} K_{p_4}}{K_{p_1}^2} (2\pi kT)^{5/2} \frac{m_F^3}{m_{UF_5}^{1/2}} R_F^6 \quad [88]$$

or

$$\begin{aligned} 2Z_{F_2} = R_F + \frac{2}{K_{p_1}} (\alpha T)^{1/2} \frac{m_F}{m_{F_2}^{1/2}} R_F^2 + \frac{4K_{p_2}}{K_{p_1}^2} (\alpha T)^{3/2} \frac{m_F^2}{m_{UF_4}^{1/2}} R_F^4 \\ + 5 \frac{K_{p_2} K_{p_3}}{K_{p_1}^2} (\alpha T)^2 \frac{m_F^{5/2}}{m_{UF_5}^{1/2}} R_F^5 + 6 \frac{K_{p_2} K_{p_4}}{K_{p_1}^2} (\alpha T)^{5/2} \frac{m_F^3}{m_{UF_6}^{1/2}} R_F^6 \end{aligned} \quad [89]$$

where Z_{F_2} and R_F are expressed in $\frac{\text{molecules}}{\text{cm}^3\text{-sec}}$;

T is in $^{\circ}\text{K}$;

the m 's are in amu;

$$\alpha = 1.40 \times 10^{-51} \left(\frac{\text{sec-cm}^2}{\text{molecule}} \right)^2 \frac{\text{atm}^2}{(^{\circ}\text{K})} \quad [90]$$

Therefore, if the value of Z_{F_2} can be assessed from experimental conditions and if the K_p 's can be calculated from thermodynamic data, then Eq. [89] can be solved for R_F and R_{F_2} , R_{UF_4} , R_{UF_5} , R_{UF_6} can be calculated from Eq. [84-87].

5.1.1. Thermodynamic data

The required thermodynamic data have been taken from Kubaschewski⁶⁴ for F_2 , F , O_2 , UO_2 and from references (65-66) for UF_4 , UF_5 , UF_6 . They are listed in Table VI.

Table VI. Thermodynamic Properties.

Species	State	H_{298}^0 cal/mole	S_{298}^0 cal/mole-°K	C_p cal/mole-°K
F_2	gas	0	48.50	$8.29 + 4.4 \times 10^{-4} \times T - \frac{8 \times 10^4}{T^2}$
F	gas	18,900	37.93	4.97
O_2	gas	0	49.00	$7.16 + 1.0 \times 10^{-3} \times T - \frac{4 \times 10^4}{T^2}$
UO_2	solid	-259,000	18.60	$19.2 + 1.62 \times 10^{-3} \times T - \frac{3.96 \times 10^5}{T^2}$
UF_4	gas	-366,000 ⁶⁵	S^0 and C_p are given from 600° to 4000°K for UF_4 , UF_5 and UF_6 in reference (66)	
UF_5	gas	-440,000 ⁶⁵		
UF_6	gas	-505,000 ⁶⁵		

It is therefore possible to tabulate the values of $\frac{-(G-H_{298})}{T}$ as a function of T for the different species. This is done in Table VII.

Table VII. $-\frac{(G-H_{298})}{T}$ in $\frac{\text{cal}}{\text{mole}^\circ\text{K}}$ as a function of temperature.

T °K	F ₂	F	O ₂	U	UF ₄	UF ₅	UF ₆
800	51.38	39.72	51.66	24.11	88.60	95.29	102.28
1000	52.60	40.46	52.78	27.11	92.21	99.57	107.51
1200	53.71	41.11	53.80	30.11	95.47	103.48	112.25
1400	54.71	41.70	54.73	32.11	98.40	107.00	116.47
1600	55.62	42.24	55.59	34.11	101.06	110.21	120.34
1800	56.45	42.72	56.37	36.11	103.49	113.13	123.87

With the help of Table VII, the evaluation of K_{P_1} , K_{P_3} and K_{P_4} corresponding to Eq. [64, 67-68] is straightforward. The evaluation of K_{P_2} by Eq. [70] requires the knowledge of the Gibbs energy change for Eq. [66], which, in turn, requires the stoichiometry of UO_2 to be known. If we assume that UO_2 is at the stoichiometry, then $\Delta G_{\text{O}_2} \approx -100 \text{ kcal/mole}$ in the temperature range considered.⁶⁷ The values of the K_p 's are listed in Table VIII.

