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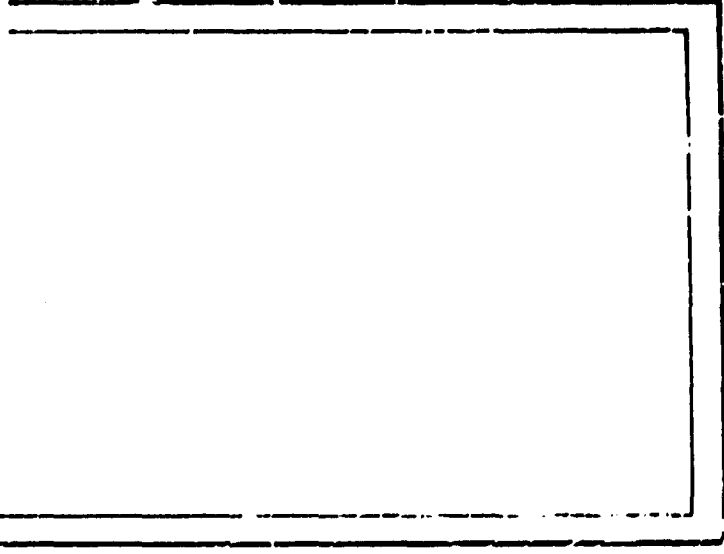
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KINETIC AND AERODYNAMIC ASPECTS
OF THE OXIDATION OF METALS BY
PARTIALLY DISSOCIATED OXYGEN.

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⑨ Semiannual Progress Report, 15 Nov. - 15 May 64

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RESULTS

Using a resistance monitoring technique, the oxidation rate of electrically heated molybdenum and tungsten filaments has been studied over a wide range of oxygen atom concentrations ($2 \times 10^{-1} \leq p_{O} \leq 5 \times 10^{-1}$ Torr) and surface temperatures ($1000^\circ K \leq T \leq 2600^\circ K$) at flow rates such that the observed oxidation kinetics are not falsified by diffusional limitations. Partially dissociated streams are produced in the pressure range 0.7-10 Torr using a microwave discharge and O-atom concentrations are determined using the NO_2 light titration technique. Under the conditions investigated the oxides of molybdenum and tungsten volatilize as rapidly as they are formed and the unprotected metal is subjected to direct attack by oxygen atoms. On molybdenum and tungsten surfaces oxidation probabilities for atomic oxygen are found to be higher than corresponding values for molecular (diatomic) oxygen by up to one to two orders of magnitude, whereas the corresponding activation energies are considerably lower. Moreover, while ^{present} studies of the pressure dependence of the rates reveal complex departures from simple "power-law kinetics" for O_2 attack, the O-atom data reported here follow simple first order kinetics. The lowered activation energy and first order kinetics observed in this work suggest that the enhanced oxidation probability exhibited by O-atoms on both molybdenum and tungsten is due to direct (Rideal-type) attack of O-atoms on chemisorbed O-atoms rather than merely the result of an increased steady state oxygen adatom coverage associated with an increased sticking probability.

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1. INTRODUCTION

Refractory metals are essential to the construction of current and anticipated high performance rocket nozzles, gas turbine power plants and hypersonic vehicles. Since the oxidation rate of these materials is often the property that limits their performance, data must be accumulated on the kinetics of oxidation under extreme environmental conditions. This information is also required to make a proper choice of materials test facilities to assure reliability and minimize the need for expensive full-scale flight testing of components.

1.1 Materials Response in the Presence of Molecular Fragments

Although the materials of advanced vehicles are exposed to highly reactive molecular fragments, the designer has not been provided with adequate basic information on the consequences of this exposure. Existing heat shield calculations are subject to large systematic errors owing to the exclusion of the kinetic effects of oxygen atom and excited molecule bombardment. For example, as a result of basic chemical kinetic work done under this program (cf. Section 2) and a company-sponsored program at this laboratory, it is now known that the oxidation probability of O-atoms can exceed that for O₂ molecules incident upon molybdenum,^{1,2} tungsten (cf. Section 2.3b) and polyolefin surfaces³ by more than an order of magnitude. An immediate implication is that materials test procedures in which no attention is paid to O-atom nonequilibrium scaling will give an erroneous picture of the relative merits of structural and ablation heat shields.⁴

1.2 Engineering Applications of Refractory Metals in Oxidizing Environments

Radiation cooled⁵ refractory metal alloys hold great promise in the design of light weight rocket engines,⁶ particularly for applications requiring long firing times with dimensional stability, and modulated or interrupted thrust. Similarly, radiation cooled structures are efficient for parts of re-entry vehicles of both the ballistic and lifting types.⁵ Refractory metals also play an important role in the development of turbojet engines for long range supersonic aircraft.⁷ In each of these applications it is clear that oxidation rates can be catastrophic even in undissociated gas mixtures and, for this reason, a coatings development program

has been undertaken for the Air Force.^{8,9} However, uniform coatings are difficult to obtain on complex aerodynamic shapes and coating life is adversely affected by transient high temperature-low pressure operation.⁹ In the event of a localized coating failure, little is known about the rate at which the substrate oxidizes,¹⁰ particularly in the presence of appreciable concentrations of free radicals and excited molecules. The surfaces of a lifting re-entry vehicle in flight would, for example, experience the pressures and oxygen atom mole fractions shown in the shaded region of Fig. 1. On the basis of experiments discussed below (cf. Section 2), which fall within this region of interest, it can be said that oxygen atoms would play a very important role in determining the oxidation rate of either molybdenum or tungsten surfaces.

It has also been suggested that refractory metals such as molybdenum and tungsten can be used unprotected,¹¹ for short duration, expendable applications at sufficiently low pressures. However, since a low pressure-high temperature environment is thermodynamically conducive to dissociation this suggestion bears careful re-examination in the light of the work described below.

1.3 Kinetics and Mechanism of Refractory Metal Oxidation

On a fundamental level, the mechanism of refractory metal oxidation at the pressures and temperatures of interest in propulsion applications is not well understood for attack by either stable molecules or atoms and free radicals. In many cases diffusional effects have complicated or completely falsified kinetic studies^{10, 12-14} since the oxidation rate can become limited by oxygen transport through the carrier gas (e.g., N_2 in the case of air) and/or product gases surrounding the specimen rather than by the true kinetics at the gas/solid interface.¹⁵⁻¹⁷ Thus, there has been a need for (i) kinetic studies carried out in an apparatus which allows the kinetics of attack by both unstable as well as stable species to be studied under diffusion-free conditions,^{1, 2} and (ii) clarification of the role of transport phenomena in determining the oxidation rate of refractory metals. This will enable the correct interpretation of oxidation rate data obtained under different experimental conditions.^{1, 15-17}

