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KINETICS AND MECHANISMS IN THE OXIDATION OF METAL VAPORS

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KINETICS & MECHANISMS IN THE OXIDATION OF METAL VAPORS

General Electric - RESD

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13. ABSTRACT
This report presents the preliminary results of a laboratory experiment involving (1) The production of metal vapor, utilizing two techniques (laser radiation and RF induction heating), and (2) the measurements of reactants and products resulting from the mixing of metal vapors with oxygen by the utilization of time of flight mass spectrometry.

Preliminary values for the heat of vaporization, ionization potential (for metal, monoxide, and dioxide) for thorium, as well as the reaction rate are reported.

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OF METAL VAPORS

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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 laser radiation and RF heating 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:

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

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

were made and the rate-constant ratio was determined, $\frac{k_{Th}}{k_U} = 1.23 \pm 0.13$. using a value[10] of $k_U = 4 \times 10^{-12}$ cm^3 $molecule^{-1}$ sec^{-1}, k_{Th} was calculated equal to 4.9×10^{-12} cm^3 $molecule^{-1}$ sec^{-1}. Measurements on the reduction of the thorium signal as a function of oxygen pressure resulted in a preliminary value for the total rate constant at least as high as 10^{-10} cm^3 $molecule^{-1}$ sec^{-1}.

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 solid-piece form) were obtained from Ventron Metal Hydride Division, Beverly, Mass. The specified purity of such samples was 99% by weight, the balance most probably being oxygen.

When Knudsen crucibles were used as containers, the structural material was tantalum.

B. APPARATUS

The two heating methods that were considered for this study are induction RF heating and laser radiation.

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 inc. 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. 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.