Table VIII. Equilibrium Constants as a Function of Temperature.

T °K	K_{P_1} atm	K_{P_2} atm ⁻¹	K_{P_3} atm ⁻¹	K_{P_4} atm ⁻²
800	6.39×10^{-5}	2.08×10^{59}	1.45×10^{18}	8.52×10^{33}
1000	8.47×10^{-3}	7.93×10^{47}	1.18×10^{13}	2.0×10^{24}
1200	2.22×10^{-1}	1.79×10^{40}	4.86×10^9	7.93×10^{17}
1400	2.34×10^0	5.85×10^{34}	1.86×10^7	2.10×10^{13}
1600	1.39×10^1	4.34×10^{30}	2.87×10^5	7.36×10^9
1800	5.58×10^1	2.56×10^{27}	1.12×10^4	1.77×10^7

The results are plotted in Fig. 26 for the values of $2Z_{F_2}$ equal to 10^{14} , 10^{15} and 10^{16} molecules/cm²-sec.

It can be seen:

a) that UF_4 is the major reaction product for our experimental conditions. UF_5 would become the main reaction product at low temperature ($< 700^\circ K$) and high fluorine pressures. UF_6 would appear at very low temperatures and high beam pressures. The formation of F atoms is favored when the temperature is high and the fluorine pressure low. The F_2 evaporation rate is always negligible.

b) In a large temperature range ($1000^\circ - 1400^\circ K$) all consumed fluorine is transformed in UF_4 and the evaporation rate of UF_4 is therefore first order with the fluorine pressure. At very high temperatures, all consumed fluorine is transformed in F atoms and the

XBL768-7309

Fig. 26. Evaporation rates of UF_5 , UF_4 , and F as a function of temperature and $2Z_{\text{F}_2}$ equal to 10^{14} , 10^{15} , 10^{16} molecules/ $\text{cm}^2\text{-sec}$. (Quasi-equilibrium analysis).

evaporation rate of F atoms is first order with the fluorine pressure; in these conditions, the UF_4 evaporation rate (which is very small) is proportional to the fourth power of the fluorine pressure. In the transition region, as the fluorine pressure is increased, the order varies in a continuous way from four to one.

5.1.2. Conclusions

The quasi-equilibrium analysis using thermodynamic considerations only, confirms the presence of UF_4 as the only reaction product in a wide temperature range for the fluorine pressures corresponding to our experiments.

The gradual shift from a UF_4 first order to a higher order formation as the temperature is increased and the fluorine pressure is decreased could also be explainable in terms of thermodynamic considerations.

5.2. Reaction Vector Temperature Dependence

The apparent reaction probability as a function of $1/T$ has been plotted in Fig. 20. By measuring the slope of the curves in the low temperature range, an apparent Arrhenius activation energy of about 40 kcal/mole is observed.

On the other hand, following the discussion given by I.E. Wachs and R. J. Madix,⁶⁹ one can plot

$$k_{eff} = \frac{\omega}{\tan \phi}, \quad [91]$$

in an Arrhenius fashion, k_{eff} being called an effective rate constant. The result is shown in Fig. 27 for the phase lags taken from Fig. 20.

XEL 768-7308

Fig. 27. $\log_{10} k_{eff}$ as a function of temperature.

The value of the slope corresponding to the highest apparent activation energy is: $\frac{E}{R} = 4500^\circ\text{K}$ or $E_{\text{app}} \approx 9000 \text{ cal/mole}$. Although, for a complex and non-linear mechanism, E_{app} is, in general, a function of modulation frequency, order of reaction,..., this value is low compared to the 40,000 cal/mole obtained from the amplitude data.

This fact points out to a mechanism where the sticking probability depends strongly upon the temperature.

5.3. Reaction Modeling

Based on the quasi-equilibrium analysis and on the reaction vector temperature dependence, the following model is proposed

Followed by the surface reactions,

and finally, UF_4 desorption

Also at $T > 1600^\circ\text{K}$,

Equation [92] corresponds to a physisorption of F_2 on the uranium dioxide surface, the activation energy of which is close to zero.

Equation [93] is the reverse reaction and corresponds to the desorption of F_2 . Equation [94] represents a dissociative chemisorption step.

