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KINETICS AND MECHANISM IN THE OXIDATION OF THORIUM AND URANIUM

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General Electric Company

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KINETICS & MECHANISM IN THE OXIDATION OF THORIUM & URANIUM

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The results of a laboratory investigations which involve (1) the vaporization of Thorium metal utilizing rf heating, laser radiation heating by chemical reactions, and (2) the oxidation of thorium and Uranium, are presented. It has been, determined that the heat of vaporization for monoatomic thorium vapor is 143 Kcal/mate. The ionization potentials of Thorium (gas) and Thorium oxide (gas) are quite low (5.5 -6.0eV), while that of

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→ (ThO_2^+)

thorium dioxide (ThO_2) is higher by 3eV. The rate constant for the production of Thorium dioxide ion (ThO_2^+) was determined to be 4.9 x 10^{-12} cm^3 $molecule^{-1}$ $sec.^{-1}$. The results of the laser blow-off study indicate that the spectrum from uranium metal produces both neutral and singly ionized uranium atoms.

ABSTRACT

In an effort to understand the kinetics and mechanisms of gas-phase reactions between metal vapors and oxygen, an experiment was set-up which utilizes RF heating and laser radiation for the production of the metal vapor and time-of-flight mass spectrometry for the measurement of reactants and products.

Measurements on the vaporization of thorium produced a value for the heat of vaporization (ΔH^{o}_{298}) equal to 143±1.5 kcal/mole. Ionization efficiency measurements on Th(g), and ThO_2(g) produced values for the ionization potential, (5.5-6)eV for the metal and the monoxide, and 8 eV for the dioxide.

Measurements on the relative rates of the following reactions:

$$Th + O_2 \xrightarrow{k_{ThO_2^+}} ThO_2^+ + e$$

$$U + O_2 \xrightarrow{k_{UO_2^+}} UO_2^+ + e$$

were made and the rate-constant ratio was determined. $k_{ThO_2^+}/k_{UO_2^+} = 1.23 \pm 0.13$; using a value[10] of $k_U = 4 \times 10^{-12}\ cm^3 molecule^{-1} sec^{-1}$, $k_{ThO_2^+}$ was calculated equal to $4.9 \times 10^{-12}\ cm^3 molecule^{-1} sec^{-1}$. Quantitative measurements on the reduction of the thorium signal and the production of ThO and UO as a function of oxygen pressure resulted in values for the rate constants of the following reactions:

$$Th + O_2 \longrightarrow ThO + O, \; k_{ThO} = (5.1 \pm 1.1) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

$$U + O_2 \longrightarrow UO + O, \; k \quad = (4.9 \pm 2.4) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

Spectra were recorded from plumes generated by laser heating of uranium metal and by chemical reaction of Al-Pd and Th-MoO_3 (seeded with U and Al). The laser heating results showed continuum radiation overlaid with UI and UII emission lines. Al-Pd and Th-MoO_3 showed strong Al and AlO emission.

I. INTRODUCTION

Although a considerable amount of information is available concerning the oxidation kinetics of metal surfaces, relatively little is known about the oxidation of metals in the gas phase. It follows that the more refractory the metal, the more difficult it is to produce it in the vapor state, and the more difficult it is to obtain kinetic data. Metals such as thorium and uranium fall in this category. Since W. Fite(1) has recently published results on the oxidation of uranium vapor, the main objective of this task was to investigate the thorium-oxygen system. For this purpose, several methods of producing the metal vapor were considered in conjunction with time-of-flight mass spectrometry for the identification of reactants and reaction products.

II. EXPERIMENTAL

A. Materials

Samples of thorium and uranium in powder and "crystal bar" form were obtained from Ventron Metal Hydride Division, Beverly, Mass.

When Knudsen crucibles were used as containers, the structural material was tantalum or tungsten. Best results, in terms of reducing background ThO signal, were obtained with tungsten.

B. Apparatus

The heating methods considered for this study are induction RF heating laser radiation and exothermic chemical reactions in the solid state.

1. Induction Heating

The use of RF heating in high-temperature mass spectrometric work has been previously demonstrated(2) and utilized in obtaining temperatures as high as 3000°K.

The experimental arrangement is shown in Figures 1 and 2. Figure 1 shows the inductively heated Knudsen cell in-place in the Bendix Model 12 time-of-flight mass spectrometer. The water-cooled induction coil enters the furnace chamber from the bottom flange. The crucible and its holder are supported on three tantalum rods on the inlet assembly.

The Knudsen crucible dimensions are 0.25 in. I.D. x 0.45 in. deep with a 0.05 in. wall with a crucible cover, 0.125 in. thick x 0.35 in. dia., 60° conical orifice whose minor diameter is 0.03 in.

The temperature of the crucible is measured with a Leeds and Northrup manual optical pyrometer by sighting into the orifice (as shown in Figure 1). Corrections due to prism and window were made in all the reported temperature values.

The vapor generated in the crucible in Chamber II, after traveling 2 cm through a vacuum of $P_{II} 10^{-6}$ torr, enters Chamber I (through a slit 0.5 cm x .05 cm) and reacts with oxygen whose pressure P_I can be as high as 2×10^{-3} torr. The vapor travels 6 cm in Chamber I before it reaches point G where an electron beam of controlled energy is directed perpendicular to the metal vapor beam and its reaction products with oxygen.

A - INDUCTION COIL
B - TANTALUM HEAT SHIELD
C - KNUDSEN CRUCIBLE AND LID
D - WATER COOLED PORTION OF CHAMBER
E - MOVABLE SHUTTER
F - TOF SOURCE ENTRANCE SLIT
G - IONIZING ELECTRON BEAM
H - ION GRID
I - VIEWING WINDOW ON MULTIWINDOW ASSEMBLY
J - PRISM
K - OPTICAL PYROMETER

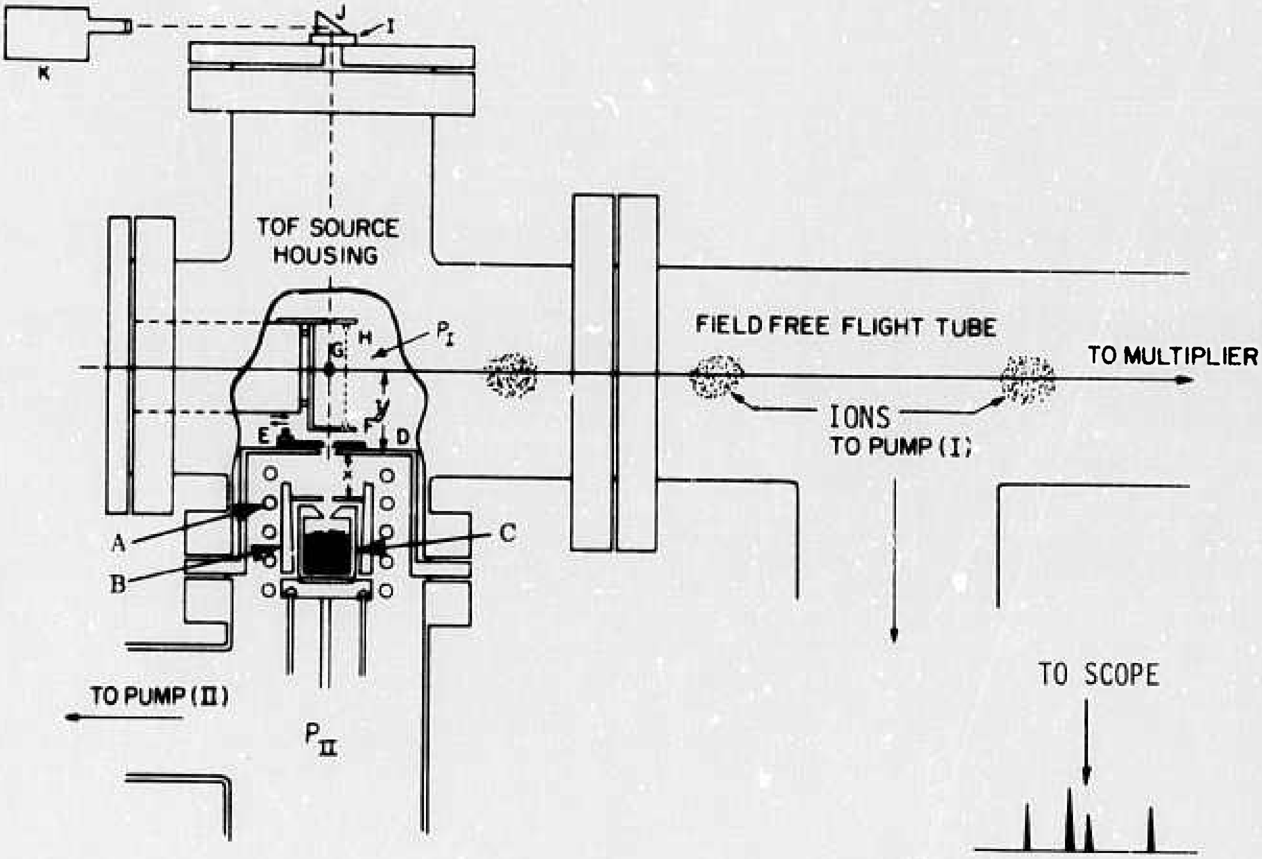


Figure 1 - KNUDSEN CRUCIBLE MASS SPECTROMETER APPARATUS

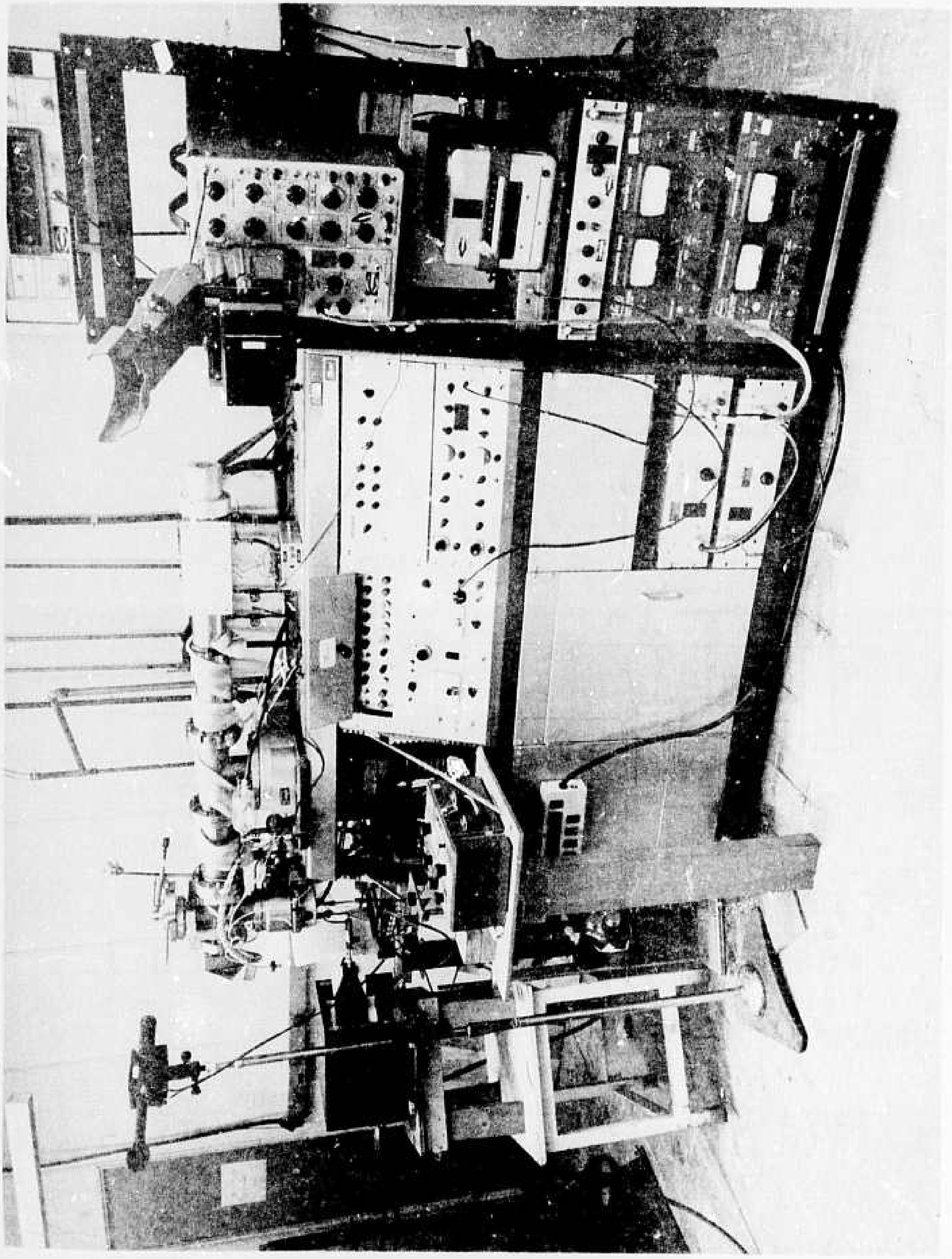


Figure 2: INDUCTIVELY HEATED FURNACE IN TIME-OF-FLIGHT MASS SPECTROMETER

At this point, the ratio of unreacted metal to metal oxide can be determined mass spectrometrically as a function of oxygen pressure and metal vapor density.