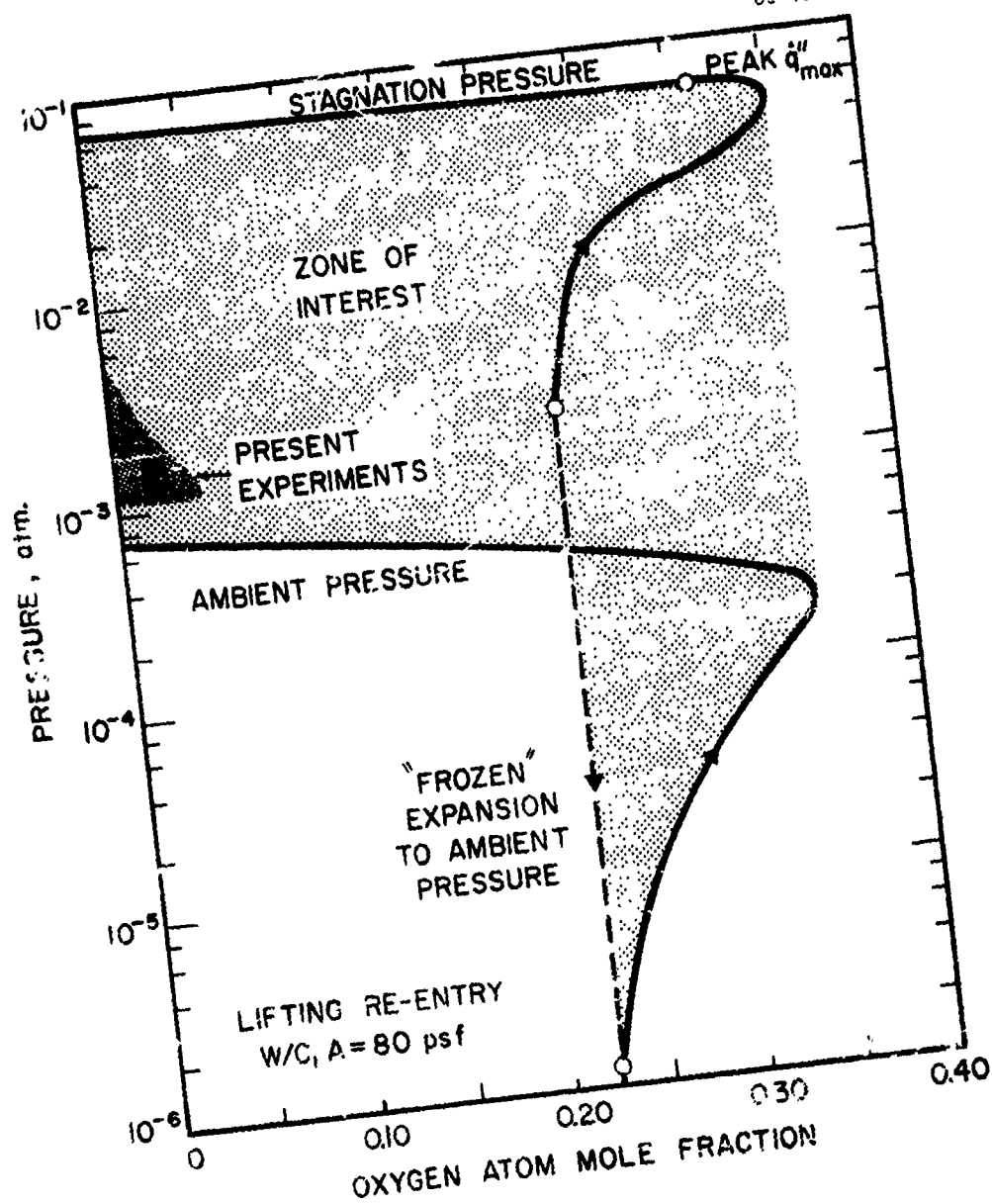


FIG. 1 PRESSURES AND OXYGEN ATOM CONCENTRATIONS EXPERIENCED DURING LIFTING RE-ENTRY

1.4 Nature and Objectives of the Present Research Program

In March of 1962, these considerations led the senior author to propose a basic research study of the rate of refractory metal oxidation in activated gas streams. With AFOSR support this study was initiated at AeroChem in December of 1962 and is currently providing basic kinetic data on the effects of dissociation on oxidation rates of molybdenum and tungsten over a wide range of environmental conditions (oxygen atom concentration, surface temperature) as well as insight as to the important role aerodynamic factors (flow rate, carrier gas identity) can play in actual practice. In what follows we will outline (i) the basic experimental techniques that have been successfully applied to this problem at this laboratory, (ii) the kinetic results^{1, 2} obtained during the present reporting period and their interpretation (iii) new kinetic studies now planned in the light of (ii).

2. CURRENT TECHNICAL STATUS

In the present program we are studying the kinetics of both O-atom and O₂ attack of molybdenum and tungsten surfaces at high temperature under diffusion-free conditions in the same apparatus. In particular, we have found that for molybdenum the oxidation probability for O-atom attack can exceed that for O₂ attack by more than two orders of magnitude. Since our experimental technique and results for molybdenum in the temperature range $1050 < T < 1500^{\circ}\text{K}$ have recently been described in the open literature^{1, 2} we will concentrate here primarily on our most recent work (e.g., experiments on molybdenum oxidation at temperatures above 1500°K , tungsten oxidation by O-atoms and O₂ and the kinetics of excited oxygen molecule[†] attack). However, a brief description of the apparatus is given below for orientation (cf. Section 2.1) together with a summary of our experimental results (cf. Sections 2.2 and 2.3) on

- a. the absolute value of the oxidation probability, ϵ , for both O and O₂ attack of molybdenum and tungsten
- b. the activation energies for both O and O₂ attack of molybdenum and tungsten.

[†]cf. Section 2.2c

All of the 1 Torr data contained herein (molybdenum: $T \geq 1050^\circ\text{K}$; tungsten: $T \geq 1450^\circ\text{K}$) pertain to the temperature range in which the metal oxide volatilizes as fast as it is formed.