As it can be expected for a chemisorption process occurring on a nonmetal, the limiting step in the adsorption process is the need to increase the vibrational amplitude of the molecule (or of the surface sites) to permit both of its atoms to bind to the surface.⁷⁰ For most nonmetal systems, the rate of chemisorption is comparatively slow, and is characterized by a significant activation energy. This fact seems to be well-documented in our experiments. The energy required to break a fluorine molecule into two atoms is about 37 kcal/mole which is of the order of the observed apparent activation energy calculated from Fig. 20. McKinley postulates a similar mechanism in

his investigation of the Ni-F_2 reaction (17). Equation [94] represents the desorption of F atoms.

Equations [96-98] represent a sequence of reactions leading to the major reaction product, UF_4 , whereas Eqs. [100-101] represent the vaporization of postulated oxyfluoride species at high temperature.

5.4. Reaction Vector Modulation Frequency Dependence

As mentioned in 4.4.3, the variation of the reaction phase lag with modulation frequency can be described by:

$$\tan \phi \propto \omega^z; \quad z = 0.25 - 0.3).$$

The relation fits surprisingly well for all experimental conditions. The phase response is therefore controlled by a process which acts as a "flywheel" which smooths the time response of the system when the frequency is modified.

Mechanisms which have been identified to show similar effects involve branch reactions, bulk diffusion and surface diffusion.^{20,71}

5.4.1. Multi-branch reaction mechanism

As pointed out by Jones,⁷² multi-branch mechanisms may be tailored to give a satisfactory match to virtually any linear reaction process. Plots of the apparent reaction vector locus as frequency is varied are useful for analyzing branch processes since they generally show humps, the number of which is an indication of the number of branches. Polar plots of (ϕ, ϵ) at constant temperature and beam intensity when the modulation is varied all appear as flattened semi-circles and do not support the existence of a multi-branch mechanism.

5.4.2. Bulk diffusion

Bulk diffusion and second order reaction on the surface were assumed to govern the kinetics. For fluorine atoms diffusing in the bulk of the specimen, the equations governing the process are:

$$\frac{dn(t)}{dt} = 2\eta^* I_0 g(t) - 4kn^2(t) + D_v \left. \frac{\partial C(z,t)}{\partial z} \right|_{z=0} \quad [102]$$

where $n(t)$ is the surface concentration of fluorine atoms, η^* represents a temperature-dependent sticking probability, I_0 is the fluorine beam intensity at the target, $g(t)$ is the modulation function conveniently expressed for analyzing a non-linear mechanism as $g = \frac{1}{2} + \frac{1}{2} g_1 e^{j\omega t}$ (73), k is a second order rate constant, D_v is a bulk diffusion coefficient, z is the distance between a given point in the bulk and the surface, t is the time.

$$\frac{\partial C(z,t)}{\partial t} = D_v \frac{\partial^2 C(z,t)}{\partial z^2} \quad [103]$$

where $C(z,t)$ is the fluorine atom bulk concentration related to n by

$$C(0,t) = Hn(t) \quad [104]$$

where H is a solubility coefficient. For a semi-infinite medium, the apparent reaction probability and the phase lag, according to this model, are given by:

$$\tan \phi = \frac{\omega + \frac{H\sqrt{D_v}}{\sqrt{2}} \sqrt{\omega}}{\sqrt{16k\eta^* I_0} + \frac{H\sqrt{D_v}}{\sqrt{2}} \sqrt{\omega}} \quad [105]$$

$$\epsilon = \frac{\eta \sqrt{4k\eta^* I_0}}{\left(\sqrt{16k\eta^* I_0} + \frac{H\sqrt{D_v}}{\sqrt{2}} \sqrt{\omega} \right)^2 + \left(\omega + \frac{H\sqrt{D_v}}{\sqrt{2}} \sqrt{\omega} \right)^2} \quad [106]$$

Although these expressions can be fitted part of the data, they fail most dramatically when the apparent order of the reaction is one. This would occur when:

$$\sqrt{16k\eta^* I_0} \gg \frac{H\sqrt{D_v}}{\sqrt{2}} \sqrt{\omega} . \quad [107]$$

For these conditions, $\tan \phi$ should be proportional to the inverse of the square root of I_0

$$\tan \phi \propto I_0^{-1/2} ,$$

which contradicts the experimental data for which

$$\tan \phi \propto I_0^{-1/4} .$$

5.4.3. Surface Diffusion

Surface diffusion can be responsible for a sluggish phase response (71).