2. Laser Heating

Another heating arrangement involves use of pulsed laser, ruby or CO_2. The beam enters a chamber through a window (glass for ruby, NaCl for CO_2) and strikes a metal target as shown in Figure 3. The generated vapor plume moves away from the metal surface and reacts with the surrounding oxygen. The ratio of metal vapor to oxidation products is measured with the time-of-flight mass spectrometer.

Spectral measurements on reactants and products are also made.

3. Heating by Chemical Reactions

This method capitalizes on the highly exothermic nature of certain solid state reactions. These include inter-metallic reactions as well as oxidation of metals.

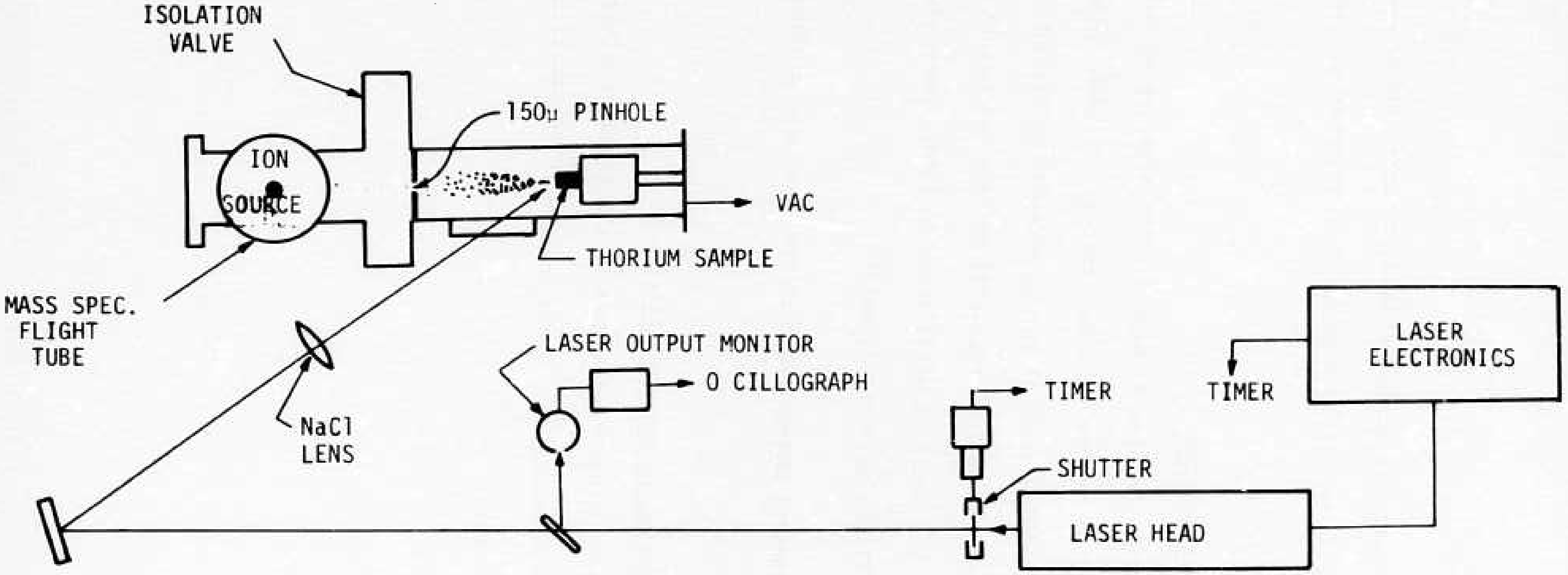


Figure 3 - LASER HEATING EXPERIMENT

III. RESULTS

A. INDUCTION HEATING

1. The Heat of Vaporization of Thorium

In an effort to fully characterize the behavior of starting materials, thorium metal was first heated in a tantalum crucible and the mass spectrum of the effusing vapor was recorded. It became immediately apparent that ThO (g) was present in the vapor in significant amounts due to residual oxygen present in the starting material as well as in the crucible itself. This result suggests that previous work on the heat of vaporization of Th based on weight loss[3] might be in error and the reported ΔH^{o}_{298} is lower than the true value. It is for this reason that the task was undertaken to measure the heat of vaporization of thorium.

According to the Clausius-Clapeyron equation:

$$d \log P/d \left(\frac{1}{T}\right) = -\Delta H^{o}_{T}/2.3R$$

or

$$d \log IT/d \left(\frac{1}{T}\right) = -\Delta H^{o}_{T}/2.3R$$

where ΔH^{o}_{T} = heat of vaporization at the average temperature of the experiment $T^{o}K$, P = vapor pressure $\propto IT$ and I = ion intensity as observed by the mass spectrometer. A plot, therefore, of IT vs $\frac{1}{T}$ can produce the heat of vaporization according to the second-law method. Figure 4 shows such a plot for thorium in the temperature range 2473°K - 2773°K; the energy of the electron beam was 12 eV. Using ΔH^{o}_{T} and tabulated thermodynamic data, the heat of vaporization at 298°K can easily be calculated by: $\Delta H^{o}_{298} = \Delta H^{o}_{T} - \Delta(H^{o}_{T} - H^{o}_{298})$.

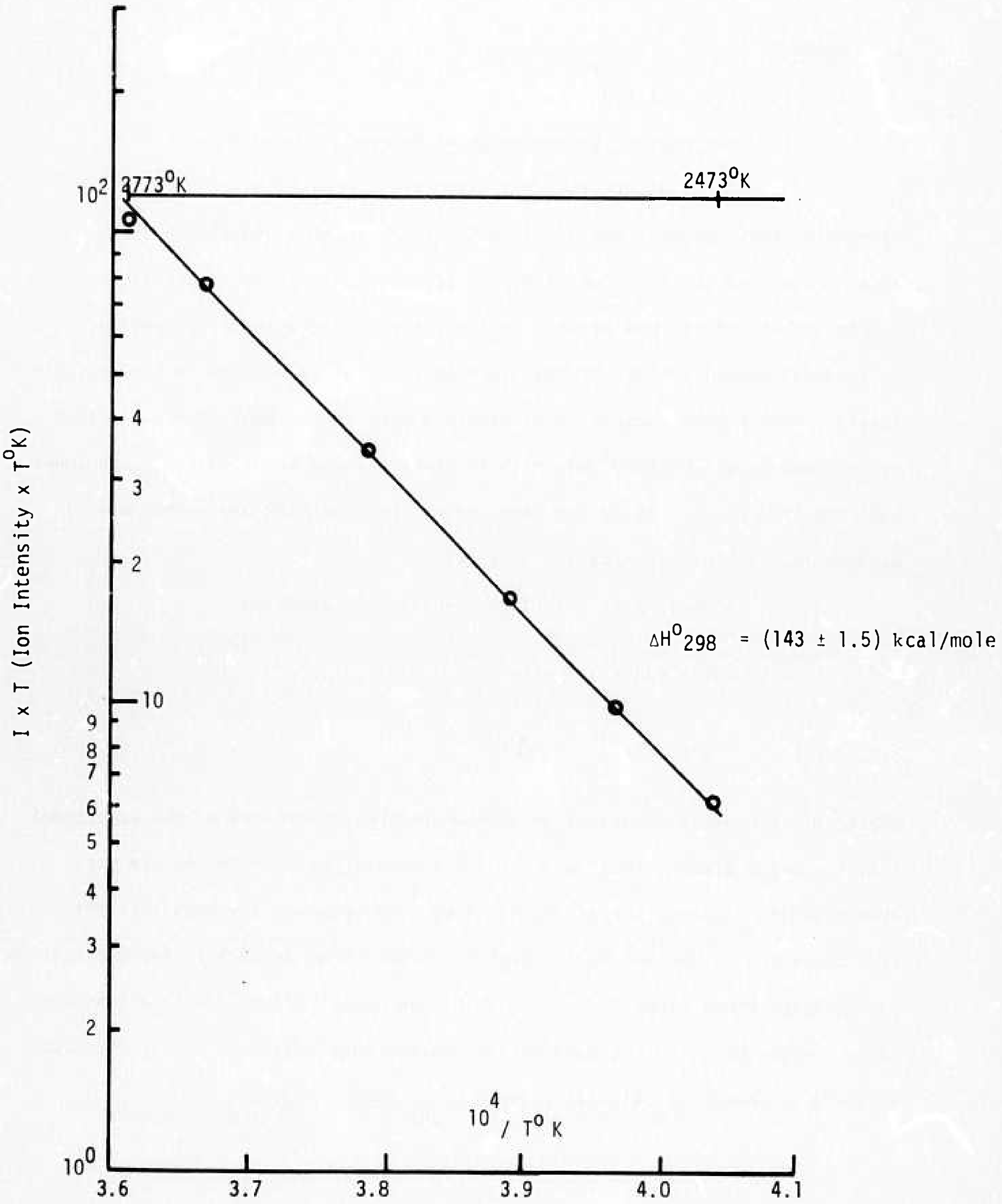


Figure 4 - Heat of Vaporization of Thorium

The heat of vaporization obtained by this work is 143 ± 1.5 kcal/mole to be compared to Darnell's value[3] of 134.7 ± 2.8 kcal/mole and to the value of 143.1 ± 1 kcal/mole, recently published by Ackerman and Rauh[4]. Table I provides additional information on the methods of experimentation as well as the temperature ranges of the three studies. In view of the very good agreement between second and third-law values of Ackerman and Rauh (in the temperature range 2010°K - 2460°K) and, further, agreement with the second-law value from this work (in a higher temperature range 2473°K - 2773°K), it is concluded that the correct value for the heat of vaporization at 298°K is 143 ± 1.5 kcal/mole and the original value of 134.7 ± 2.8, reported by Darnell et al, is in error possibly due to the presence of oxygen in the sample.

2. Ionization Potentials

Ionization efficiency plots were made for Th(g), ThO(g) as generated from a thorium sample and ThO_2 (g) generated from a ThO_2 sample. Similar plots were made for UO(g) and UO_2 (g) generated from a UO_2 sample. Ion intensities as a function of energy of the ionizing electron beam showed that the ionization potentials of Th and ThO are about equal and in the vicinity of 5.5 - 6 eV while that of ThO_2 is about 3 eV higher.[7] The ionization potentials of UO and UO_2 on the other hand (as obtained by the same method) are closer to each other and between 5.3 and 5.5 eV.

3. Thorium Vapor Oxidation

a. Chemi-Ionization

Thermochemical calculations on chemi-ionization processes such as

$$U + O_2 \xrightarrow{k_1} UO_2^+ + e \qquad (1)$$

TABLE 1

THE HEAT OF VAPORIZATION OF THORIUM

METHOD	ΔH^o_{298} (kcal/mole)	REFERENCE
WEIGHT LOSS 1747-1956°K 3rd Law	134.7 ± 2.8	(3)
MASS SPECTROMETRY 2nd & 3rd Law 2010-2460°K	143.1 ± 1	(4)
MASS SPECTROMETRY 2nd Law 2473-2773°K	143 ± 1.5	THIS WORK

$$U + O \xrightarrow{k_2} UO^+ + e \qquad (2)$$

$$Th + O_2 \xrightarrow{k_3} ThO_2^+ + e \qquad (3)$$

$$Th + O \xrightarrow{k_4} ThO^+ + e \qquad (4)$$

suggest that they are all exothermic by several electron-volts (see Table II for details on the thorium system).