2.1 Experimental Technique

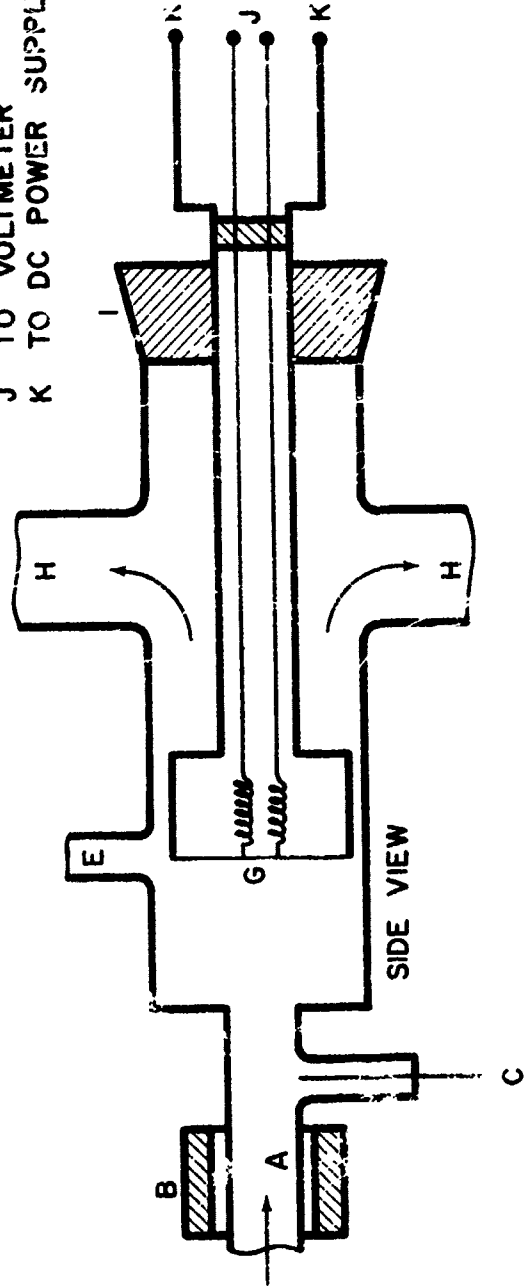
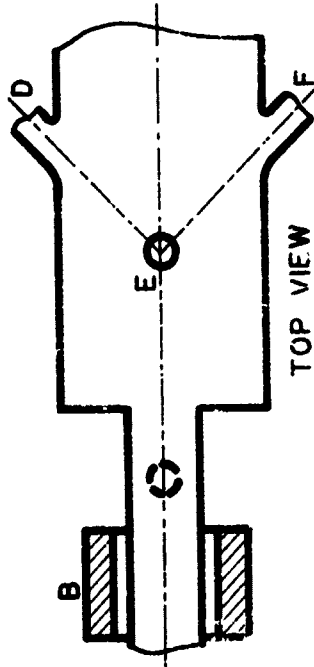
Our apparatus (cf. Fig. 2) consists of a part vycor-part pyrex vacuum flow system coupled to a 12 liter/sec mechanical pump.[†] Metered noble gas/O₂ mixtures are passed through a 2450 Mc/sec, 100 w microwave discharge cavity, downstream of which the gas encounters an electrically heated filament fed by a regulated dc power supply. Simultaneous with a current measurement the voltage drop across the central 0.55 cm of the filament is monitored using spring loaded contacts leading to a recording potentiometer. During an experiment the filament is maintained at constant temperature ($\pm 5^\circ\text{K}$) by altering the filament power in accord with an optical pyrometer output, thereby allowing the decrease in filament diameter caused by the oxidation reaction to be related to the increase in filament electrical resistance.¹⁸ The absolute value of the filament surface temperature is determined from the filament resistance in accord with its known resistivity-temperature relation. O-atom concentrations in the vicinity of the filament are obtained using the NO₂ light titration technique. The data reported here were obtained using commercially available .0381 cm (15 mil) diameter wire (Westinghouse Lamp Division, Bloomfield, N. J.). In all cases, diffusional limitations were ruled out on the basis of the absence of flow rate and carrier gas effects on the observed rates.

2.2 Kinetics of the Oxidation of Molybdenum

Our earlier data¹⁹ on the oxidation kinetics of unalloyed molybdenum have been corroborated and considerably extended during the present reporting period. The principal results in the temperature range: $1050^\circ\text{K} - 2600^\circ\text{K}$ are reported below.

[†] for studying the kinetics of O-atom attack of molybdenum and tungsten above 1500°K this capacity was increased by the addition of a second 12 liter/sec mechanical pump in parallel with the first.

- A DISCHARGE TUBE (VYCOR)
- B OPTHOS MICROWAVE CAVITY
- C NITRIC OXIDE INLET
- D ATOM DETECTION INLET
- E PRESSURE TAP
- F PYROMETER SIGHT TUBE
- G OXIDIZING FILAMENT
- H TO VACUUM PUMP
- I GROUND JOINT
- J TO VOLTMETER
- K TO DC POWER SUPPLY



2.2a Oxidation by atomic oxygen With the microwave discharge off we have studied the kinetics of O_2 attack of molybdenum at high temperature. In addition to their intrinsic interest these data are necessary to correct data obtained with partially dissociated oxygen for the O_2 contribution at high temperatures. Our results for the pressure dependence of the oxidation rate in air were reported in Ref. 19 and compared with the data of Ref. 11. Extensive measurements for molybdenum oxidation by O_2 reveal (i) important departures from simple power-law kinetics[§] (cf., e.g., Fig. 3) (ii) that the oxidation rate at a given surface temperature is not a function of oxygen partial pressure alone.¹ This is evident upon comparing the slopes of our rate data in Figs. 3 and 4, the latter pertaining to runs at constant pressure but variable O_2 mole fraction.^{§§} Rate data at several temperature levels are included in Fig. 4 for comparison. The activation energy for the oxidation of molybdenum by O_2 will be discussed with reference to the corresponding value for O-atom attack.

2.2b Oxidation by oxygen atoms^{1,2} Figure 5 shows our results for the temperature dependence of the oxidation probability[†] ϵ , defined here as the ratio of the flux of molybdenum atoms (regardless of their chemical state of aggregation^{§§}) away from the surface to the collision flux of O (or O_2) with the surface.^{††}

[§] We believe that these departures account for the apparent scatter in the reaction order data (4 data points) at 1073°K reported in Ref. 13.

[†] Control experiments in, for example, partially dissociated nitrogen rule out the possibility that the observed probability is merely a sputtering efficiency associated with the evaporation of molybdenum (or tungsten) caused by the heat of atom recombination.

^{§§} This probability, ϵ , should be distinguished from the fraction of the incident oxygen atoms or molecules which react. The definition adopted here has the advantage that, in computations based on the observed data, no assumption regarding the stoichiometry of the reaction product need be made. For example, if an author has assumed that the trioxide is the major reaction product²⁰ then ϵ (as defined here) would be smaller than the reported fraction of O_2 molecules which react by the factor $\frac{2}{3}$.

^{††} Computed using simple kinetic theory (Hertz-Knudsen equation)

^{§§§} These data, which correspond to an order with respect to X_{O_2} of 0.8, supersede the preliminary data leading to the value 0.9 quoted in Ref. 1.