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

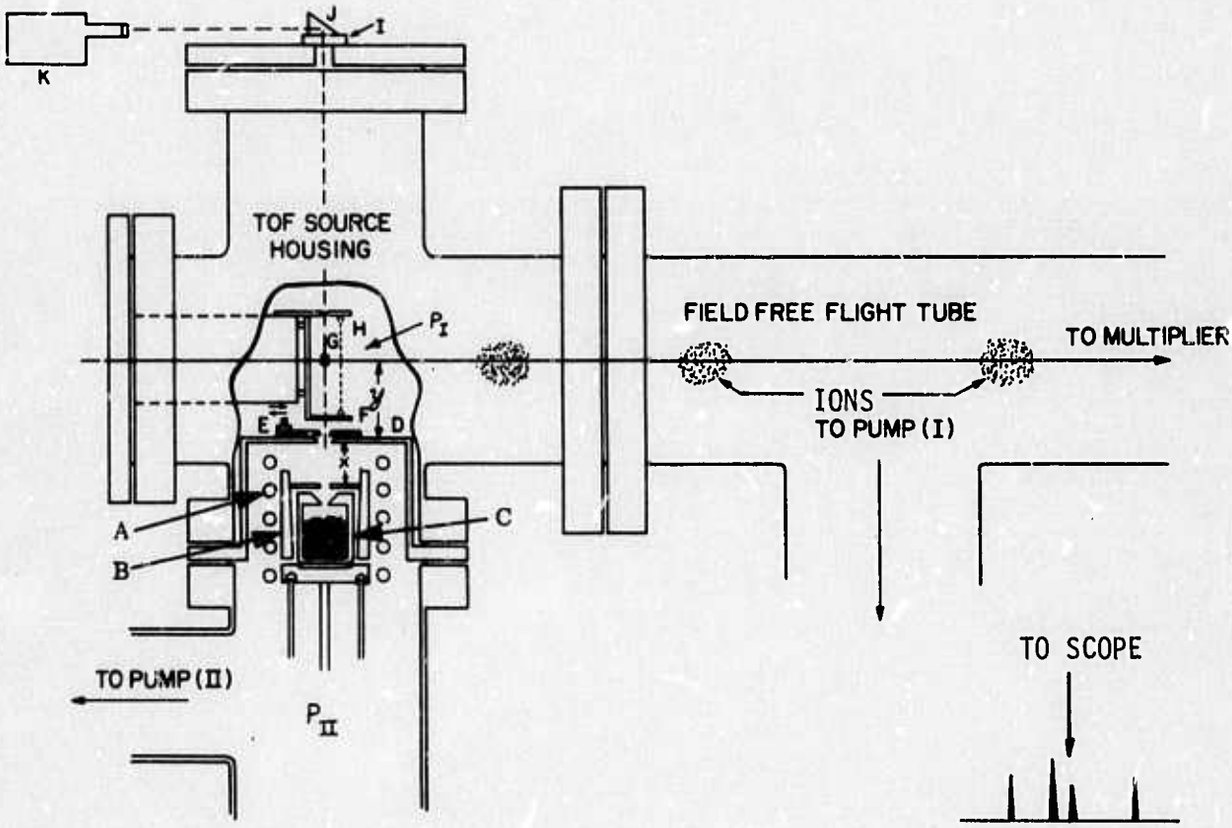


Figure 1 - KNUDSEN CRUCIBLE MASS SPECTROMETER APPARATUS

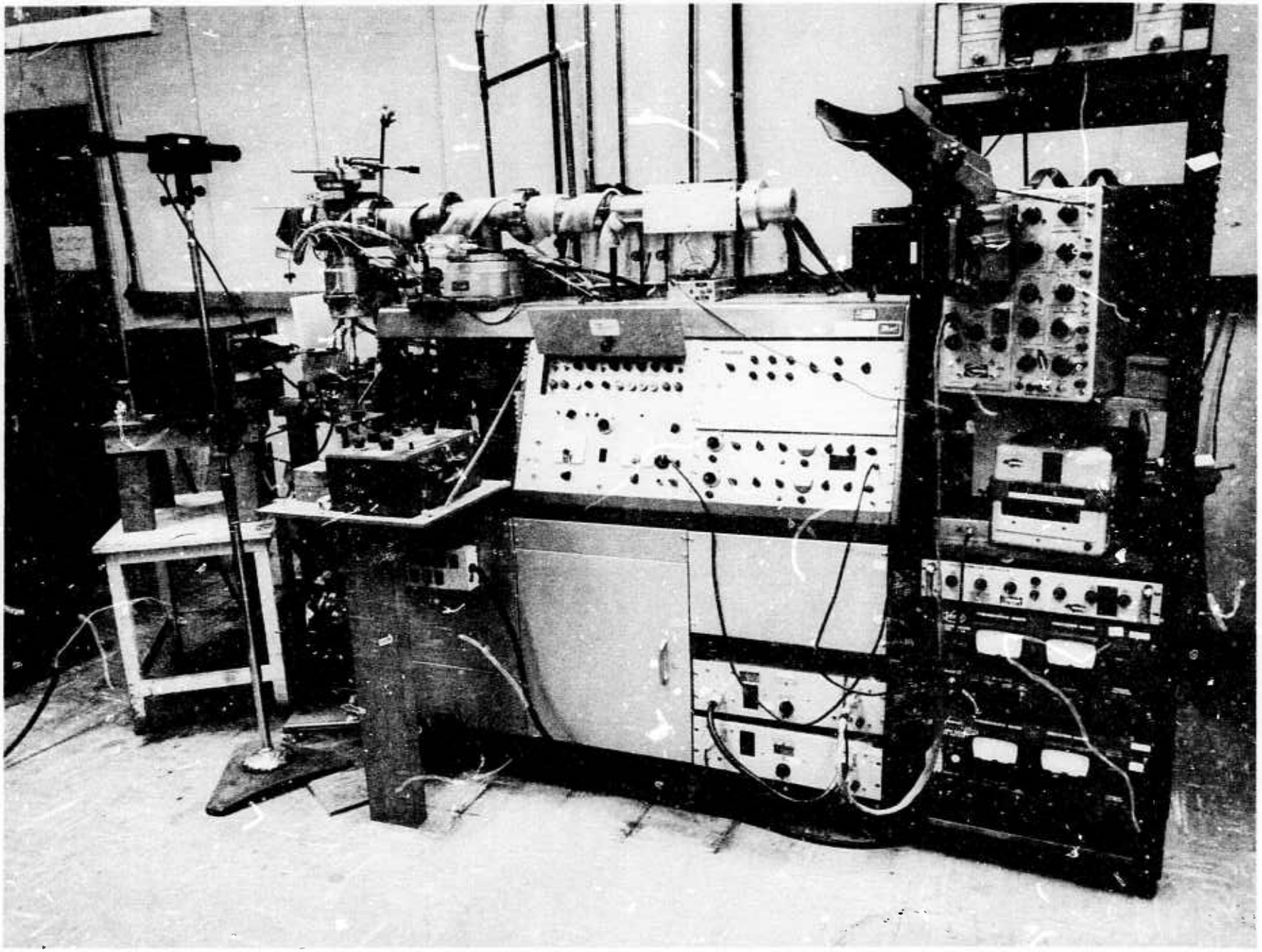


Figure 2: INDUCTIVELY HEATED FURNACE IN TIME-OF-FLIGHT MASS SPECTROMETER

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.