Experimental verification of process (1) and (2) was recently reported by Fite and Irving[1]. All of the above processes were observed in this work by reacting thorium and uranium atoms with O_2 and O inside a time-of-flight mass spectrometer.

In these experiments, the metal vapors were generated by heating metal samples in tantalum and tungsten Knudsen crucibles (with a 25 KW GE Induction Heater). The effusing vapor beam, after traveling 2 cm in vacuum of 10^{-6}, enters (through a slit) a vacuum system which is pressurized with static oxygen up to 3×10^{-4} torr. The metal atoms travel 6 cm in this environment before they enter the ion source of the mass spectrometer. At this point, mass spectrometric analysis of the mixture of reactants and products is carried out.

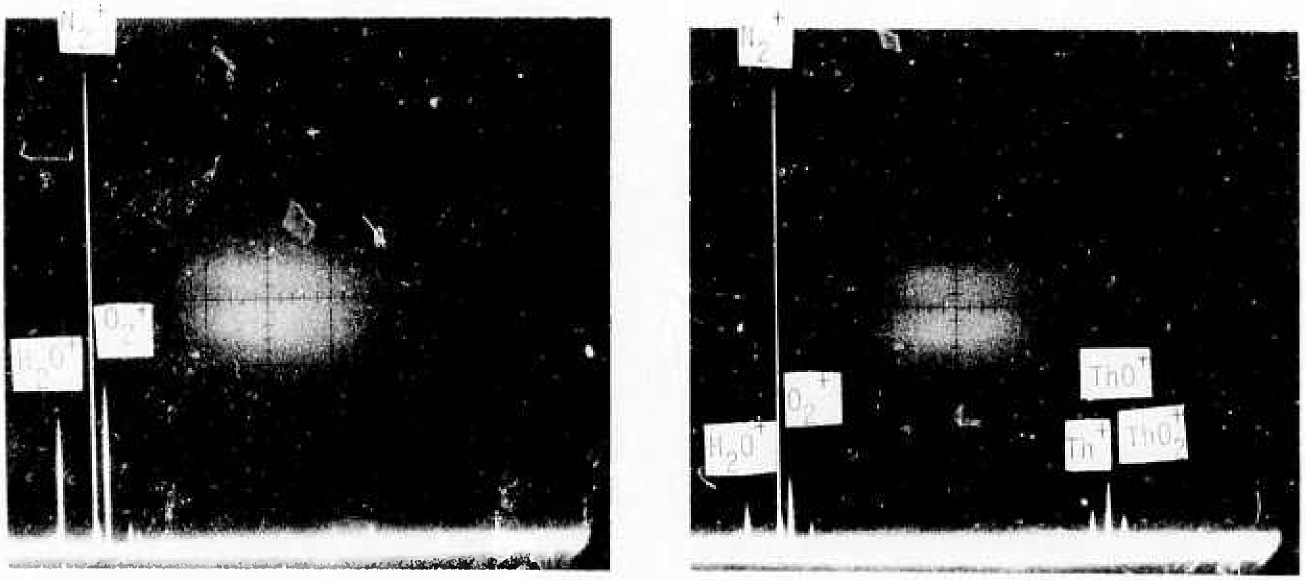
The experimental procedure is first to turn on the electron beam of the mass spectrometer and observe the metal vapor effusing from the Knudsen crucible. Data were obtained with the electron beam set at 20 eV and 12 eV; the pressure in both chambers was about 10^{-6} torr.

Typical mass spectra of air background and vapor effusing from the crucible are shown in Figure 5, A and B. The addition of O_2 in the upper chamber enhances the intensity ThO_2^+ peak and decreases the intensity of

TABLE II

THERMOCHEMISTRY OF THORIUM-OXYGEN SYSTEM

REACTION	$\Delta H^o_{298} (\frac{kcal}{mole})$	REFERENCE
$Th(s) \longrightarrow Th(g)$	143	THIS WORK
$ThO_2(s) \longrightarrow ThO_2(g)$	158.7	(5)
$Th(s) + O_2(g) \longrightarrow ThO_2(s)$	-293	(6)
$\frac{1}{2}Th(s) + ThO_2(s) \longrightarrow ThO(g)$	152	
$ThO_2(g) \longrightarrow ThO_2^+ + e$	195-207	THIS WORK
$ThO(g) \longrightarrow ThO^+ + e$	126-138	THIS WORK
$Th(g) + O_2 \longrightarrow ThO_2^+ + e$	- 86	COMPUTED
$Th(g) + O \longrightarrow ThO^+ + e$	- 83	COMPUTED
$Th(g) + O_2 \quad ThO(g) + O$	- 70	COMPUTED



A. BACKGROUND

B. THORIUM AT 2623°K

C. ADDITION OF O_2

D. SAME CONDITION AS C BUT ELECTRON BEAM TURNED OFF

Figure 5 - MASS SPECTRA IN THE OXIDATION OF THORIUM VAPOR

Th^+ Figure 5C. When the electron beam is turned off, all peaks disappear with the exception of ThO_2^+ which proves that this ion is formed directly through a chemi-ionization process such as shown by equation reaction (3).

When mixtures of U and Th were heated in the same manner, U^+ and Th^+ peaks were observed along with UO^+ and ThO^+ (both due to residual oxygen in the samples). When the electron beam was turned off, all signals disappeared. As soon as molecular oxygen at room temperature was introduced in the upper chamber, strong UO_2^+ and ThO_2^+ signals from processes (1) and (3) were observed. See Figure 6 for data at 2423°K.

The production rates of ThO_2^+ and UO_2^+ through equations (3) and (1) are given by:

$$\frac{dThO_2^+}{dt} = k_3 \times [Th] \times [O_2] \qquad \text{and}$$

$$\frac{dUO_2^+}{dt} = k_1 \times [U] \times [O_2] \qquad \text{or}$$

$$\frac{k_3}{k_1} = \frac{d\,ThO_2^+/dt}{d\,UO_2^+/dt} \times \frac{[U]}{[Th]} = \left(\frac{I_{ThO_2^+}}{I_{UO_2^+}}\right)^{**} \times \left(\frac{I_{U^+}}{I_{Th^+}}\right)^{*} \frac{\sigma_{Th}}{\sigma_U} \times \frac{(E-A_{Th})}{(E-A_U)}$$

where I = ion intensity observed by mass spectrometry.

* = Electron beam on

** = Electron beam off

σ = Ionization Cross Section

E = Electron Energy

A = Appearance Potential

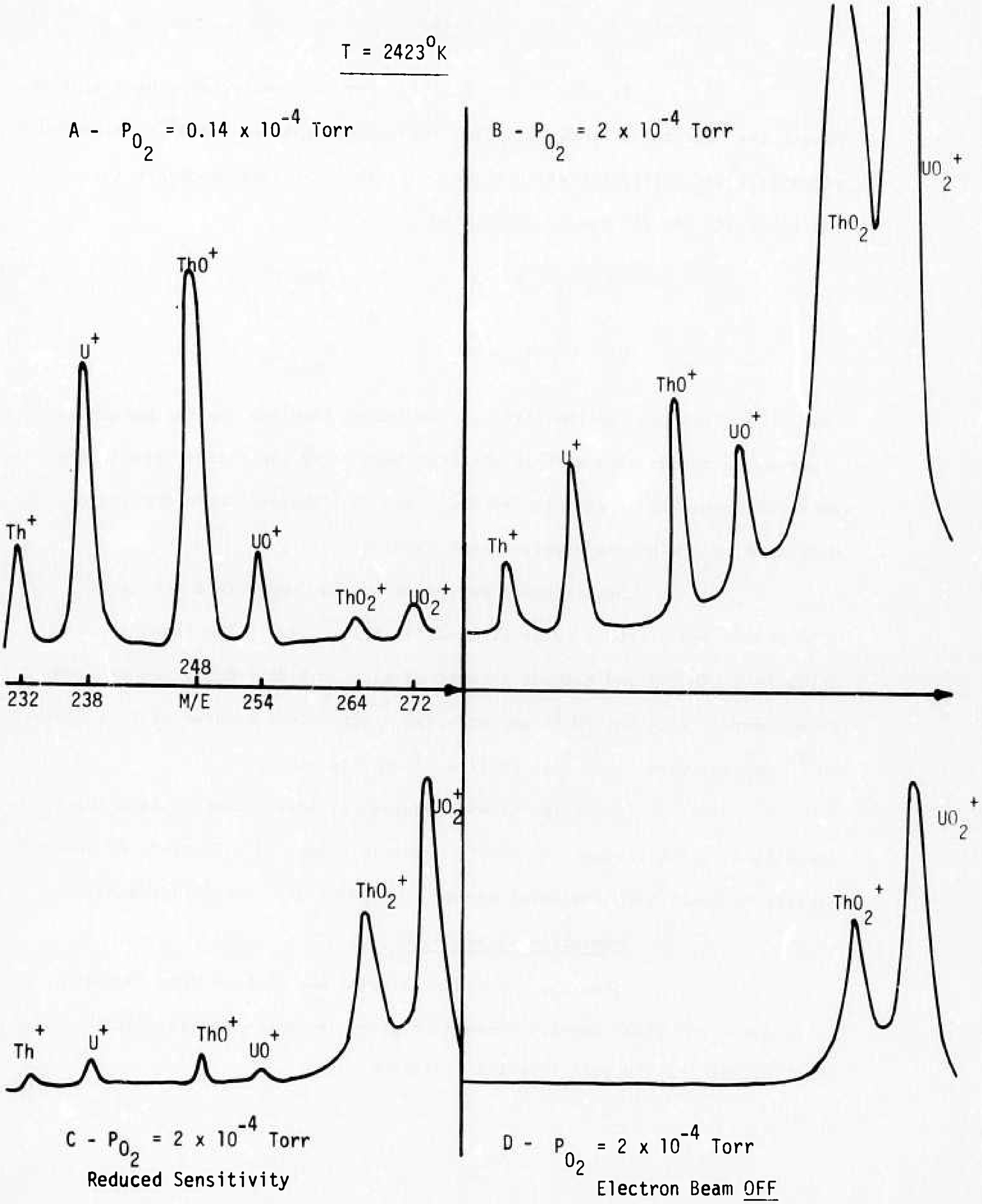


Figure 6 - MASS SPECTRA IN THE OXIDATION OF Th-U MIXTURES

In view of the fact that thorium and uranium have similar properties concerning atomic weights, ionization cross sections[8], ionization potentials[9] and multiplier efficiencies, the ratio of rate constants for reactions (1) and (3) can be simplified to:

$$\frac{k_3}{k_1} \left(\frac{I_{U^+}}{I_{Th^+}}\right)^{*} \times \left(\frac{I_{ThO_2^+}}{I_{UO_2^+}}\right)^{**},$$

where the first term is the ratio of ion intensities for the two metals as observed in vacuum with a 20 eV electron beam while the second term is the ratio of chemi-ion intensities of ThO_2^+ and UO_2^+ observed upon the introduction of O_2 (with the electron beam turned off).

Measurements were made in the temperature ranges of 2253-2423°K and pressure range $(0.14-2.84) \times 10^{-3}$ torr. The results are shown in Table III and suggest a ratio of $k_3/k_1 = 1.23 \pm 0.13$. Since from Fite's work[10] $k_1 = 4 \times 10^{-12}$ cm^3 molecule^{-1} sec^{-1} then a value of $k_3 = 4.9 \times 10^{-12}$ cm^3 molecule^{-1} sec^{-1} is obtained from this work.

Reaction (4) was observed by introducing O_2 into the crucible from the bottom. At 2900°K, certain amount of O is produced which appears to react with the metal vapors to produce ThO^+ very efficiently.

b. Formation of Neutrals

When the container material was changed from tantalum to tungsten and after several hours of heating in vacuum it was possible to eliminate the ThO peak from the background.