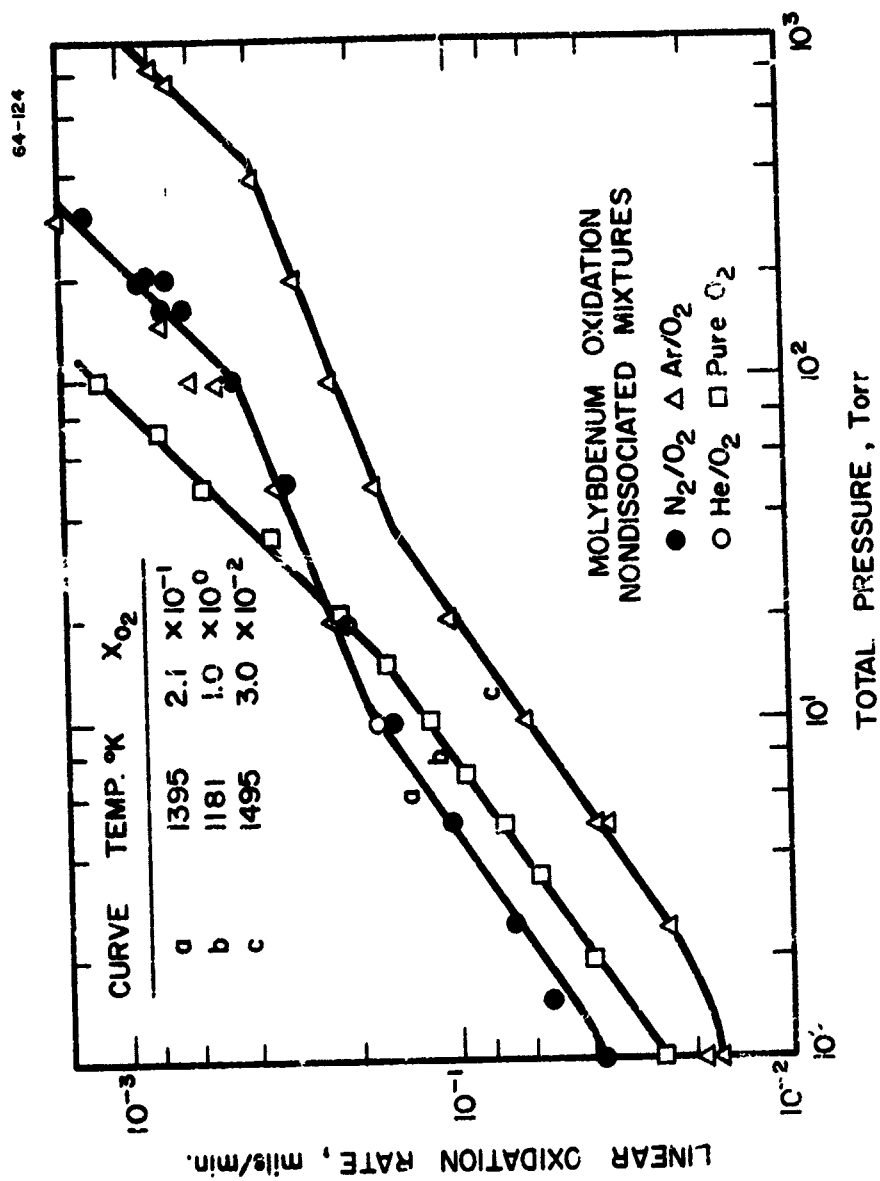


FIG. 3 PRESSURE DEPENDENCE OF MOLYBDENUM OXIDATION
RATES IN NONDISSOCIATED GAS MIXTURES

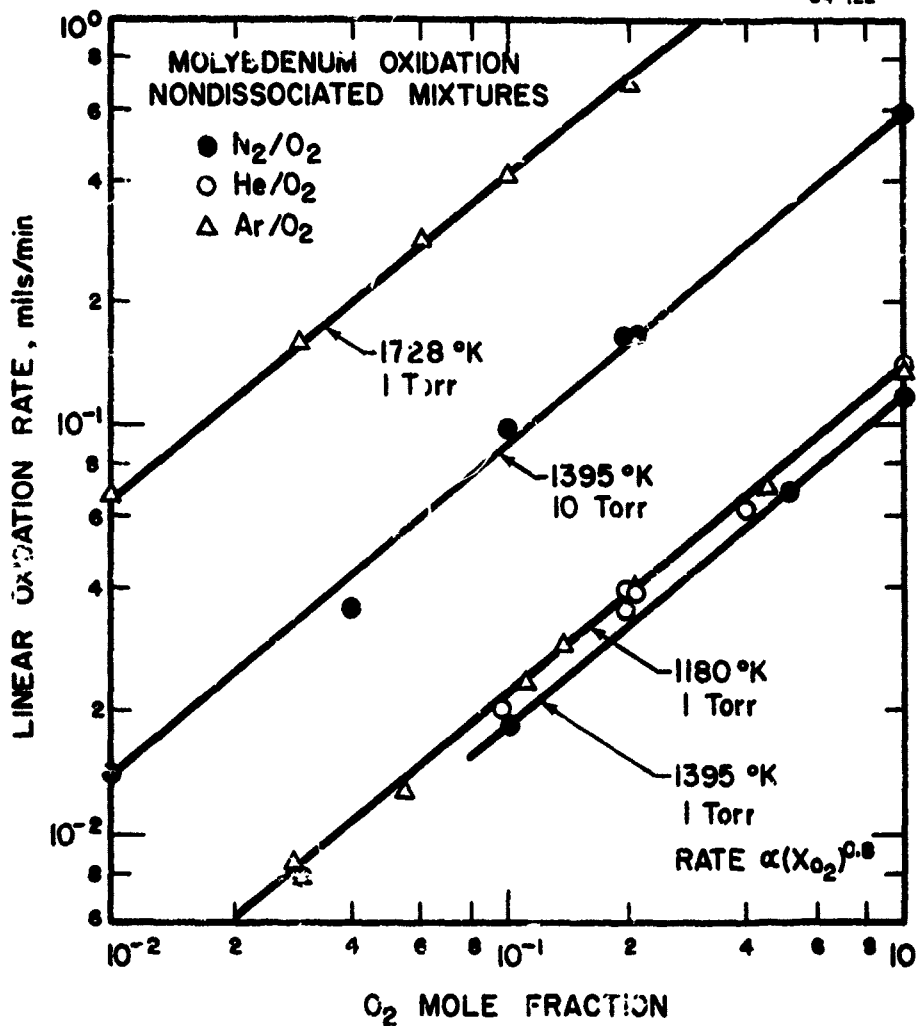


FIG. 4 DEPENDENCE OF MOLYBDENUM OXIDATION RATE ON OXYGEN MOLECULE MOLE FRACTION

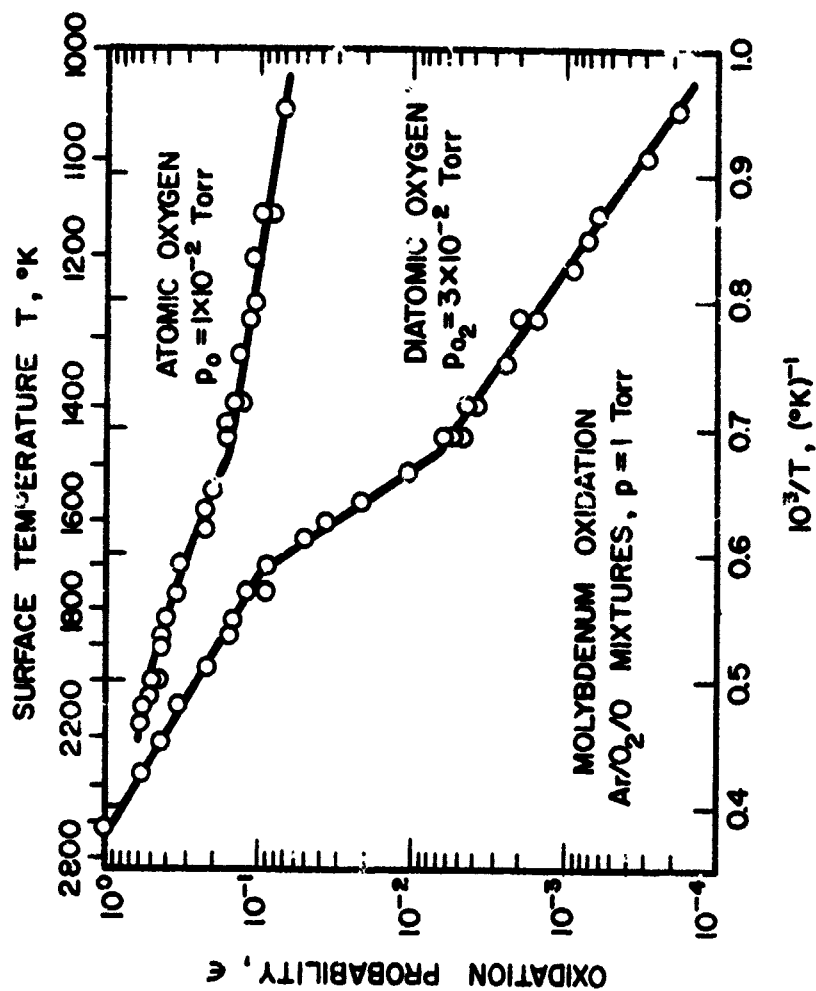


FIG. 5 ARRHENIUS PLOT OF MOLYBDENUM OXIDATION PROBABILITIES

In the range $1050^{\circ}\text{K} < T < 1500^{\circ}\text{K}$ the data are well represented by straight lines on the Arrhenius plot, with the O-atom activation energy (~ 6 Kcal/mole) being smaller than that for O_2 (26 Kcal/mole) by a factor of 4.4. At comparable arrival rates, ϵ for O-atoms is seen to be some two orders of magnitude higher than for O_2 at 1200°K . On the average, it is seen that about one Mo atom is ejected for every ten O-atoms striking a 1200°K filament.

At temperatures above 1500°K departures from simple Arrhenius behavior occur for both the O-atom and O_2 oxidation probabilities. These departures are most likely related to shifts in the relative importance of the reaction products MoO_2 and MoO_3 (cf., e.g., Ref. 21), a hypothesis which will be investigated in greater detail during the next reporting period. At the highest temperatures shown it appears that, on the average, every incident oxygen atom or molecule leads to the production of one MoO_2 molecule.

Preliminary studies of the pressure dependence of the rates at 1400°K and 1150°K led to complex departures from first order kinetics for O_2 attack, but our O atom data reveal simple first order kinetics (cf. Fig. 6 and 7) over the range of pressures investigated thus far ($2 \times 10^{-3} < p_{\text{O}} < 5 \times 10^{-2}$ Torr; $1 < p < 5$ Torr), i.e., ϵ for the reaction is pressure independent, with O_2 playing no role in the kinetics.[§]

The lower activation energy and first order kinetics strongly suggest that the enhanced oxidation probability exhibited by O-atoms is due to direct attack in accord with a Rideal-type mechanism (gas phase strikes near oxygen chemisorbed on molybdenum) rather than merely the result of an increased steady state oxygen adatom coverage associated with an increased sticking probability.[†] Thus, for the production of $\text{MoO}_2(\text{g})$ we envision the sequence of steps:^{§§}

[§] The oxidation rate was linear in p_{O} alone, despite the fact that p / p_{O_2} varied by a factor of ten for these experiments.

[†] This mechanism may also apply to the enhanced oxidation of platinum.²²

^{§§} (g) $\equiv$ gas phase; (s) $\equiv$ solid surface; --- bonds with metal lattice; ‡ activated complex