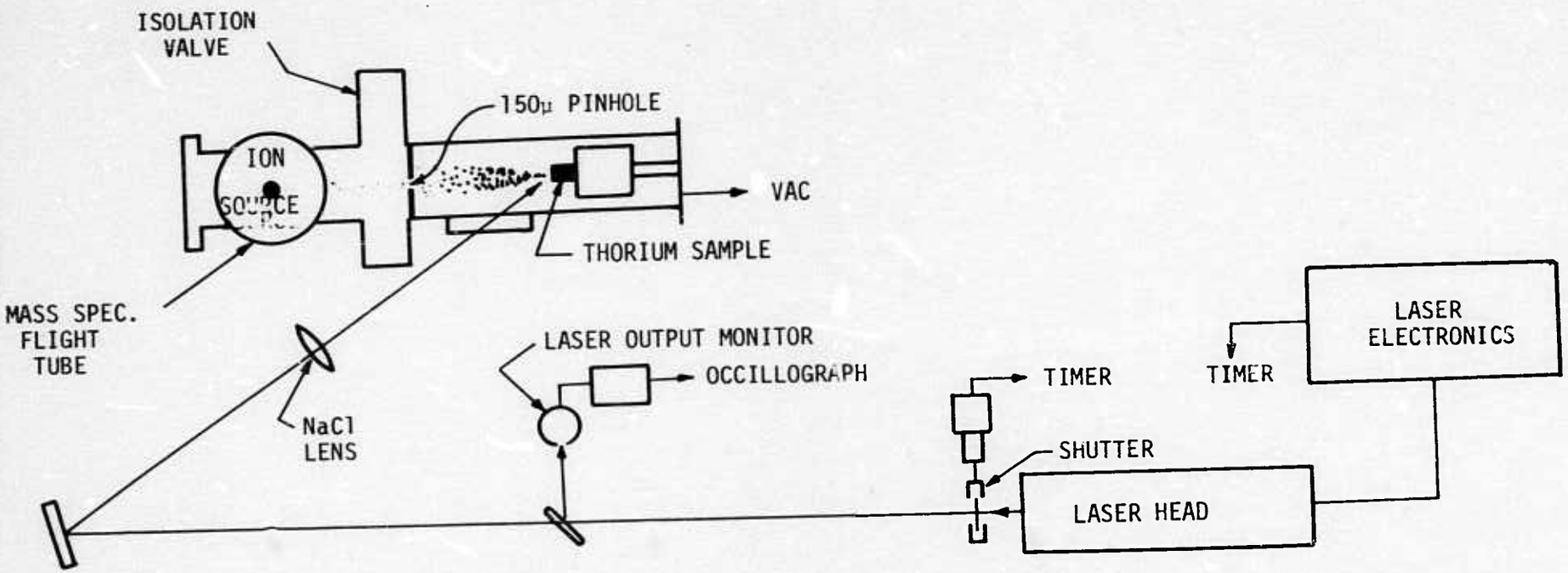


Figure 3 - LASER HEATING EXPERIMENT

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. 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^oK, 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^oK - 2773^oK. Using ΔH^o_T and tabulated thermodynamic data, the heat of vaporization at 298^oK can early be calculated by:

$$\Delta H^o_{298} = \Delta H^o_T - \Delta(H^o_T - H^o_{298}).$$

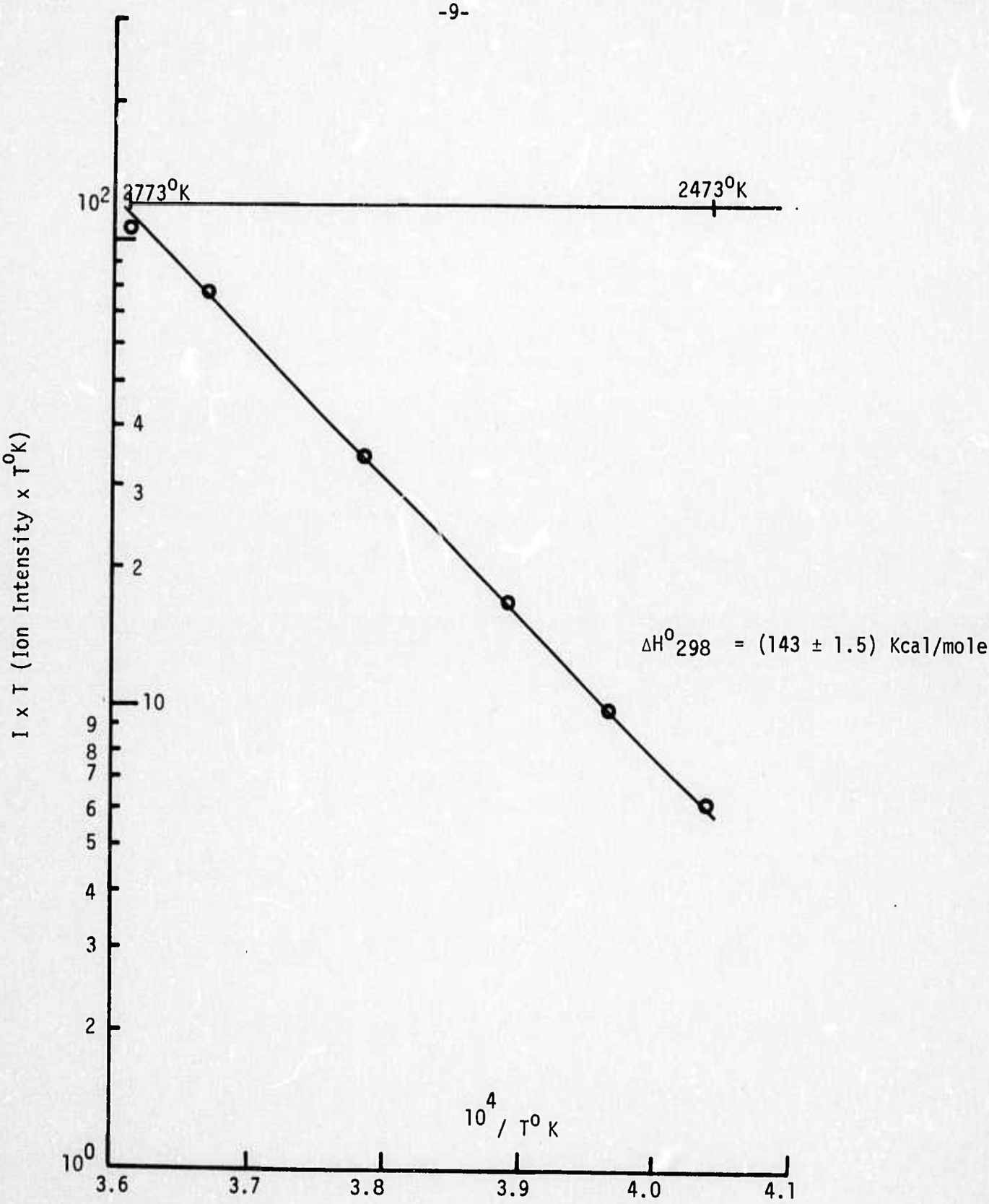


Figure 4 - Heat of Vaporization of Thorium

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. Ion intensities as a function of energy of the ionizing electron beam are shown in Figure 5. From these data, it is apparent 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.

3. Thorium Vapor Oxidation

Thermochemical calculations on chemi-ionization processes such

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

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

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

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

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

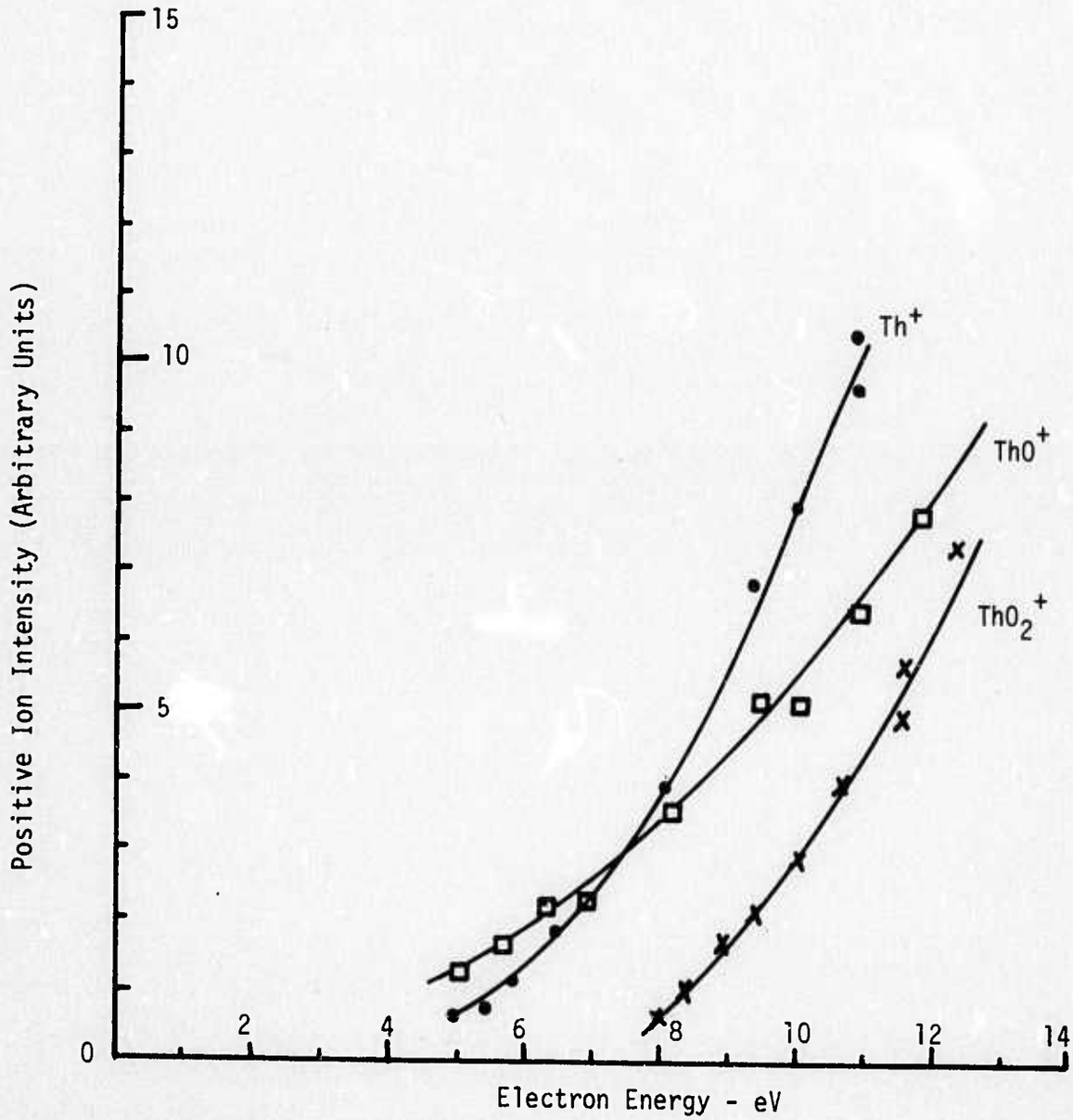


Figure 5 - IONIZATION EFFICIENCY OF THE THORIUM OXYGEN SYSTEM

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

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 a tantalum Knudsen crucible (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.