TABLE III

RELATIVE RATE CONSTANTS FOR THE OXIDATION OF URANIUM AND THORIUM

T°K	P_{O_2} (Torr)x10^{-4}	Ratios of Ion Intensities $\left(\frac{I_{U^+}}{I_{Th^+}}\right)^*$	$\left(\frac{I_{UO_2^+}}{I_{ThO_2^+}}\right)^{**}$	Ratio of Rate Constants k_3/k_1
2253	0.14	10.60	10.00	1.06
	0.44	8.21	6.67	1.23
	0.74	6.92	6.00	1.15
	1.64	5.00	5.55	0.90
	0.14	7.20	5.50	1.30
2353	0.14	6.43	5.50	1.16
2423	0.14	3.00	2.00	1.50
	1.04	2.54	1.85	1.38
	2.04	2.14	2.00	1.07
	2.84	2.33	1.84	1.27
	0.44	2.20	1.63	1.35
	0.14	2.28	1.67	1.37
				1.23 ± 0.13

* = ELECTRON ENERGY - 20 eV

** = ELECTRON BEAM TURNED OFF

Typical spectra obtained with tungsten crucibles are shown in Figures 7 and 7A at two different oxygen pressures. It is apparent that the addition of O_2 reduces the Th signal and increases both ThO and ThO_2^+. The total rate of Th removal by O_2 can be computed as follows:

$$-\frac{d\,Th}{dt} = k\,[Th] \times [O_2]$$

or

$$k = \frac{-d\,Th}{[Th]} \quad \frac{1}{[O_2] \times dt}$$

where dt = the reaction time (i.e. the time required by the Th atoms to travel 6 cm distance in O_2) or $dt = \frac{6\ cm}{\bar{c}} = \frac{6}{1.868 \times 10^{-8}\sqrt{\frac{T}{M}}}$ sec

where T = crucible temperature in °K

M = mass of thorium atom

For $T = 2648\,^{o}K$

$\bar{c} = 4.87 \times 10^{4}$ cm/sec

and $dt = 1.23 \times 10^{-4}$ sec

It is then possible to calculate the rate constant from measurements of the reduction of the thorium if the oxygen density is known. In this experiment the oxygen pressure is measured with a McLeod gauge and the intensity of the thorium ion peak is measured in a vacuum of 10^{-6} torr and also as a function of imposed oxygen pressure. The conditions of these experiments were such that the metal density was at least two orders of magnitude less than that of oxygen. A typical series of runs depicting the reduction of the thorium signal as a function of oxygen pressure is shown in Figure 8. It is apparent that after every measurement when the oxygen is removed the signal returns to its original value thus suggesting that the change is primarily due to reaction.