The total surface area is divided into independent circular unit cells of radius R . Reaction is assumed to occur on a circular band of width "a" on the perimeter of the unit cell. F_2 molecules dissociatively adsorb on the entire surface. Adsorbed F atoms may diffuse on the surface, desorb from the surface or dissolve in the

bulk solid. Fluorine atoms reaching the perimeter of the cell may react according to a second order mechanism. Desorption of fluorine atoms from the surface is allowed but recombination is neglected since it is thermodynamically unfavorable as it was shown in the quasi-equilibrium analysis.

For a system in which the atoms diffuse to annular reaction sites (equivalent to grain boundaries), the equations describing the mechanism, in cylindrical coordinates, are:

$$\frac{\partial n(r,t)}{\partial t} = D_s \left(\frac{\partial^2 n}{\partial r^2} + r \frac{\partial n}{\partial r} \right) + 2\eta^* I_0 g(t) + D_v \frac{\partial C}{\partial z} \Big|_{z=0} - k_d n(t) \quad [106]$$

where D_s is a surface diffusion coefficient and k_d is the first-order fluorine atom desorption rate constant. The boundary conditions are:

$$\frac{\partial n}{\partial r} \Big|_{r=0} \text{ is finite at all times;}$$

and

$$2 \left(-2\pi R D_s \frac{\partial n}{\partial r} \Big|_{r=R} \right) = 4kn^2 \Big|_{r=R} (2\pi Ra)$$

or

$$- D_s \frac{\partial n}{\partial r} \Big|_{r=R} = 2kan^2 \Big|_{r=R} \quad [107]$$

is the boundary condition at the reaction site; "a" is the reaction site width.

Expressions for the reaction probability and phase can be obtained in terms of modified Bessel functions with complex argument. They fit the phase data best when large values of the parameter $\frac{R^2}{D_s}$

are assumed. However, at low modulation frequencies, when the phase lags become smaller than 45° , the approach to zero phase shift by a surface diffusion process is rapid; this rapid approach is often considered as a criteria to distinguish a bulk diffusion from a surface diffusion process.²² The data do not show such a behavior. Moreover large surface diffusion times as expressed by R^2/D_s can only be explained by a highly activated diffusion process; this, however, contradicts the phase lag versus temperature data as discussed in 5.2 and shown in Fig. 27.

5.4.4. Surface coverage effect

Surface coverage effects are not believed to play an important role since a steady first-order behavior is obtained when the fluorine beam pressure is increased (Fig. 21).

5.4.5. Conclusions

Among the remaining possibilities are back-to-back diffusion processes and diffusion through a film formed on the surface. This latter mechanism has encouraging features such as: a) reaction rates at the UO_2 -film interface may be fast compared to the diffusion times through the film. Therefore differences associated with the nature of the reacting plane (crystallographic orientation) would not show up as experimentally observed; b) the relationship between film thickness determining the diffusion time and modulation frequency could conceivably introduce the "flywheel" effect suggested by the data.

Since the differential equations describing these phenomena have to be coupled with non-linear kinetics, present efforts are

concentrated on the tantalum-fluorine reaction which appears to obey similar, although simpler, kinetics.

Attempts to find evidence of the presence of a film on the uranium dioxide target have failed. However since our system is not equipped with a in situ surface analysis system, it was necessary to let the sample sit for several days in ambient atmosphere before attempting a fluorine identification analysis (see section 4.5.4). Therefore, interaction of the film with the moisture of the air leading to the removal of fluoride species cannot to be ruled out.

6. CONCLUSIONS

For our experimental conditions, the reaction between fluorine and uranium dioxide results in the formation of uranium tetrafluoride as predicted by thermodynamic considerations only.

The kinetics are strongly non-linear as evidenced by beam intensity-dependent phase lags and apparent reaction orders (with respect to fluorine) higher than one.

The activated nature of fluorine chemisorption has been established by comparing the apparent activation energies derived from reaction probability and phase lag versus temperature data.