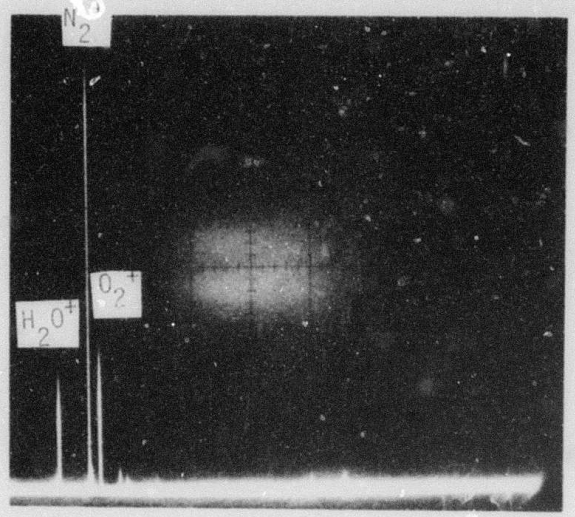
The experimental procedure is first to turn on the electron beam of the mass spectrometer and observe the metal vapor effusing from the Knudsen crucible. The energy of the electron beam was set at 20 eV, and the pressure in both chambers was about 10^{-6} torr.

Typical mass spectra of air background and vapor effusing from the crucible are shown in Figure 6, A and B. The addition of O_2 in the upper chamber enhances the intensity ThO_2^+ peak and decreases the intensity of Th^+ Figure 6C. 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).

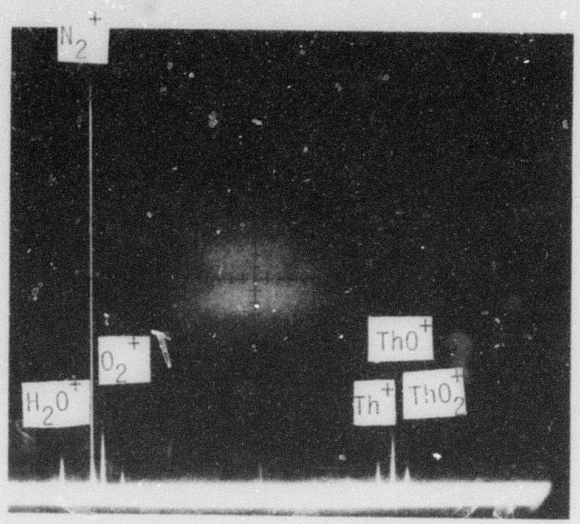
TABLE II

THERMOCHEMISTRY OF THORIUM-OXYGEN SYSTEM

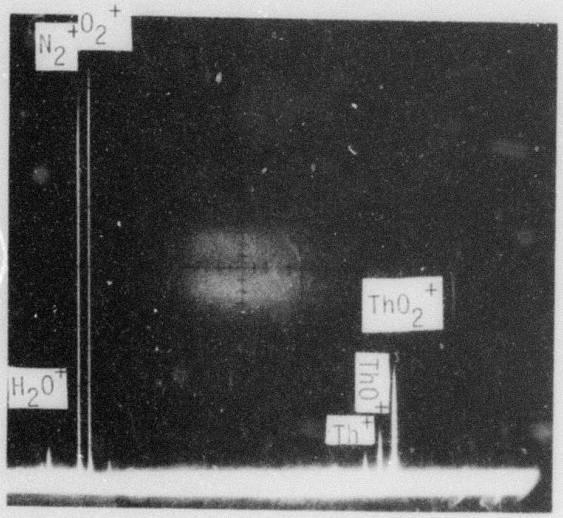
REACTION	ΔH^{o}_{298} $(\frac{kcal}{mole})$	REFERENCE
$Th(s) \longrightarrow Th(g)$	143	THIS WORK
$ThO_2(s) \longrightarrow ThO_2(g)$	158.7	(5)
$Th(s) + O_2(g) \longrightarrow ThO_2(s)$	-293	(6)
$\frac{1}{2}Th(s) + ThO_2(s) \longrightarrow ThO(g)$	152	
$ThO_2(g) \longrightarrow ThO_2^{+} + e$	195-207	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



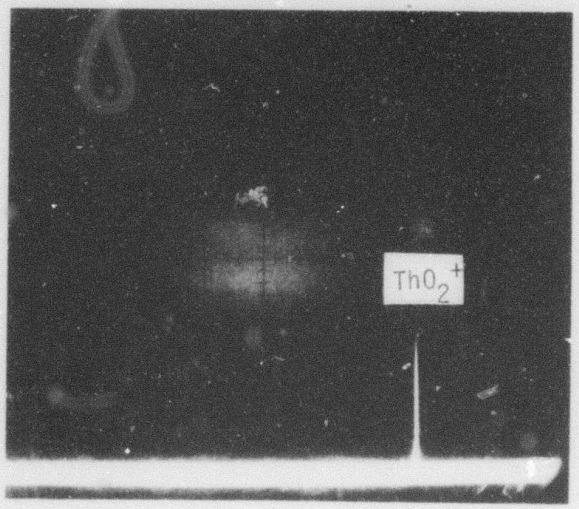
A. BACKGROUND



B. THORIUM AT 2623 ^{o}K



C. ADDITION OF O_2



D. SAME CONDITION AS C BUT ELECTRON BEAM TURNED OFF

Figure 6 - MASS SPECTRA IN THE OXIDATION OF THORIUM VAPOR

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 7 for data at 2423°K.