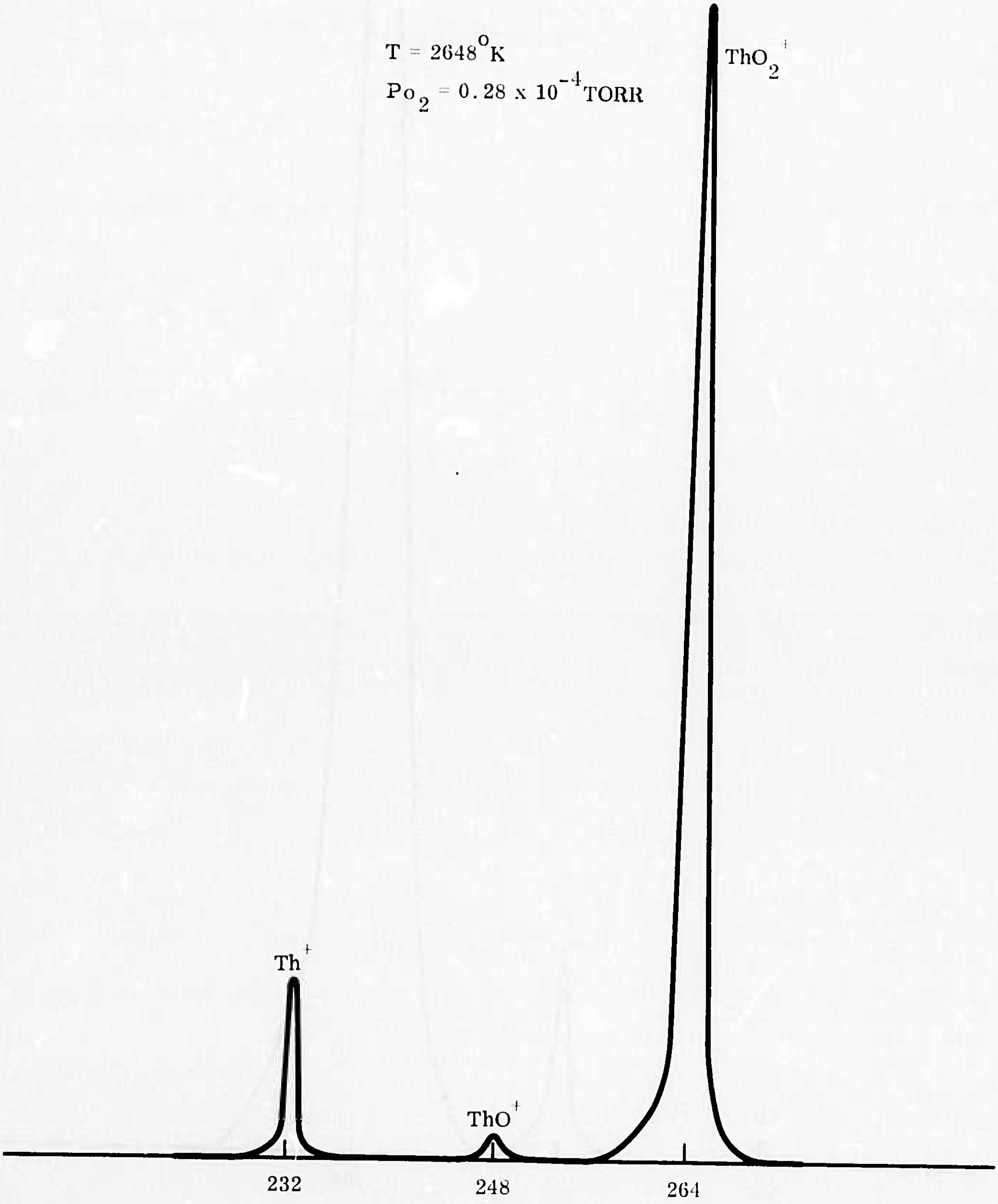


Figure 7. Mass Spectra in the Oxidation of Thorium Vapor

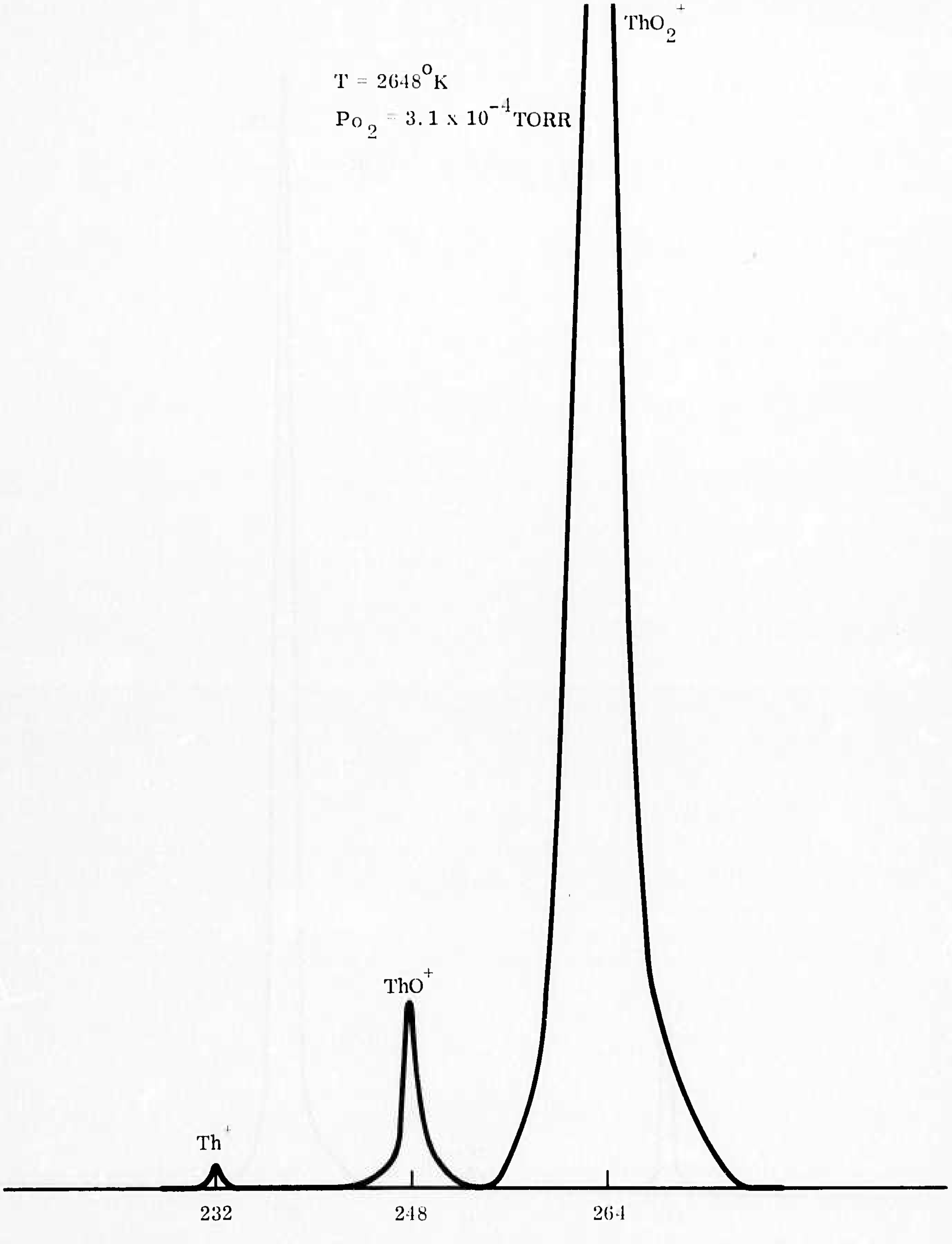


Figure 7A. Mass Spectra of Thorium Oxidation At Higher Oxygen Pressure

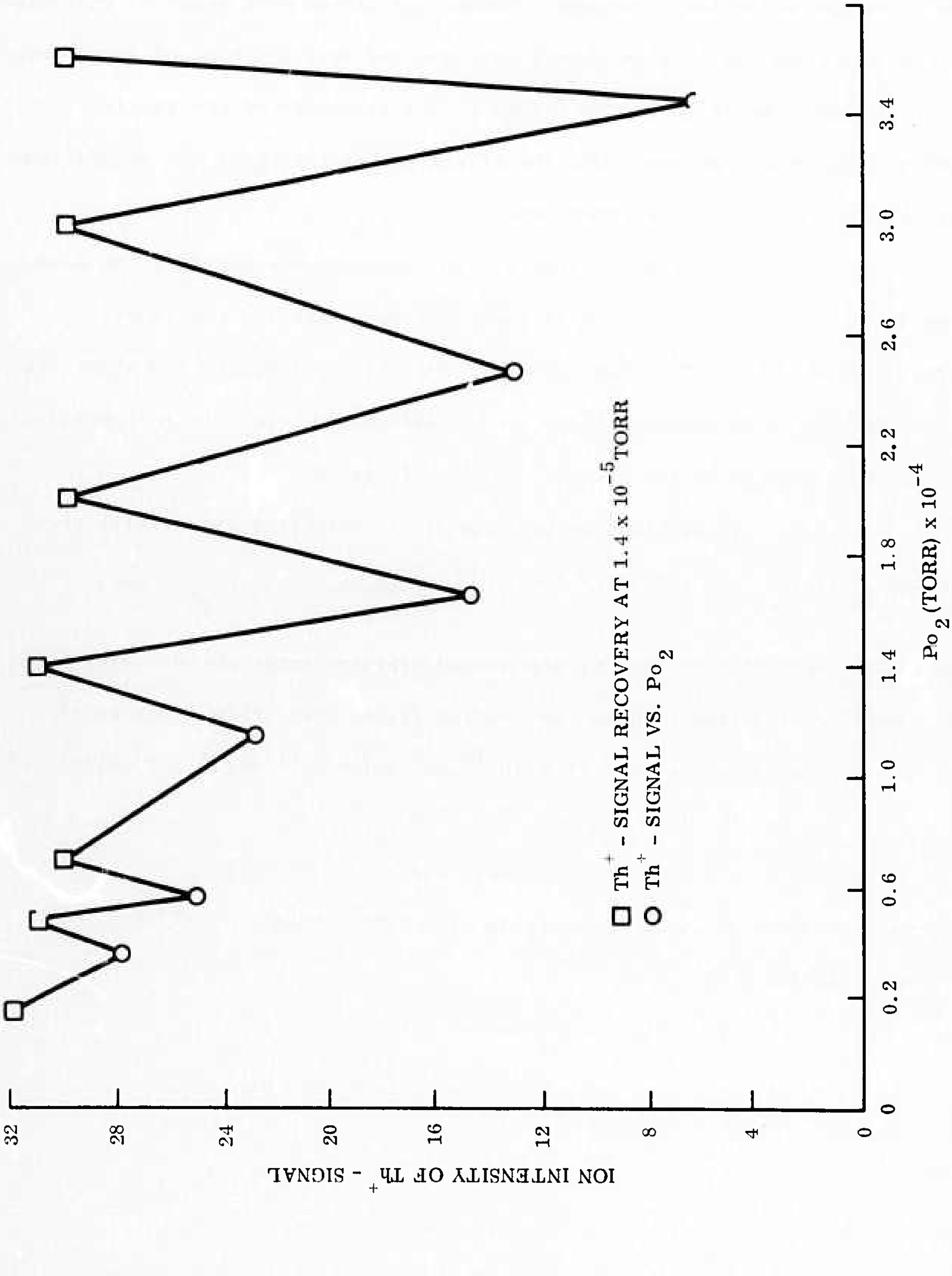


Figure 8. The Oxidation of Thorium as A Function of Oxygen Pressure.

In an effort to assess the extent of scattering of thorium atoms by oxygen molecules, the upper chamber was filled with argon of equivalent pressure range and the thorium signal was measured as a function of argon pressure. The measurements showed no change in the intensity of the thorium signal and was thus concluded that the effect of scattering is not significant under the conditions of this experiment.

When the products of the reaction were carefully measured it was found that ThO^+ was formed at about the same rate Th^+ was removed Figure 9. Since Th and ThO have the same ionization potentials and about the same ionization cross section (based on the additivity rule[8]) it is concluded that the main product in the reaction of $Th + O_2$ is ThO.

It should then be possible to calculate essentially the same rate constant from intensity ratios of $\frac{ThO}{Th + ThO}$ vs. P_{O_2}. Many measurements were made at 2648°K, and oxygen pressure range $(0.28 - 5) \times 10^{-4}$ torr. Based on the reduction of the thorium signal (See Table IV) a total rate constant equal to $(5.1 \pm 1.1) \times 10^{-10}$ cm^3 $molecule^{-1}$ sec^{-1} was calculated for

$$Th + O_2 \rightarrow \begin{matrix} ThO + O \\ ThO_2 + e \end{matrix}$$

Based on the formation of ThO (See Table V) a rate constant equal to 5.5×10^{-10} was calculated for

$$Th + O_2 \rightarrow ThO + O$$

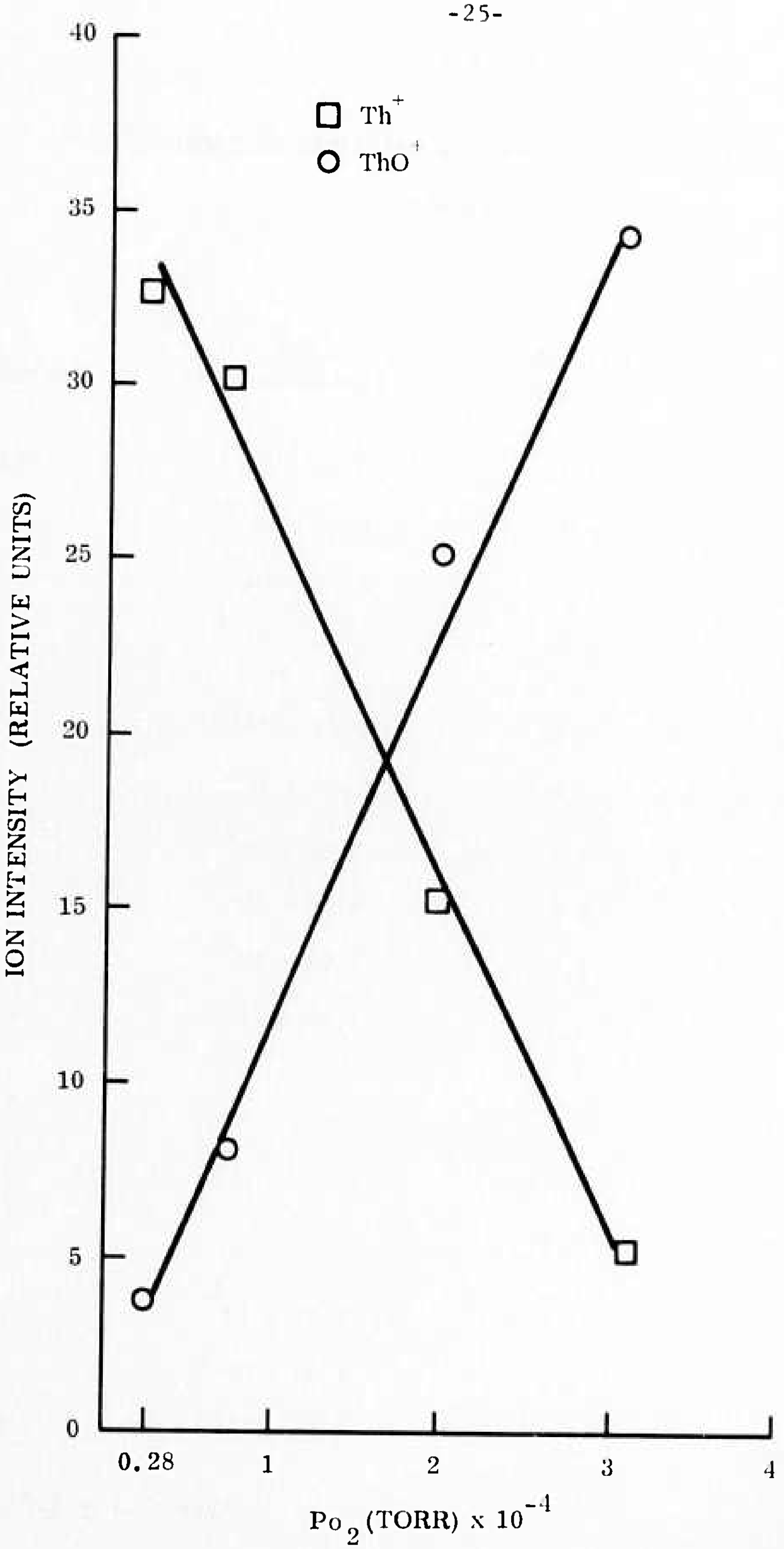


Figure 9. Formation of ThO vs. Oxygen Pressure

TABLE IV

THE RATE CONSTANT FOR THE OXIDATION OF THORIUM AT 2648°K

Run	$\frac{-d\ I_{Th^+}}{I^o_{Th^+}}$	$PO_2 \times 10^{-4}$ (torr)	$[O_2]$ (molecules/cm^3)	k_t (cm^{3}molecule^{-1}sec^{-1})
#1	0.281	1.14	3.65×10^{12}	6.0×10^{-10}
	0.553	2.0	6.44×10^{12}	6.8
	0.584	3.3	1.06×10^{13}	4.3
	0.797	4.7	1.50×10^{13}	4.1
#2	0.125	.55	1.75×10^{12}	5.9
	0.194	.84	2.63×10^{12}	5.7
	0.233	1.15	3.68×10^{12}	4.9
	0.516	2.0	6.40×10^{12}	6.3
	0.567	3.4	1.09×10^{13}	4.1
	0.813	4.6	1.47×10^{13}	4.4
#4	0.577	3.7		3.8
	0.155	0.75		5.0
	0.859	4.2		4.8
#5	0.247	1.02	3.26×10^{12}	5.9
	0.579	2.5	8.00×10^{12}	5.6
	0.605	3.9	1.25×10^{13}	3.8

Average $(5.1 \pm 1.1) \times 10^{-10}$

TABLE V

RATE CONSTANT FOR THE FORMATION OF ThO AT 2643°K

Run	$\frac{I_{ThO^+}}{I_{Th^+} + I_{ThO^+}}$	$P_{O_2} \times 10^{-4}$ (torr)	k_{ThO} ($cm^3 molecule^{-1} sec^{-1}$)
#4	.09	.40	5.45×10^{-10}
	.20	.90	5.5
	.62	2.6	6
	.87	4.1	5.1

Average $(5.5 \pm 0.3) \times 10^{-10}$

The second value is in agreement with the first (within the experimental error) and entirely consistant with the chemi-ionization rate constant of 4.9×10^{-12} for the formation of ThO_2^+.

4. The Oxidation of Uranium

In an effort to further check the validity of the method and compare the reactivity of thorium with that of uranium the experiment was repeated with high purity uranium. Measurements on the formation of neutral UO as a function of oxygen pressure at 2448°K are shown in Table VI. Based on these data a rate constant equal to $4.9 \pm 1.2 \times 10^{-10}$ is calculated for the reaction

$$U + O_2 \longrightarrow UO + O$$

This value is in good agreement with the value of 4×10^{-10} obtained by Fite[10] by a different method.

B. LASER HEATING

When a laser beam strikes the surface of a metal, there is a great difference in the behavior of surfaces struck by laser pulses with millisecond (or higher) durations as compared to those with pulse duractions in the nanosecond region. Typically, very high-power short pulses do not produce much vaporization, but instead produce a small amount of vapor in an excited and frequently ionized state, whereas longer, lower-power pulses from normal pulse or CW lasers produce vapor which is characterized by a temperature close to the boiling point of the target metal.

TABLE VI

RATE CONSTANT FOR THE FORMATION OF UO FROM U + O_2 AT 2448°K

$\frac{I_{UO^+}}{I_{U^+} + I_{UO^+}}$	$PO_2 \times 10^{-4}$ (torr)	k_{UO} ($cm^3 molecule^{-1} sec^{-1}$)
0.08	0.6	3.1×10^{-10}
0.22	1.0	5.3
0.45	1.6	6.8
0.80	4.5	4.3
0.73	2.8	6.4
0.79	5	3.8
		Average $(4.9 \pm 1.2) \times 10^{-10}$

The time, Δt, required for the surface of the material to reach a vaporization temperature is given by:

$$\Delta t = (\pi/4)\ (K\rho\ C/\dot{E}d^2)\ (Tv-To)^2$$

where K, C, ρ and $\dot{E}d$ are the thermal conductivity, heat capacity per unit mass, density and laser flux (power density), respectively, and Tv and To are the vaporization temperature and initial temperature. Based on the above expression times were calculated for reaching the boiling points of several metals as a function of power density. The results are shown in Table VII.

It can then be easily calculated that a normal pulse laser of 10 joules output and 5×10^{-4} sec duration, focussed to 10^{-2} cm^2 can provide a flux of 10^6 w/cm^2, which is capable of raising the surface temperature of thorium and uranium to the boiling point in a few microseconds.

The maximum vaporization rate[9] during steady state vaporization (which is reached after several microseconds) would be:

$$\dot{m} = \frac{\dot{E}d - \emptyset}{(C\Delta T_1)\ \text{Solid} + \Delta H_f + (C\Delta T_2)\ \text{liquid} + \Delta Hv}$$

where $\dot{E}d$ = flux (power density)

$\emptyset$ = radiative flux from the surface after conductive flux has reached equilibrium $(\sigma\ Tv^4)$

C = heat capacity

$(C\Delta T_1)_{\text{solid}}$ = energy required to heat the solid to its melting point

ΔH_f = heat of fusion

$(C\Delta T_2)_{\text{liquid}}$ = energy required to heat the liquid to its boiling point, and

ΔH_v = heat of vaporization of liquid at its boiling point.