The unusual behavior of the phase lag dependence upon variation of the modulation frequency cannot be explained by simple transport processes like bulk and surface diffusion and further analytical modeling is required to fit the data in detail.

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REFERENCES

1. Dmitrievski, V.A., Vainov, E. M. and Tetel'baum, S. D., "Use of Uranium Hexafluoride in Nuclear Power Plants" Soviet Atomic Energy, Vol. 29, No. 4, October 1970, pp. 976-980.
2. Thom, K., and Schneider, R. T. "Nuclear Pumped Lasers," AIAA Journal, Vol. 10, No. 4, April 1972, pp. 400-405.
3. A. H. Sutton, J. C. Bishop, M. H. Cohen and K. J. Stahman, Chem. Eng. Progr. Symp. Ser. 62 (65), 20 (1966).
4. J. J. Barghusen, A. A. Jonke, N. M. Levitz, M. J. Steindler and R. C. Vogel, Progress in Nuclear Energy Series III Volume 4 pp. 347-398. Pergamon Press - Oxford and New York 1969.
5. Technical Bulletin TA-85411 "Fluorine, Elemental" General Chemical Division Allied Chemical Division, Morristown, New Jersey.
6. USAEC ANL-5924, 1958.
7. USAEC ANL-6898, 1965.
8. W. J. Mecham, J. D. Gabor and A. A. Janke, Chem. Eng. Progr. Symp. Ser. 60(47), 76 (1964).
9. L. J. Anastasia and W. J. Mecham, I & EC Process Design and Development Vol. 4, No. 3, July 1965, 338-344.
10. A. A. Jonke, At. Energy Rev. 3(1), 3 (1965).
11. USAEC ANL 6287, 147 (1960).
12. M. Iwasaki, J. Inorg. Nucl. Chem., 1964, Vol. 26, pp. 1853-1861.
13. T. Yahata and M. Iwasaki, J. Inorg. Nucl. Chem., 1964, Vol. 26, pp. 1863-1867.
14. M. Iwasaki, Journal of Nuclear Materials, 25 (1968) pp. 216-226.

15. G. Vandenbussche, CEA-R 2859, 1966
16. R. Idrissi, T. Kikindai, B. Auguin and D. Vigner, C. R., Acad. Sc. Paris, t.270 (2 mars 1970) Série C pp 765-768.
17. John D. McKinley, J. Chem. Phys. 45, 1690 (1966).
18. D. E. Rosner and H. D. Allendorf, J. Phys. Chem., 75, 308 (1971).
19. R. A. Krakowski and D. R. Olander, J. Chem. Phys. 49, 5027 (1968)
20. Richard Harold Jones, "Kinetics of the Reaction of Pyrolytic Graphite with Molecular Oxygen" (Ph.D. Thesis), LBL-104, 1971.
21. M. Balooch and D. R. Olander, J. Chem. Phys. 63, 4772 (1975).
22. R. J. Madix, Physical Chemistry of Fast Reactions, Vol. 2, "Fast Reactions on Surfaces" D. O. Haywood, Ed., Plenum Press.
23. R. L. Palmer and J. N. Smith, Jr., Catal. Rev. 12, 279 (1975).
24. R. P. Merrill, Catal. Rev. 4, 115 (1970).
25. R. H. Jones, D. R. Olander, W. J. Siekhaus, and J. A. Schwarz, J. Vac. Sci. Technol. 9, 1429 (1972).
26. C. T. Foxton, M. R. Boudry and B. A. Joyce, Surf. Sci. 44, 69 (1974).
27. J. A. Schwarz and R. J. Madix, Surf. Sci. 46, 317 (1974).
28. H. Saltsburg, Annu. Rev. Phys. Chem. 24, 493 (1973).
29. S. N. Foner and R. L. Hudson, J. Chem. Phys. 21, 1374 (1953).
30. J. N. Smith and W. L. Fite, J. Chem. Phys. 37, 898 (1962).
31. J. N. Smith and W. L. Fite, in "Proc. Third Intern. Symp. Rarefied Gas Dynamics," Vol. 1, 430 (1963).
32. D. R. Olander, Invited paper, American Chemical Society Meeting, Puerto Rico (1976).