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

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

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

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

where I = ion intensity observed by mass spectrometry

* Electron beam on

** = Electron beam off

σ = Ionization Cross Section

E = Electron energy

A = Appearnace Potential

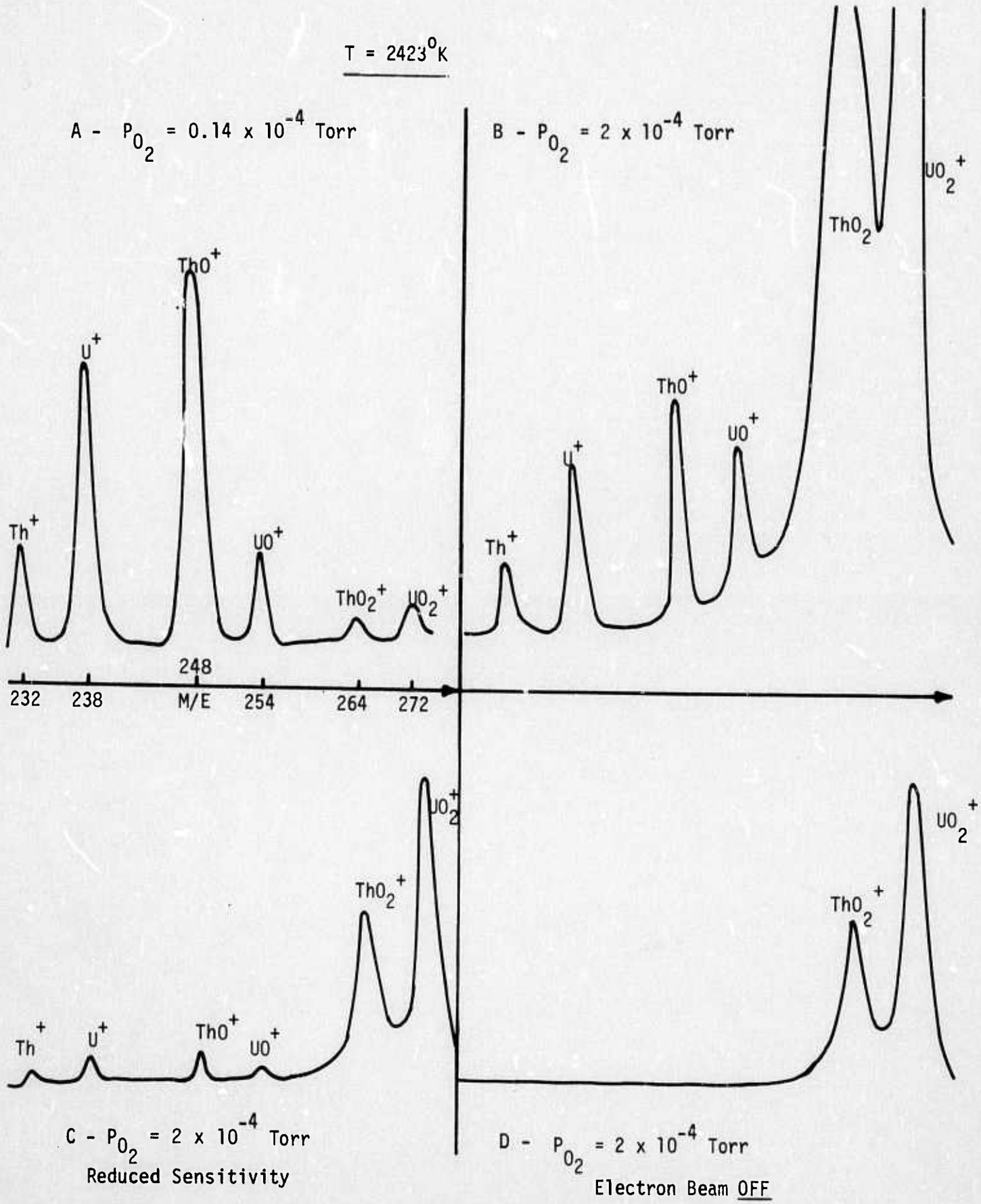


Figure 7 - MASS SPECTRA IN THE OXIDATION OF Th-U MIXTURES

In view of the fact that thorium and uranium have similar properties concerning atomic weights, ionization cross sections[7], ionization potentials[8] 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 rangs 2253-2423°K and pressure range (0.14-2.84) x 10^{-3} torr. The results are shown in Table III and suggest a ratio of $k_1/k_3 = 1.23 \pm 0.13$.

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.

Measurements are now being made on the reduction of the thorium intensity as a function of collision frequency with oxygen molecules in order to obtain absolute values of rate constants. Preliminary results are hown in Figure 8. This plot shows the increase in the ThO_2^+ signal and the decrease of the Th^+ signal as a function of oxygen pressure.