TABLE VII

TIME REQUIRED TO REACH VAPORIZATION (BOILING POINT) TEMPERATURE, Δt

	LASER FLUX (W cm^{-2})		
METAL	10^5	10^6	10^7
Fe	1.8 m sec	18 μ sec	0.18 μ sec
Al	2.6	26	0.26
U	0.2	2	0.02
Th	0.4	4	0.04
Cu	8.0	80	0.8

Thus a 10-joule laser pulse, for example, is expected to produce 10^{-5} moles of thorium vapor. The calculation assumed no energy loss due to reflection and, therefore, the actual amount should be somewhat less.

Using a 10-joule, ruby laser (lear Siegler) with a pulse duration of 5×10^{-4} sec, preliminary data were obtained with thorium metal targets vaporizing into air at several pressures. Figure 10 shows photographs of thorium vapor oxidizing in air in the pressure range 0.3 torr - 1 atm.

1. Plume Spectral Measurements

a. Plumes Generated by Laser Blow-Off

A series of experiments was performed in which the light from laser induced plumes was examined spectroscopically. The wavelength range covered was .36 to .64 microns. Plumes were generated from depleted uranium sheet metal samples in air at 1 atmosphere, and reduced pressures and in argon at reduced pressure. A diagram of the experimental arrangement is shown in Figure 11. Samples were positioned in a cylindrical vacuum chamber, A, fitted with two glass windows. The samples were irradiated by the laser beam through one of the windows and the resulting plume radiation was observed through the second window as indicated in Figure 11.

A pulsed ruby laser, B, operating at 10 joules in the burst mode was used in this work. The pulse duration was 0.5 milliseconds. The laser beam passedthrough an energy monitor, C, and was then focussed with a plan convex lens to a 0.5 mm diameter spot size at the surface of the sample. This spot size produced a density of 5×10^3 joules/cm^2 on the sample.

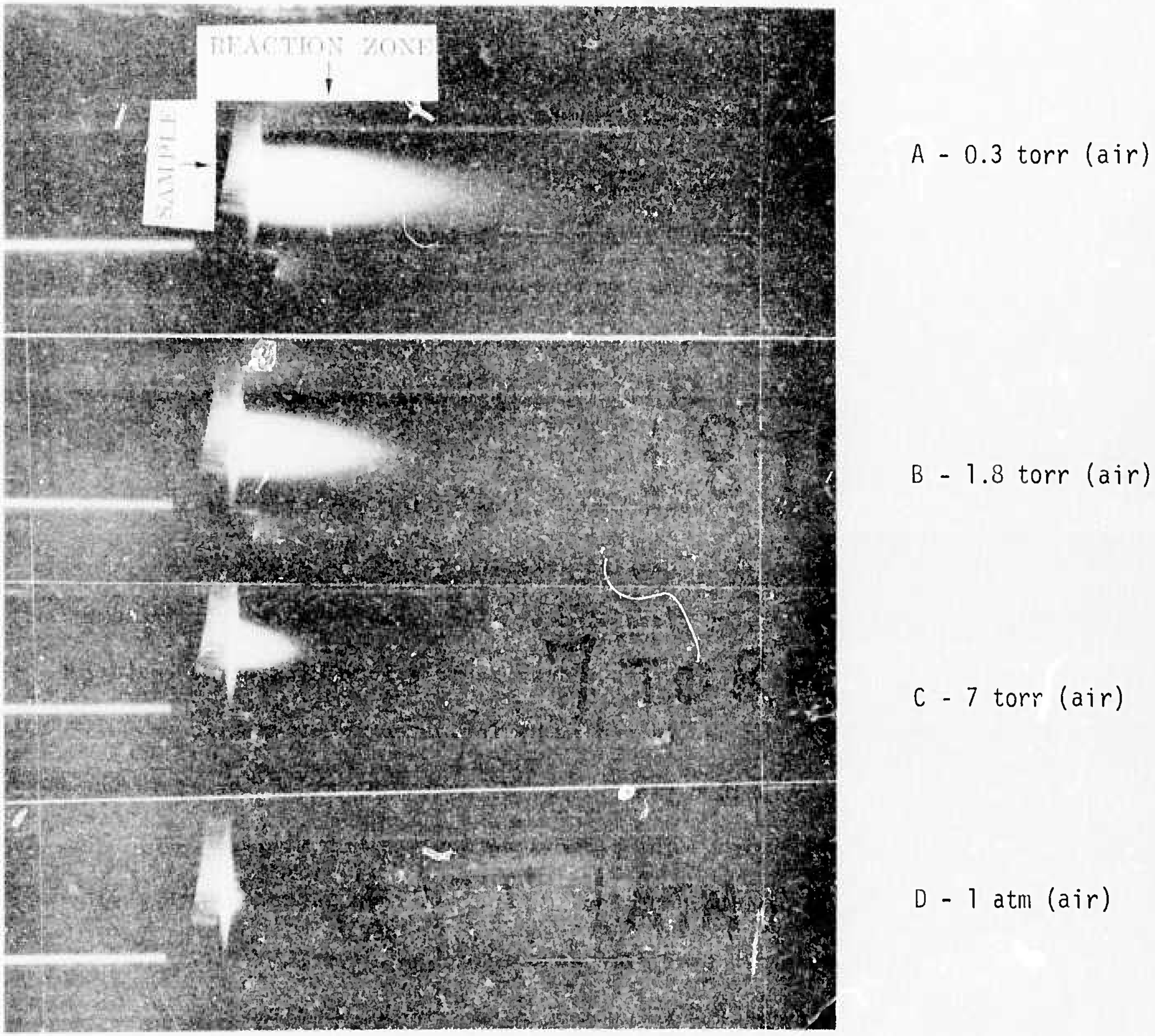


Figure 10 - COMBUSTION OF THORIUM VAPOR IN A LASER BLOW-OFF EXPERIMENT

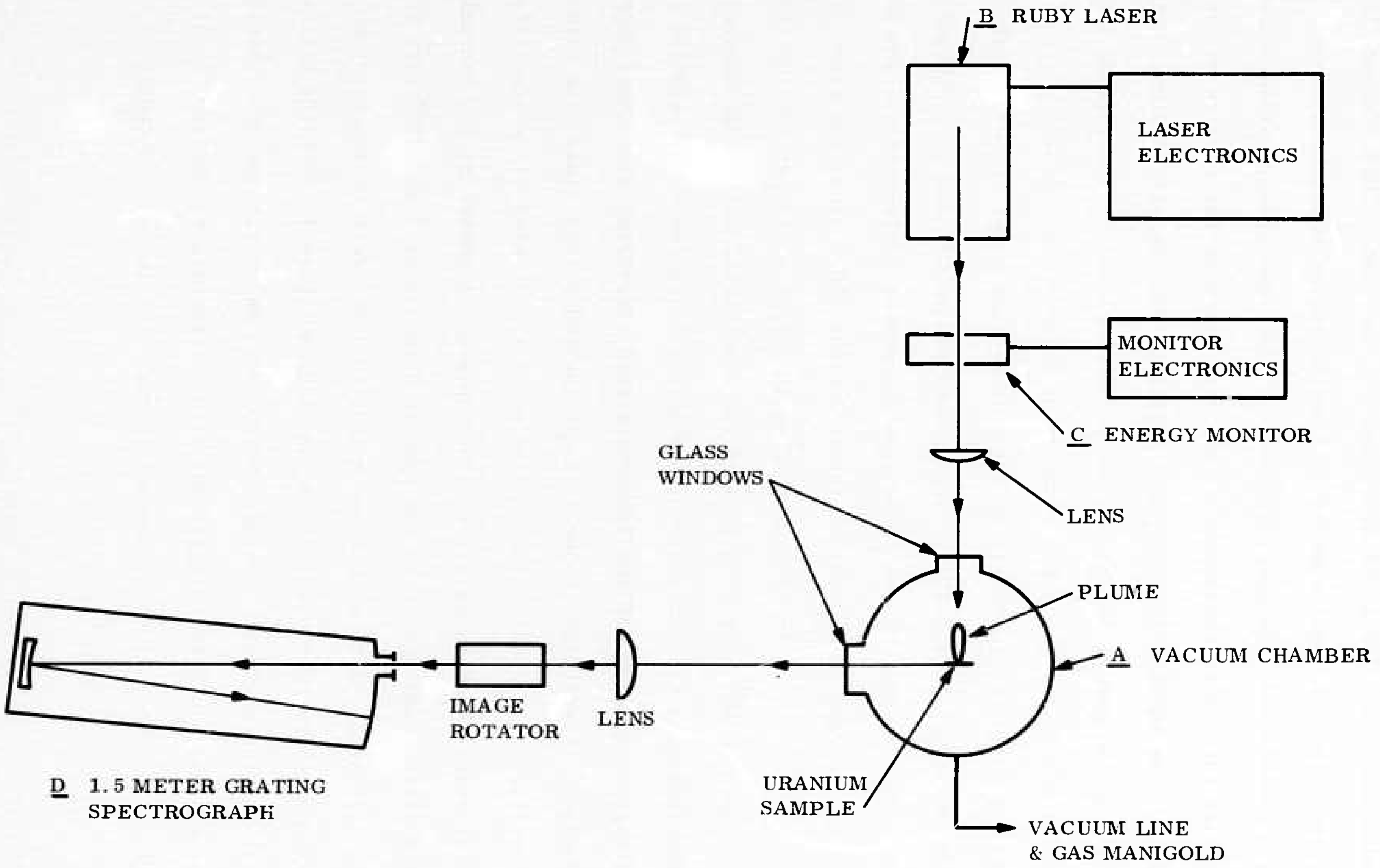


Figure 11. Diagram of Apparatus for Laser Blow-Off Experiments

Plume radiation was recorded with a 1.5 meter B&L grating spectrograph, D. The first order spectrum was used. This produced 14.5 Å/mm plate dispersion and covered the .36-.64 micron wavelength range. Kodak TRI-X emulsion was the recording medium. Each spectrum recorded represented the time integrated radiation (.5 ms) from a single laser pulse on the sample. Samples were mounted in a vertical position. The resulting plume is then normal to the sample surface (a horizontal position). In order to obtain spatial resolution along the plume axis, a lens-image rotator combination was used (as shown in Figure 11) to rotate the plume image to a vertical position along the spectrograph slit. The optical system was set up to record radiation along the axis of the plume from the sample surface to a distance 2 cm from the surface. The spatial resolution was 200 μ along the plume axis.