33. O. C. Chaykowsky and R. D. Moore, Research/Development, April 1968, pp. 32-36.
34. Thomas Coor, J. Chem. Educ. 45 (A533) 1968.
35. Thomas Coor, J. Chem. Educ. 45 (A583) 1968.
36. The Excalibur Corporation, "Operating Instructions for Excalibur Cryo-Vacuum Pumps"
37. D. White, J. H. Hu, and H. L. Johnston, J. Am. Chem. Soc. 76, 2584 (1954).
38. Instruction Book No. WAA 620.075, Pennwalt Corp., Wallace and Tiernan Division
39. Engineering Report G-115, Matheson Gas Products
40. MATHESON GAS DATA BOOK, The Matheson Company, Inc. (1971) pp. 261-265.
41. Electron beam milling was performed by TRI-D Corporation, 7 Johnson Avenue, Plainville, Connecticut 06062.
42. R. H. Jones, D. R. Olander and V. R. Kruger, J. Appl. Phys. 40 4641 (1969).
43. R. A. Olstad, "Mass Spectrometric Investigation of Laser-Induced Vaporization of Binary Solid Compounds" (Ph.D. Thesis) LBL-1177.
44. Same as (20), pp. 86-88.
45. A. T. Chapman and G. W. Clark, Am. Ceram. Soc. Journal 48, 494 (1965).
46. Same as (43), pp. 35.
47. Peter C. Held and D. R. Wilder, Am. Ceram. Soc. Journal 52, 182 (1969).

48. F. Cabannes, J. P. Stora and J. Tsakiris, C. R. Acad. Sci., Paris, Ser. B, 264 [1] 45-48 (1967).
49. J. Belle, "Uranium Dioxide Properties and Nuclear Applications" U.S. Government Printing Office Washington, D.C. (1961).
50. QUAD 250B Residual Gas Analyser, Instruction Manual, Electronic Associates Inc. .
51. Extranuclear Laboratories, Quadrupole Mass Spectrometer Systems and Components.
52. Personal Communication from GALILEO ELECTRO-OPTICS Corp.
53. W. H. Beattie, Applied Spectroscopy 29, 334 (1975).
54. Same as (20) p. 68.
55. The chopper motor power supply and the pulse amplifier have been designed and built by T. Small.
56. Ch. Biguenet, Le Vide, 159-160, 143 (1972).
57. S. Kemmler-Sack, Z. Naturforschg. 22b, 597-599 (1967).
58. G. Fonteneau and J. Lucas, J. Inorg. Nucl. Chem. 33, pp. 4061-4067 (1971).
59. V. M. Vdovenko, G. A. Romanov; L. V. Solntseva, Radiokhimiya 11(4), 466-8 (1969).
60. Mukhametshina, Z. B., Seleznev, V. P., Sudarikov, B. N., Gromov, B. V., Tr. Mosk. Khim. - Tekhnol. Inst. 75, 42-4 (1973).
61. V. M. Vdovenko, G. A. Romanov and L. V. Solntseva Radiokhimiya 9(6), 727-9 (1967).
62. H. Harrison, D. G. Hummer, W. L. Fite, J. Chem. Phys. 41, 2567 (1964).

63. J. C. Batty and R. E. Stickney, J. Chem. Phys. 51, 4475 (1969).
64. Kubaschewski, O., Evans E., Alcock, C. B., Pergamon Press,
Metallurgical Thermochemistry, 4th-Ed. (1967).
65. Godnev, I. N. and Svedlin, A. S. CEA-tr-R-1905 Commissariat à
l'Energie Atomique, Paris 1968.
66. H. A. Hassan and J. E. Deese, NASA Contract. Rep. 1974, NASA CR-2373.
67. T. L. Markin, Chem. Eng. Progress Symp. Series 80, 43 (1967).
68. Von O. Knacke, G. Lossmann and F. Müller, Z. anorg. allg. Chem.
370, 91 (1969).
69. I. E. Wachs and R. J. Madix to be published in Surface Science.
70. G. Ehrlich, J. Chem. Phys. 31, 1111 (1959).
71. A. Z. Ullman and R. J. Madix, High Temp. Sci. 6, 342 (1974).
72. Same as (20) p. 42.
73. D. R. Olander and A. Z. Ullman, to be published in Int. J. Chem.
Kinet.