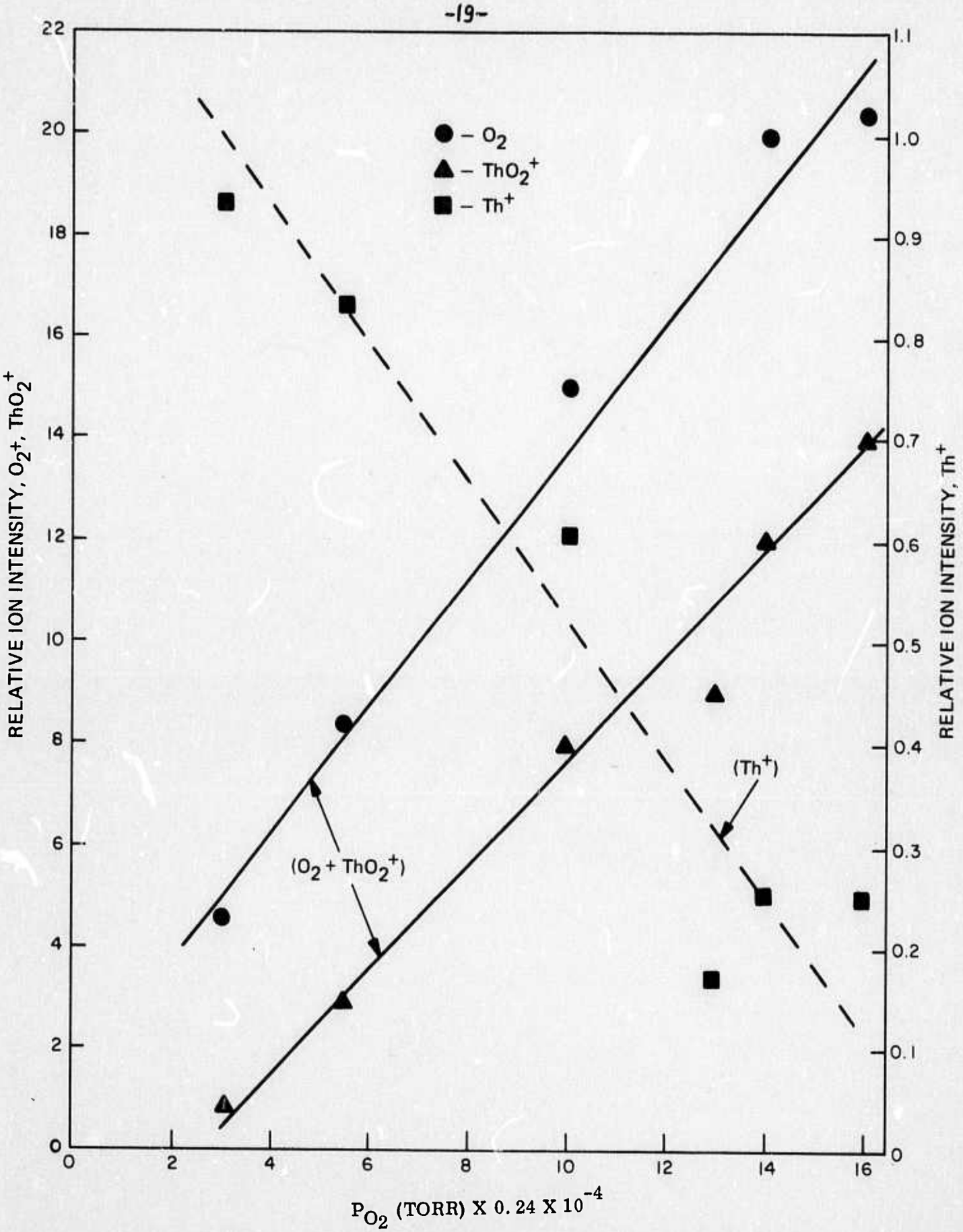


Figure 8 - THE OXIDATION OF THORIUM AS A FUNCTION OF OXYGEN PRESSURE

TABLE III

RELATIVE RATE CONSTANTS FOR THE OXIDATION OF URANIUM AND THORIUM

T^oK	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

In order 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.

Calculations based on the fact that the thorium signal decreases by 50% when the oxygen pressure approaches 2×10^{-4} torr suggests a total rate constant for the reaction of Th(q) at least as high as 10^{-10} cm^3 $molecule^{-1}$ sec^{-1}.

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.

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 IV.

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:

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

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

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

C = heat capacity

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

ΔH_f = heat of fusion

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

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

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.