Spectra were taken in air at pressures ranging from 1 atmosphere to 10^{-4} torr. A qualitative examination of the data showed continum radiation (.36-.64μ) overlaid with a large number of emission lines in all cases. A number of the lines have been identified as neutral U atom emission. In addition, several singly ionized U atom lines have also been identified. Table VIII gives a listing of the uranium lines identified from the spectrum obtained in air at 1 atmosphere. A number of the neutral and ion lines listed also appear in the spectra obtained at 5 and 10^{-4} torr in air and at 5 torr argon. Figure 12 shows a densitometer trace of the spectrum obtained at 1 atmosphere pressure. It can be seen in Figure 12 that the spectrum shows no readily recognizable features which could be attributed to a Uranium oxide band system. This is in agreement with the results of Gatterer et al(11). The work in reference 11 shows several intensity maxima in the continuum radiation

TABLE VIII

URANIUM LINE SPECTRA FROM LASER BLOW-OFF EXPERIMENTS

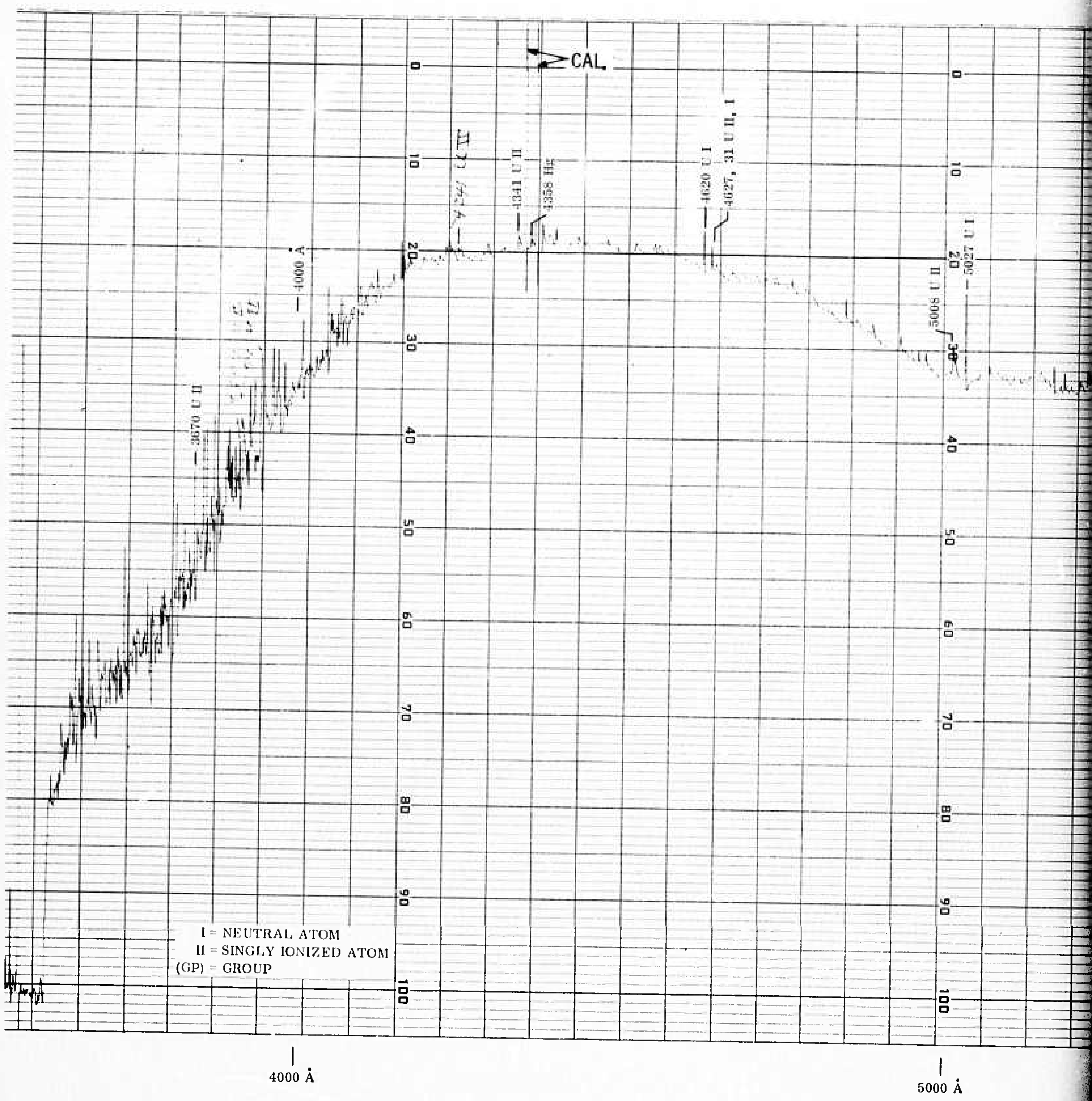
Wavelength (Å)		Spectrum
3854.7		II
3859.9		II
3670.0		II
4241.7		II
4341.7		II
4620.2		I
4627.1		II
4631.6		I
5008.2		II
5027.4		I
5280.4		I
5310	(gp)	II
5327.7	(gp)	I
5368.4		--
5510.4	(gp)	I
5527.8		II
5564.2		I
5610.9		I
5620.8	(gp)	I
5780.6		I
5915.4		I
5971.5		I
5976.3		I
5999.4	(gp)	I
6077.3		I

I = Neutral Atom

II = Ionized Atom

(gp) = Group of Lines Not Resolved With Our Instrumentation.

A


CAL.
0
10
20
30
40
50
60
70
80
90
100
3670 U II
4000 Å
4341 U II
4358 Hg
4620 U I
4627, 31 U II, I
5005 U II
5027 U I
I = NEUTRAL ATOM
II = SINGLY IONIZED ATOM
(GP) = GROUP
4000 Å
5000 Å

B

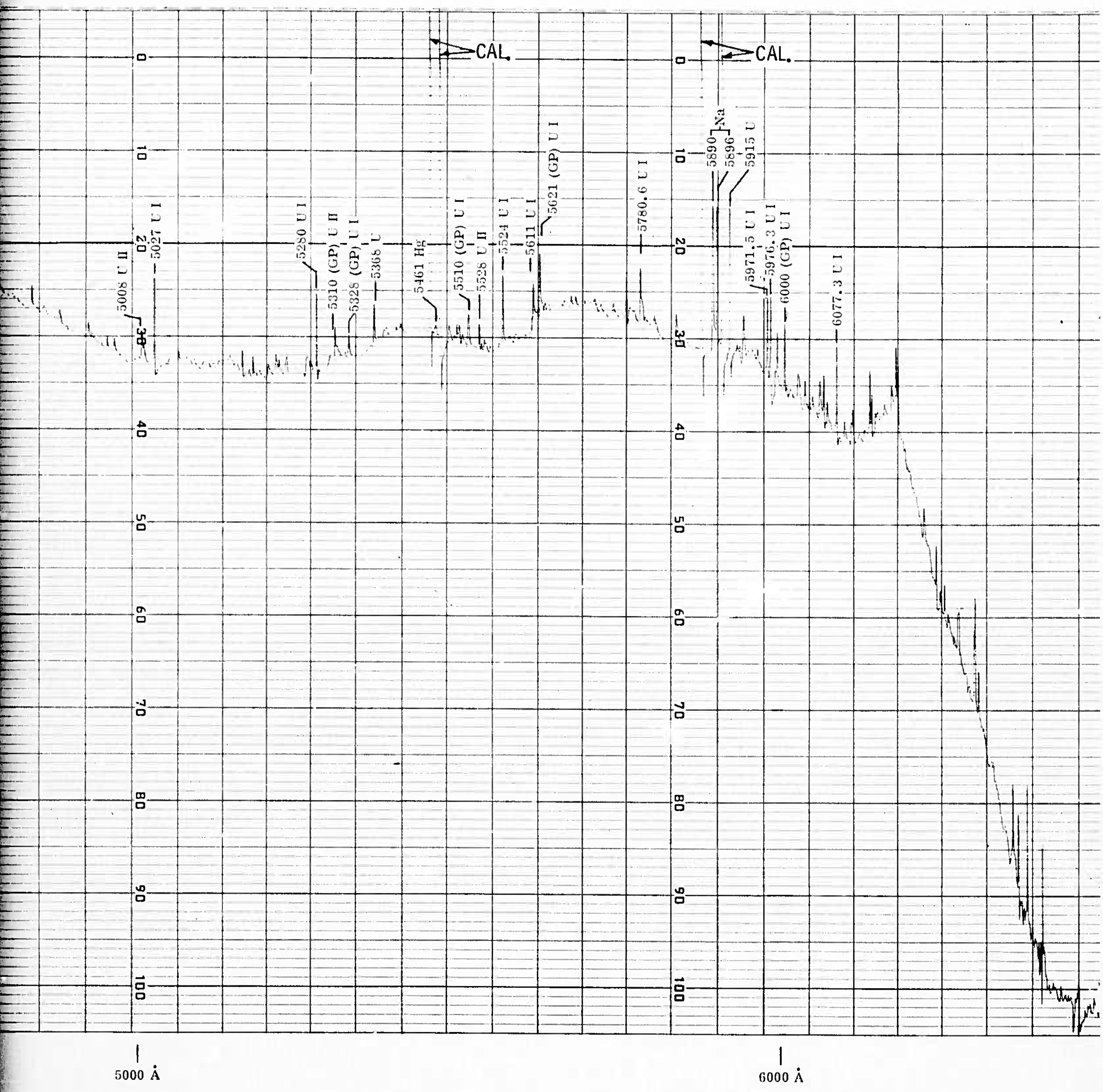


Figure 12. Densitometer Trace of Uranium Plume Spectrum

which are attributed to UO. One of the maxima appears at 4600A which is in the wavelength region covered in the work reported here. However, further work would be needed to extract intensity information from our data. The data at 1 atmosphere and 10^{-4} torr show the line (neutral and ion) and continuum radiation extending 1 cm from the sample surface whereas at 5 torr these species extended at least 2 cm (the field of view of the optical system) from the sample. A spectrum was also recorded in argon at 5 torr. This gave the same result as in air at that pressure.

c. PLUMES GENERATED BY CHEMICAL REACTION

Mixtures of Th-MoO_3-U-Al and powders were ignited in a Knudsen crucible in air at atmospheric pressure. These mixtures react explosively when heated to 500 - 600°C producing a flame which lasts 1-5 tenths of a second. Inter-metallic Al-Pd sheet metal strips react in the same manner as the powder mixtures. The flame radiation from the above reactions was examined spectroscopically and is reported herein.

A diagram of the experimental set-up is given in Figure 13. The Knudsen crucible, A, is the reaction vessel. The crucible is tantalum metal 9 mm diameter x 11 mm deep and has a removable cap. There is a 1.5 mm hole in the cap. The material to be ignited is packed in the crucible and reaction is started by heating the crucible with a propane torch. During reaction there is a plume-like flame above the hole in the lid. The light from this flame was focussed via a simple plano convex lens onto the slit of the 1.5 meter B & L grating spectrograph, B. The system was adjusted to