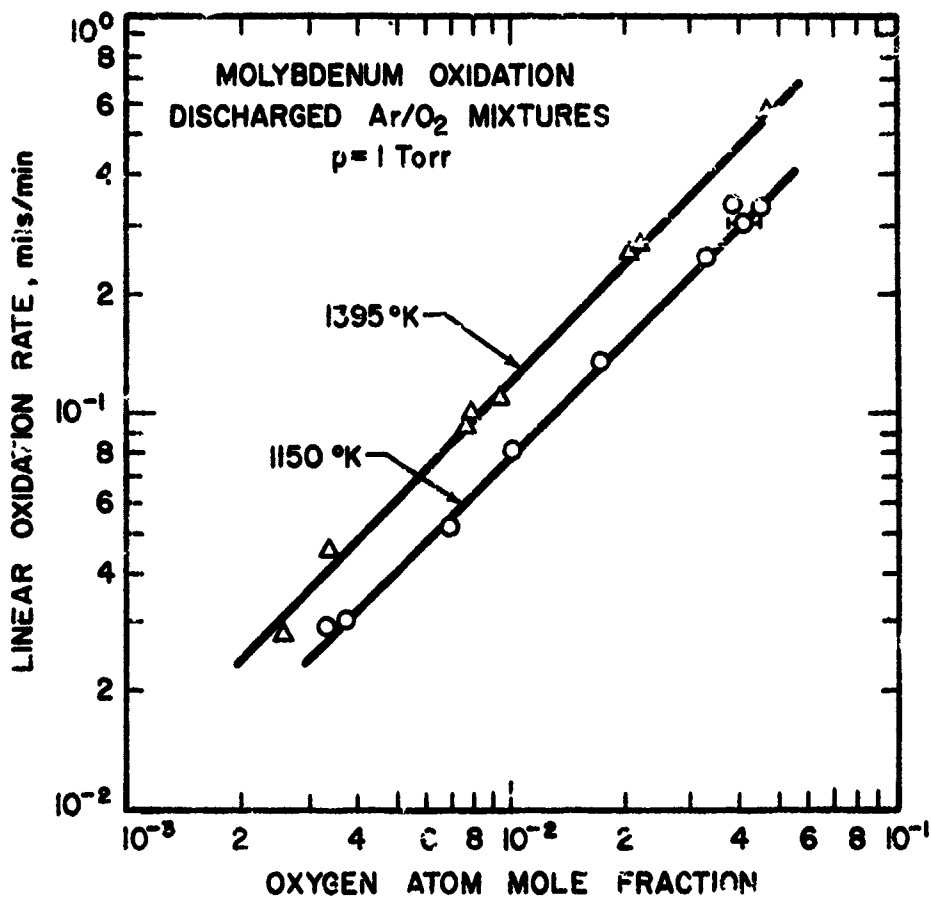


FIG. 6 DEPENDENCE OF MOLYBDENUM OXIDATION RATE
ON OXYGEN ATOM MOLE FRACTION

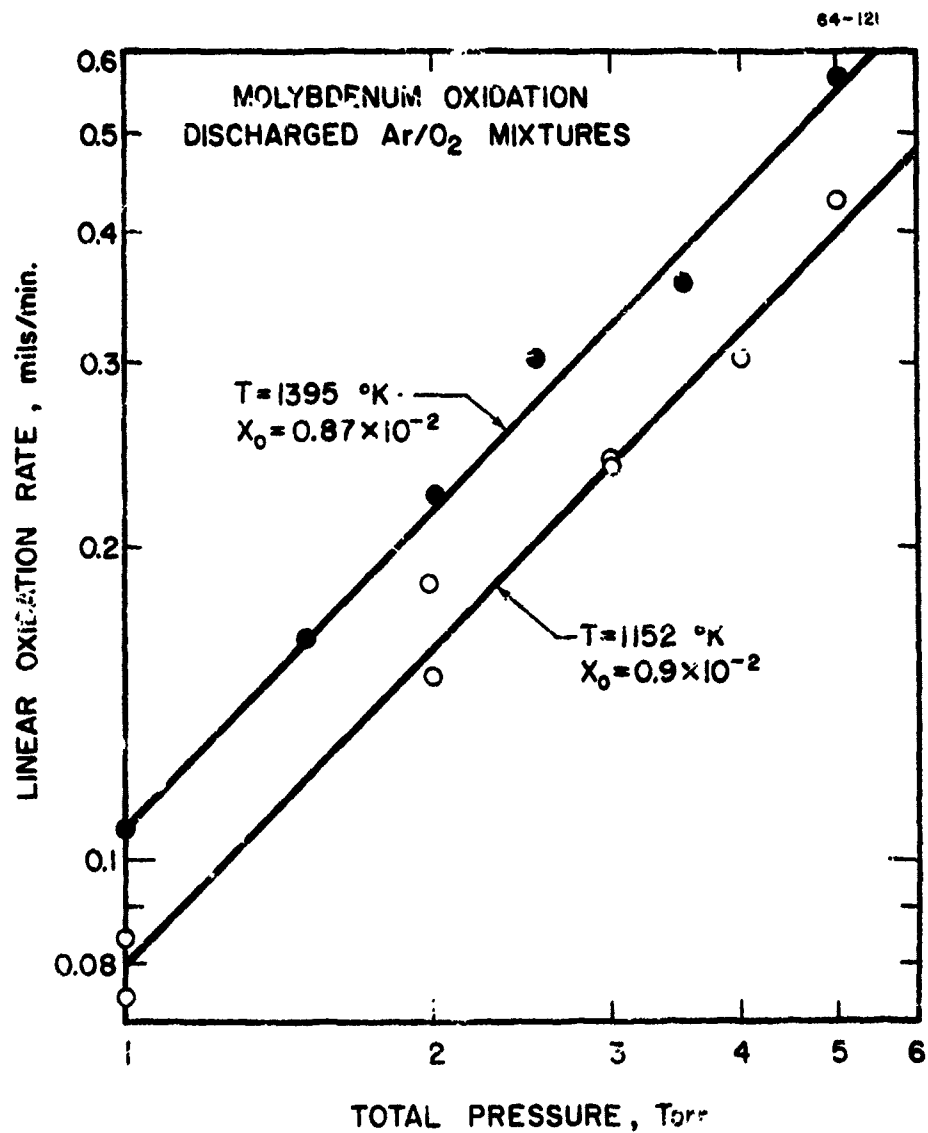
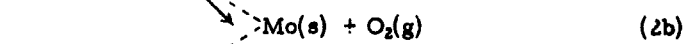
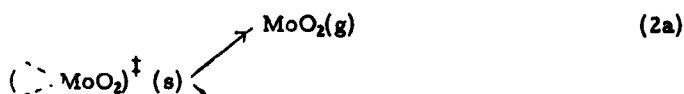


FIG. 7 DEPENDENCE OF MOLYBDENUM OXIDATION RATE ON
PRESSURE LEVEL AT CONSTANT OXYGEN ATOM
MOLE FRACTION



followed by:



Since O-atom recombination can be catalyzed on metals by a Rideal mechanism²³ (cf. Step 2b) an important implication of the above oxidation mechanism is that a simple relation should exist between the oxidation and recombination probabilities. This predicted relation will be investigated in our future work.

2.2c Oxidation by excited oxygen molecules We have initiated studies on the kinetics of excited molecule attack by introducing an oxidized silver foil upstream of the molybdenum filament when the microwave discharge is on. This foil recombines O-atoms produced in the discharge but admits electronically excited O_2 molecules²⁴ (abbreviated hereafter as O_2^*). Preliminary measurements show that the reaction probability for O_2^* in the temperature range $1050 < T < 1500^\circ K$ is somewhat greater than for O_2 but negligible compared to the O-atom probability, thereby validating our previous measurements. Yet the difference between O_2 and O_2^* is great enough to study quantitatively. By varying the filament temperature at constant discharge conditions the activation energy for O_2^* attack has been found to fall between that for O and O_2 attack, confirming the existence of a distinct oxidizing species. These studies will be continued during the next reporting period.

2.3 Kinetics of Oxidation of Tungsten

Experiments on tungsten oxidation have been initiated during the present reporting period. Our preliminary results, to be described here, indicate many similarities with the case of molybdenum discussed above. In particular, we have found that the oxidation probability for O-atom attack of tungsten can exceed that for O_2 attack by considerably more than one order of magnitude.

2. 3a Oxidation by diatomic oxygen In nondissociated gas mixtures of constant composition the oxidation rate of tungsten at 1560°K was found to increase as the 0.68 power of the pressure below 10 Torr, and linearly with pressure above 10 Torr. This behavior is shown in Fig. 8, which should be compared with the similar trends for molybdenum already shown in Fig. 3 (Curve b). As in the case of molybdenum,¹ there is also a marked difference between the pressure coefficient (0.68) below 10 Torr and the dependence of the oxidation rate on oxygen molecule mole fraction at constant pressure (cf. Fig. 9). This difference indicates that the rate of tungsten oxidation is not a simple function of local O_2 partial pressure alone. The activation energy for the oxidation of molybdenum by O_2 will be discussed below with reference to the corresponding value for O-atom attack.

2. 3b Oxidation by oxygen atoms Figure 10 includes our results for the temperature dependence of the tungsten oxidation probability ϵ , defined as in Section 2. 2b. In the temperature range 1400°K - 1600°K the activation energy for the attack by diatomic oxygen is about 32 Kcal/mole, in good agreement[§] with similar data of Langmuir,²⁵ Eisinger²⁶ and Perkins and Crooks.^{27†} In this same temperature range we find that the corresponding O-atom oxidation probabilities are higher by factors of from 50 to 20, corresponding to an activation energy for this reaction of about 4 Kcal/mole.

As shown in Fig. 11, at 1570°K we have verified that the O-atom attack is first order (i.e., ϵ is independent of oxygen partial pressure).^{§§} Once again, the lowered activation energy and first order kinetics strongly suggest that the enhanced oxidation probability exhibited by O-atoms on tungsten in this temperature

[§] Gulbransen et. al.¹⁴ report 14.3 Kcal/mole for this reaction, however it is readily demonstrated that all of the rate data contained in Ref. 14 are subject to appreciable errors due to the presence of diffusional limitations on the observed rates.