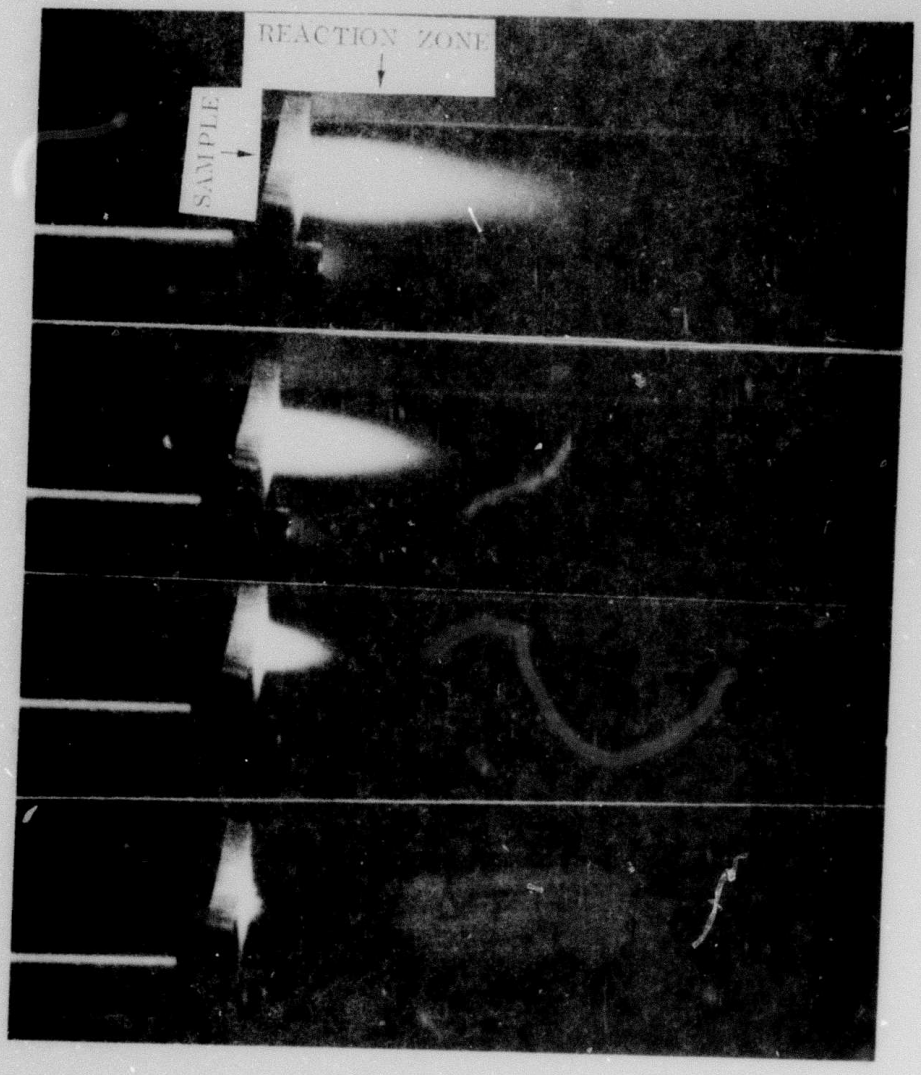
Using a 10-joule, ruby laser (Lear Siegler) with a pulse duration of 5×10^{-4} sec, preliminary data were obtained with thorium metal targets vaporizing into air at several pressures. Figure 5 shows photographs of thorium vapor oxidizing in air in the pressure range 0.3 torr - 1 atm.

TABLE IV

TIME REQUIRED TO REACH VAPORIZATION

(BOILING POINT) TEMPERATURE, Δt

METAL	LASER FLUX (W cm^{-2})		
	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



A - 0.3 torr (air)

B - 1.8 torr (air)

C - 7 torr (air)

D - 1 atm (air)

Figure 9 - COMBUSTION OF THORIUM VAPOR IN A LASER BLOW-OFF EXPERIMENT

The exposures were made using a 35 mm camera where the shutter opened just before the laser firing. Radiation from the combustion of the metal vapor produced the observed white plume image.

The dependence of plume length on external pressure suggests that, at the highest pressure, the vapor is all converted to the oxide very close to the surface, while at the lowest pressure the plume extends further out to a length of 6 cm.

Mass spectrometric analysis of the reaction products at the lowest pressure identified ThO_2^+ as an important species.

A series of experiments were performed in which plume radiation from Uranium metal was recorded in the .39 to .7 micron wavelength range. The plumes were generated by layer blow off using a pulsed Ruby laser operating in the burst mode. (single pulse, .5 ms pulse duration, 10 joules). Spectra were recorded with a B & L 1.5 meter grating spectrograph. The optical system was set up with an image rotator, in order to obtain spatially resolved spectra normal to the Uranium sample surface along the axis of the plume.

Spectra were recorded from a single layer pulse on the sample in air at 1 atmosphere, 5 torr and .20 torr. A spectrum was also recorded in an Argon atmosphere at 5 torr. The spectra showed continuium (.39-.7μ) over laid with a large number of emission lines. A half dozen or so of the lines have been identified as neutral U atom emission. These U lines also appear in the Argon atmosphere.

The optics were set up to examine the region from the sample surface to a location 2 cm in front of the surface. The data at 1 atmosphere and .2 Torr showed configuration and the line emission extending approximately 1 cm from the surface while the data at 5 torr showed continuum and U line spectra extending to the 2 cm cut off of the optics.

Further mass spectrometric and spectroscopic work is now in progress.

IV. CONCLUDING REMARKS

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

1. The vaporization of thorium produces the monoatomic vapor with a heat of vaporization 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 (3) is 4.9×10^{-12} cm^3 $molecule^{-1}$ sec^{-1}*. Preliminary measurements on the reduction of the thorium signal as a function of oxygen pressure suggests a total rate constant for $Th + O_2 \longrightarrow \begin{matrix} ThO^+ + O \\ ThO_2^+ + e \end{matrix}$ higher than 10^{-10} cm^3 $molecule^{-1}$ sec^{-1}

*This value is relative to Fite's rate for the equivalent uranium reaction 4×10^{-12} cm^3 $molecule^{-1}$ sec^{-1}.

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