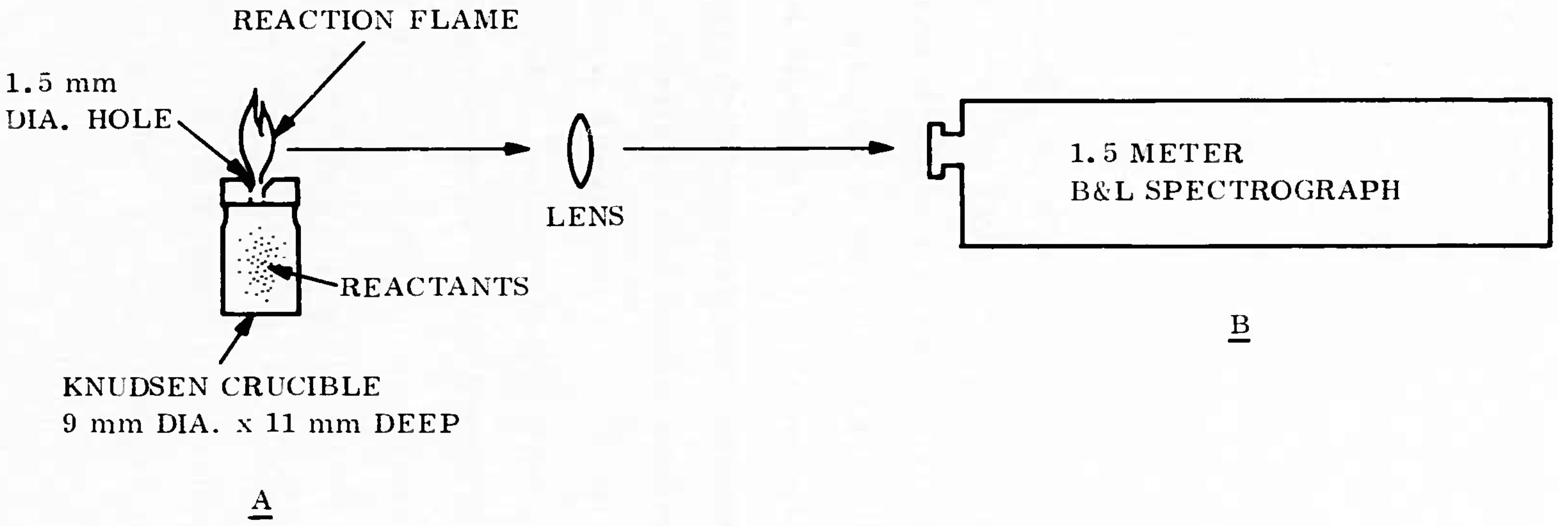
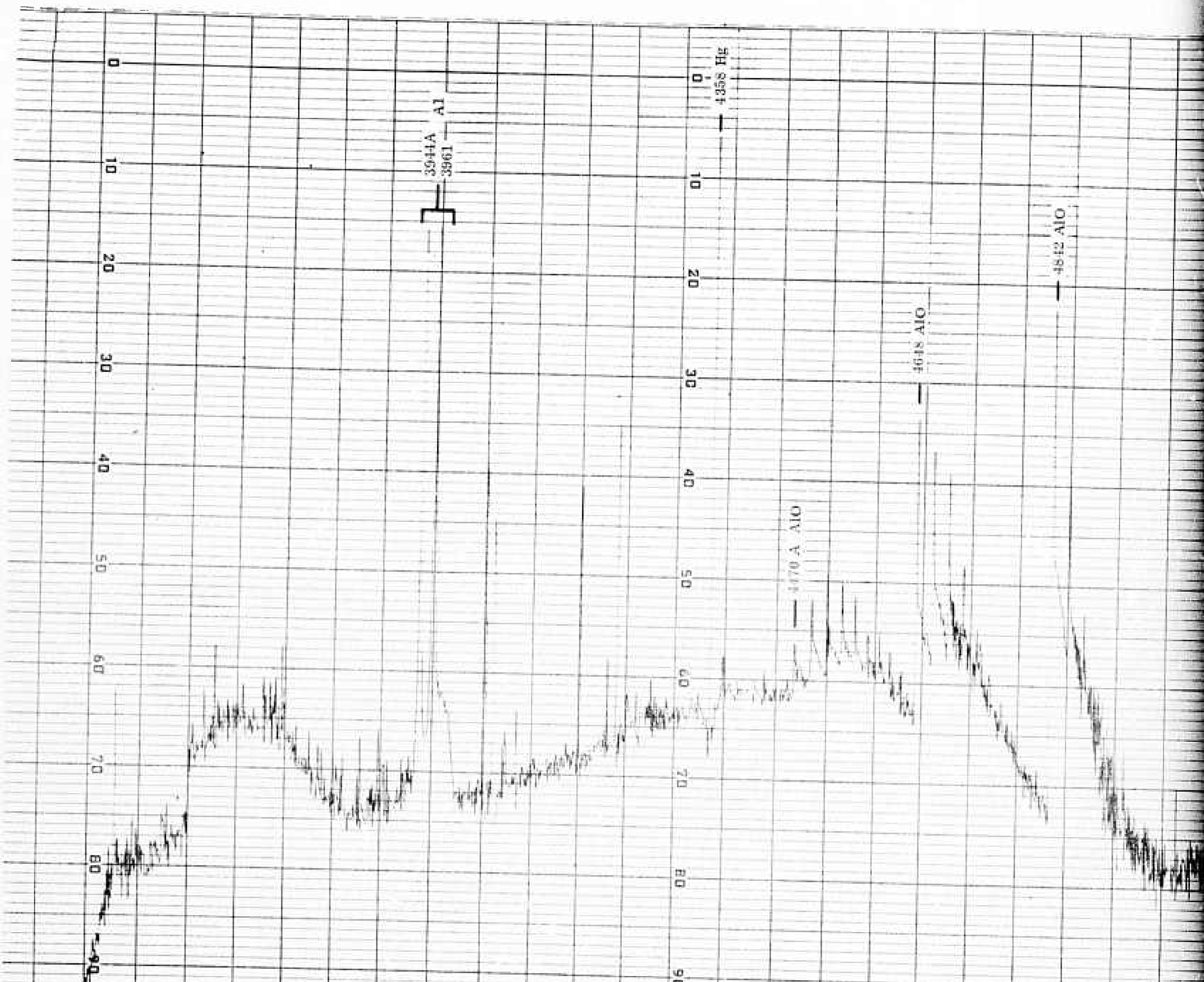


Figure 13. Diagram of Experimental Arrangement for Chemical Plume Studies.

spatially resolve the region from the top of the crucible to a distance 2 cm above the crucible on a 1:1 basis at the spectrograph film plane.

Two experiments were performed with the above set up. In the first, Al-Pd sheet .2 mm thick was cut into strips 1 x 5 mm and packed in the crucible interspersed with aluminum foil to fill the container. Upon reaction, a white flame about 5-6 mm in height and 3-4 mm diameter was seen above the crucible. The spectrum of this flame showed strong Al, AlO and moderately strong continuum radiation. Al and AlO emission extended 5 mm above the crucible while the continuum extended 3 mm. Visual examination of the film indicated little change in intensity vs distance above the crucible. A densitometer trace of this film is shown in Figure 14, and a photographic reproduction in Figure 15. The second experiment consisted of ignition of a 2 gram sample of a Stoichiometric mixture of Th and MoO_3 powders. This mixture was seeded with .1 gm Al and .1 gm U powder. Ignition of this mixture produced a plume about the same size and color as the Al-Pd. The resulting spectrum showed Al, AlO and continuum extending about 1 cm above the crucible. Also, a gradual decrease in intensity is seen on the film at 5-6 mm. No Uranium species were seen.

A


3944A Al
3961
4358 Hg
4470 A AlO
4648 AlO
4842 AlO
0
10
20
30
40
50
60
70
80
90
100
0
10
20
30
40
50
60
70
80
90
100

B

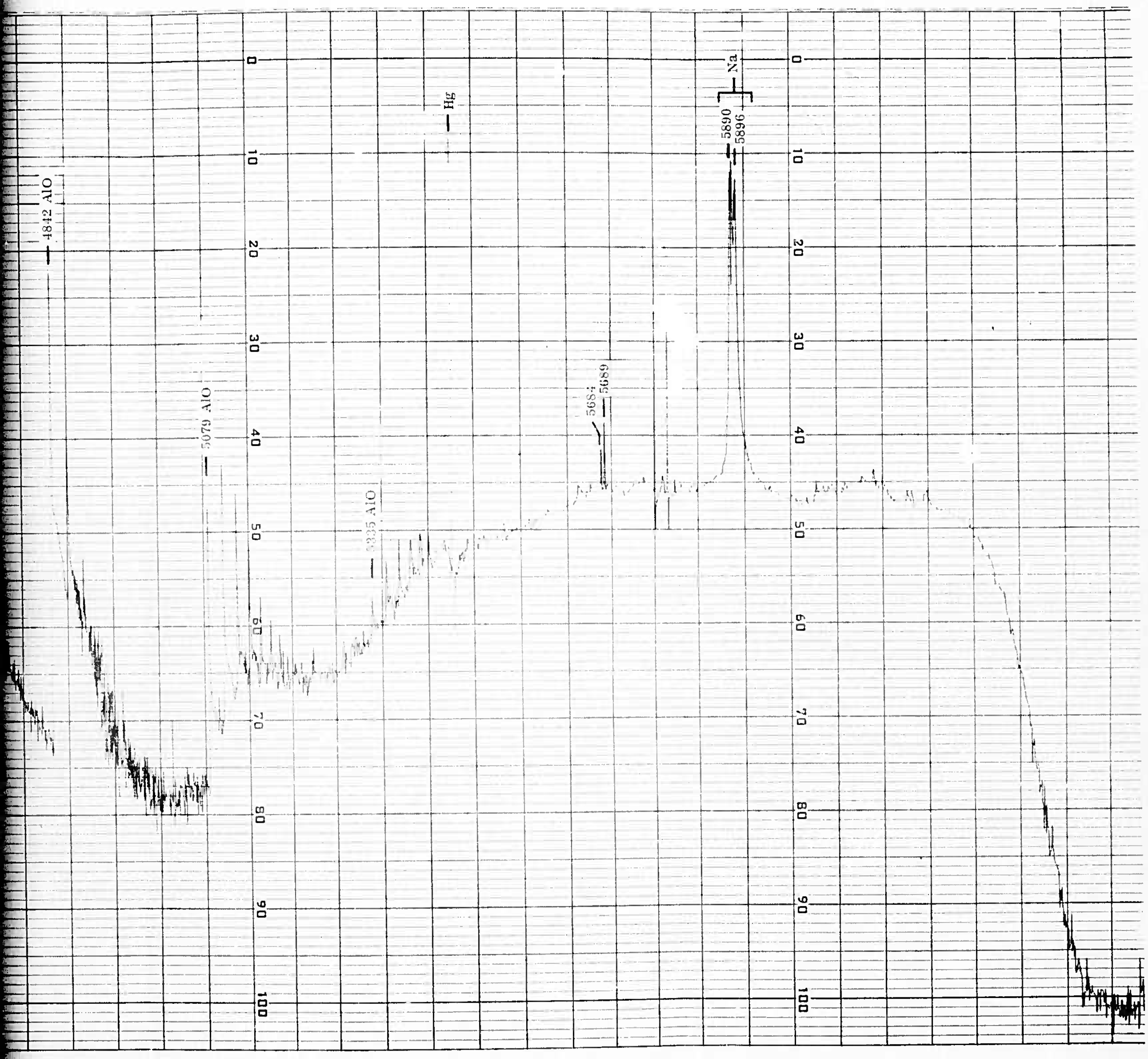


Figure 14. Densitometer Trace of AlO Spectrum Generated in an Al-Pd Plume

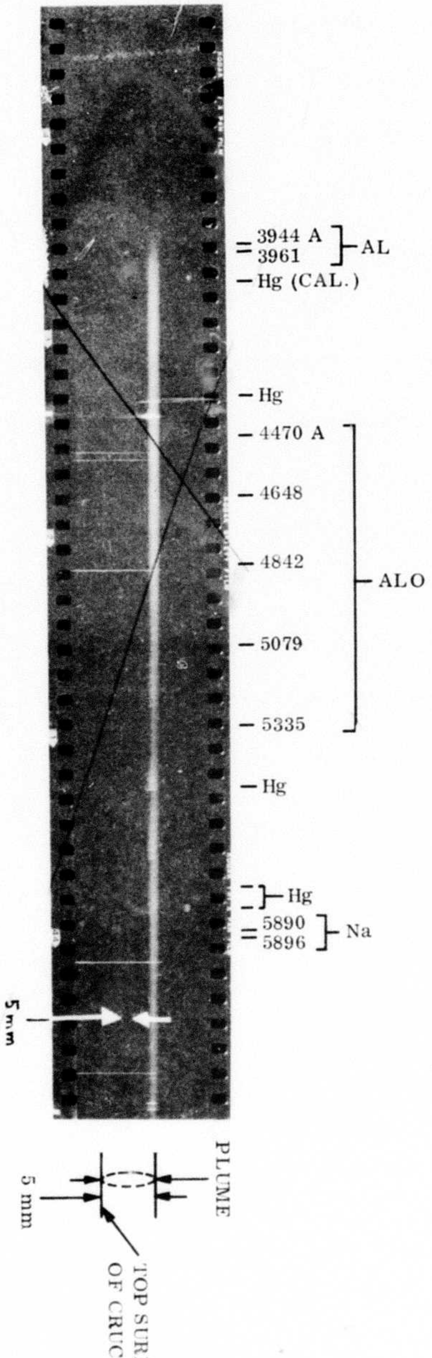


Figure 15. Photograph of Al and AlO Spectrum Generated in an Al-Pd Plume

IV. CONCLUDING REMARKS

Based on results obtained to date the following conclusions can be made:

1. The vaporization of thorium produces the monoatomic vapor species with a heat of vaporization $\Delta H^{o}298$ equal to 143 kcal/mole.
2. The ionization potentials of Th (g) and ThO (g) are quite low (5.5-6 eV) while that of ThO_2(g) is higher by 3 eV.
3. The oxidation of thorium atoms by molecular and atomic oxygen produces ions such as ThO_2^+ and ThO^+ respectively. The rate constant for the production of ThO_2^+ through reaction with O_2 is 4.9×10^{-12} cm^3 $molecule^{-1}$ sec^{-1}.
4. The formation of ThO and UO from the oxidation by O_2 of the respective metal atoms is extremely fast (gas kinetic).
5. The laser blow-off spectrum from uranium metal produces both neutral and singly ionized uranium atoms. Strong continuum radiation (.36 - .64 μ-range) was observed in air.
6. Chemically generated plumes from the reaction of both Al-Pd and Th-MoO_3 (seeded with Al) show strong Al-line and AlO-band radiation.

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