[†] However, oxidation probabilities calculated from the correlation equation suggested in Ref. 27 are appreciably lower than the remaining O_2 data shown in Fig. 10.

^{§§} Previous measurements at this temperature but in the presence of some diffusional limitation also showed that, at constant flow rate and pressure level, the oxidation rate of tungsten increased linearly with oxygen atom mole fraction. These measurements were made prior to the addition of the second 12 liter/sec vacuum pump (cf. Footnote, p. 4)

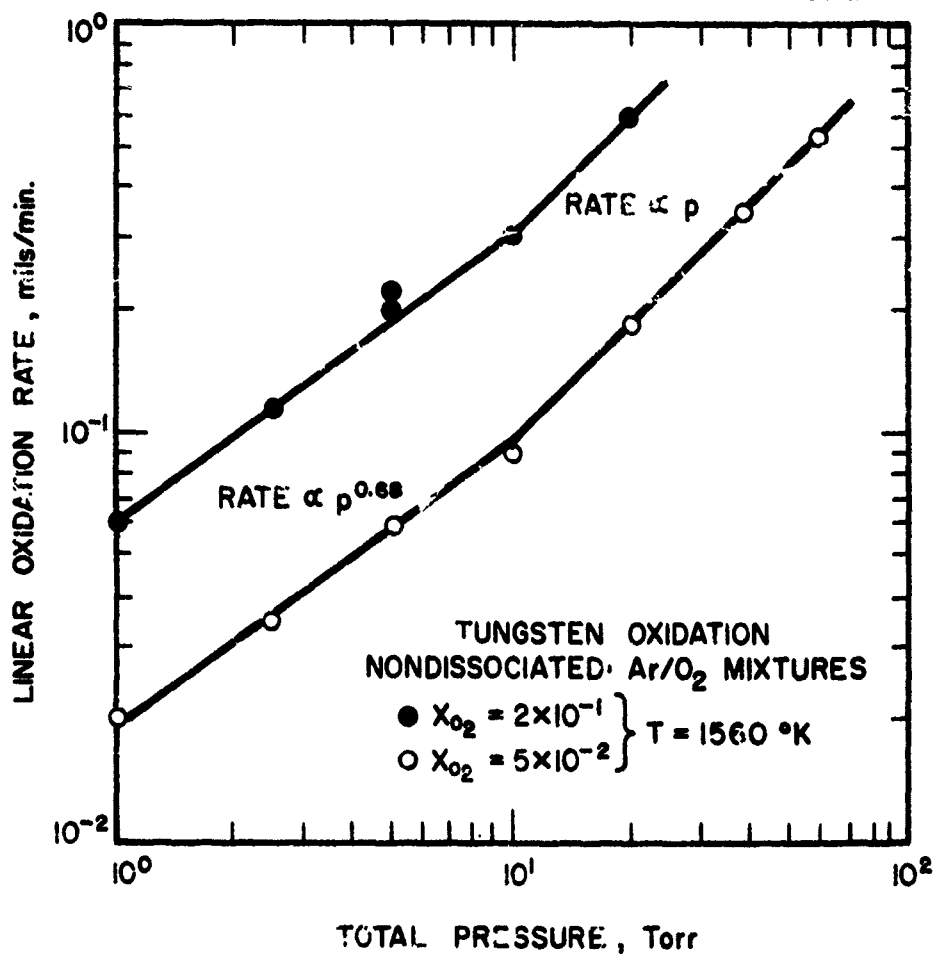


FIG. 8 PRESSURE DEPENDENCE OF TUNGSTEN OXIDATION RATES IN NONDISSOCIATED GAS MIXTURES

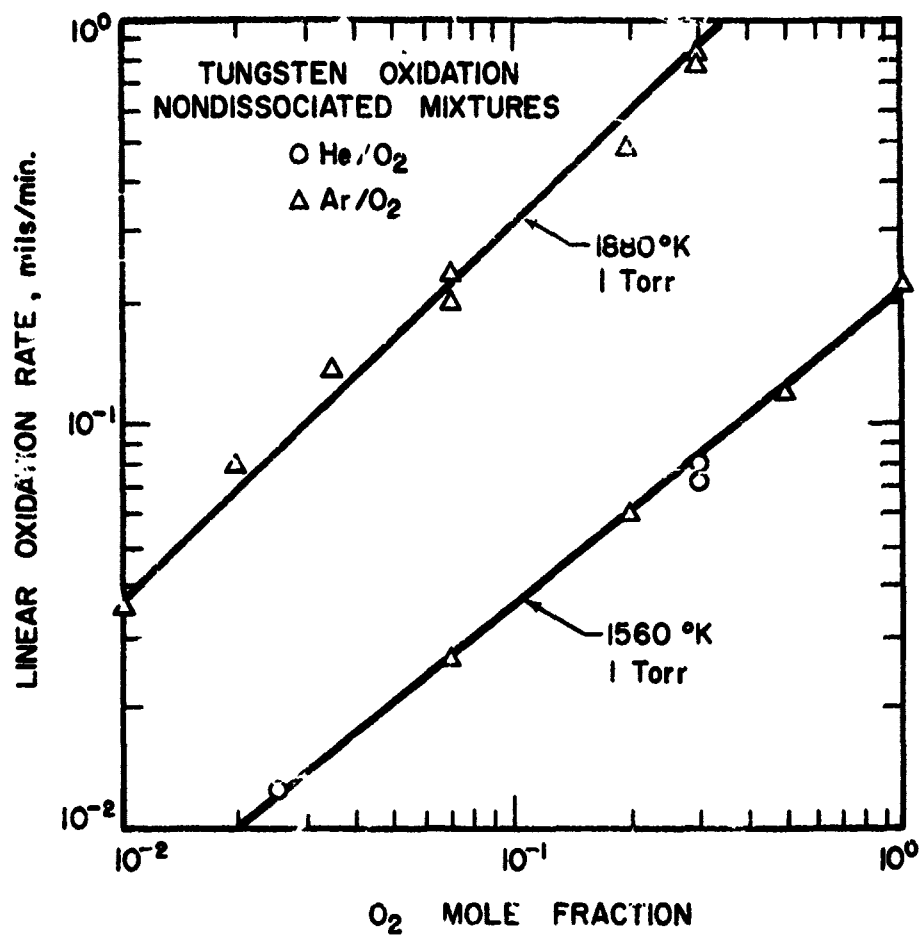


FIG. 9 DEPENDENCE OF TUNGSTEN OXIDATION RATE ON OXYGEN MOLECULE MOLE FRACTION

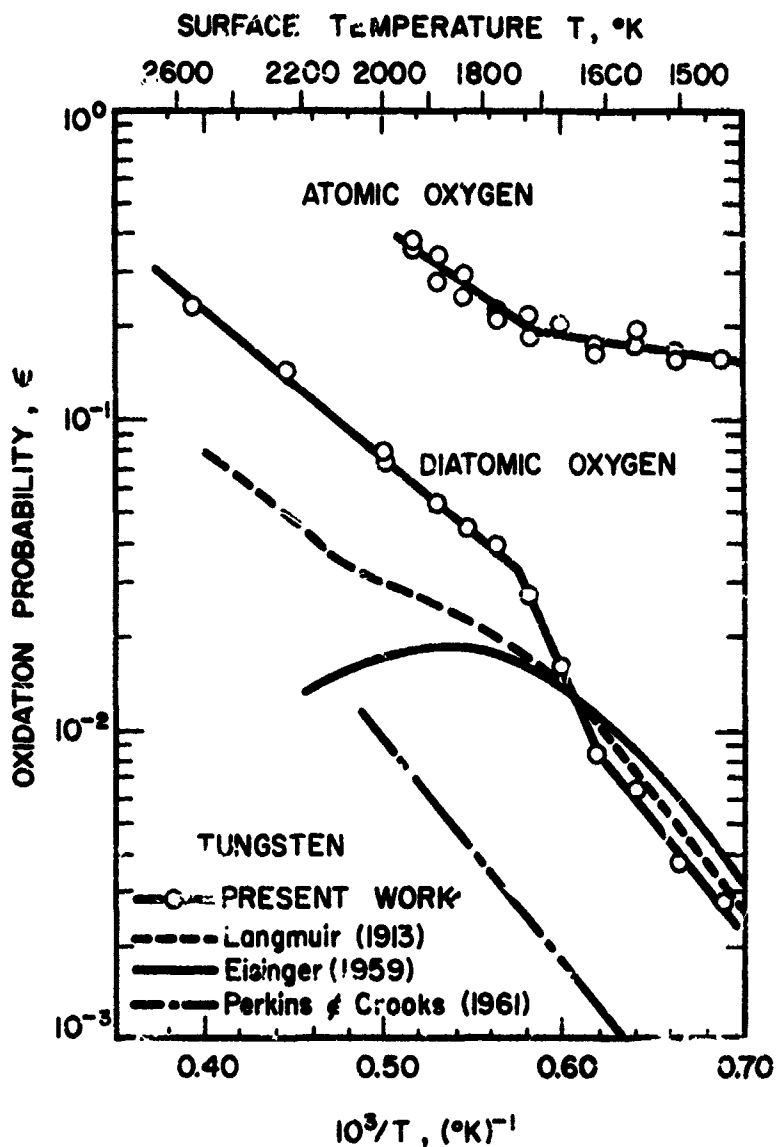


FIG. 10 ARRHENIUS PLOT OF TUNGSTEN OXIDATION PROBABILITIES

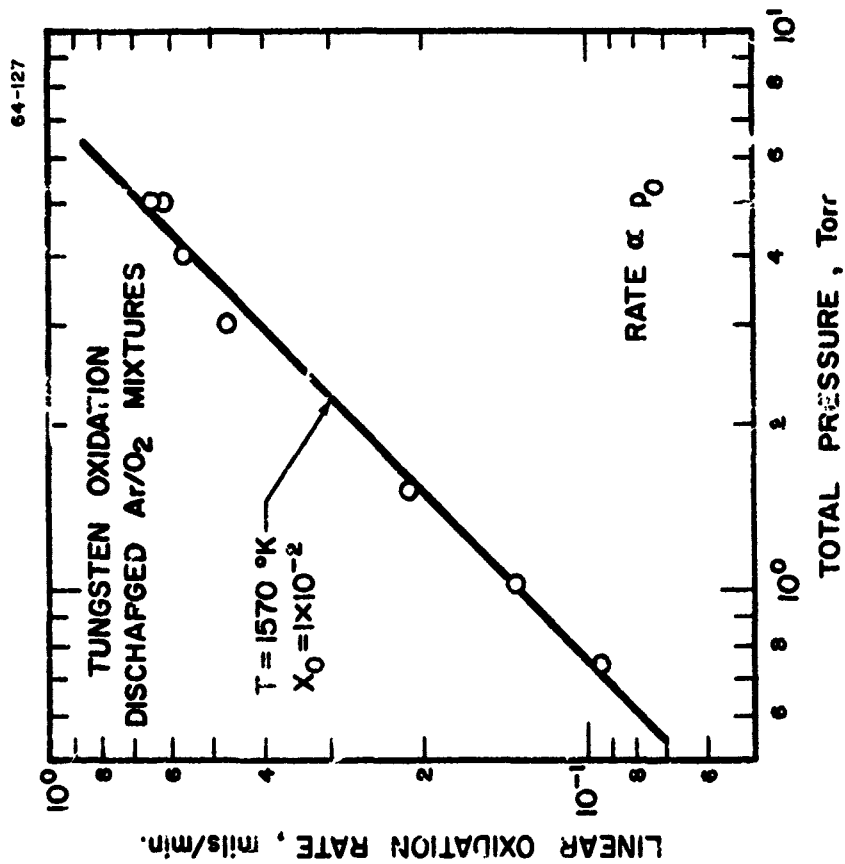


FIG. 11 DEPENDENCE OF TUNGSTEN OXIDATION RATE ON PRESSURE
LEVEL AT CONSTANT OXYGEN ATOM MOLE FRACTION

range is due to direct attack by a Rideal-type mechanism (cf. Eqs. 1, 2) rather than merely the result of an increased steady state oxygen adatom coverage associated with an increased sticking probability.

At temperatures above 1600°K departures from simple Arrhenius behavior occur for both the O-atom and O₂ oxidation probabilities. As in the case of molybdenum, these departures are most likely related to shifts in the relative importance of the reaction products (WO₂, WO₃). These and other aspects of the kinetics of high temperature tungsten oxidation are currently under investigation.

3. PLANS

During the next reporting period we plan to direct our efforts as follows:

- a. extend the range of temperatures and partial pressures over which data for molybdenum and tungsten oxidation by O₂ and O-atoms is now available.
- b. study the predicted relation between the oxidation and recombination probabilities for O-atoms on both molybdenum and tungsten
- c. study the kinetics of excited oxygen molecule attack of both molybdenum and tungsten
- d. perform exploratory tests of the effect of O-atoms on the kinetics of oxidation of other materials
- e. extend our critical analysis of existing kinetic data for O₂ attack of refractory metals, with particular attention to the role of diffusion in falsifying the kinetics. Continue reduction of available information to a common basis for comparison and the prediction of trends.

4. PUBLICATIONS

During the present reporting period Refs. 1 and 2 were prepared. In addition, Ref. 17, supported in part by the present contract, appeared in print.

5. ACKNOWLEDGEMENTS

We are grateful to Dr. A. Fontijn, R. Mantell and S. C. Kurzius for their suggestions and criticism and to W. Brenner for his assistance with the electrical instrumentation. The interest and support of the U. S. Air Force Office of Scientific Research, Propulsion Division, is also gratefully acknowledged.

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