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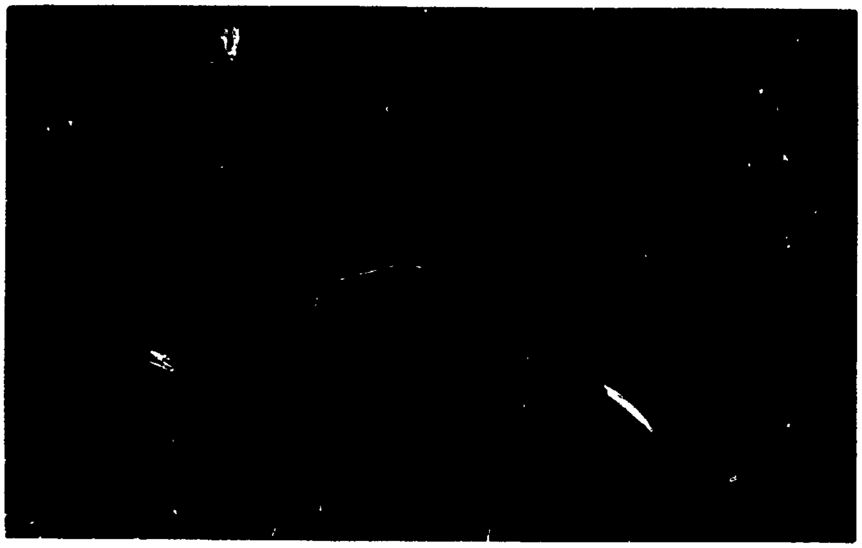

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Princeton, New Jersey

KINETIC AND AERODYNAMIC ASPECTS OF THE OXIDATION OF MATERIALS BY PARTIALLY DISSOCIATED GASES

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Final Report

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ABSTRACT

A synopsis is presented of the most significant results of a three-year research program carried out at this laboratory on the oxidation kinetics of refractory materials in dissociated gases. Microwave-discharge fast flow system techniques, coupled with electrical resistance heating and monitoring of the reacting specimens,have been used throughout. Experimental results are included for the attack of (a) polycrystalline molybdenum, tungsten, graphite, iridium and vitreous boron by atomic oxygen, (b) polycrystalline molybdenum and nickel by atomic chlorine, and (c) polycrystalline molybdenum by hydroxyl radicals. Reactant (O, Cl, and OH) partial pressures were of the order of 10^{-3} to 5×10^{-2} Torr, and surface temperatures were within the range 400 to 2600°K. A chronological list is provided of the seven publications and eleven reports describing these results and the underlying methods in greater detail.

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I. INTRODUCTION

At the temperature levels experienced in hypersonic flight and in high-performance chemical propulsion systems of interest to the Air Force, gaseous molecular fragments are produced which interact directly with solid surfaces introduced to contain and/or control the flow.[1-3] While much is known about the gas-phase reactivity of atoms and free radicals,[6-8] comparatively little is known about their reactivity with solid surfaces.[6,] Since chemical erosion rates can determine the success or failure of heat shields and control surfaces,[9-11] this lack of information is no longer acceptable from either a design or fundamental point of view.

In March of 1962, these considerations led the senior author to propose a basic experimental study of the oxidation rate of refractory materials in partially dissociated gas streams. With AFOSR support, this study was initiated at AeroChem in November of 1962 and has provided extensive kinetic data[12-14, 16-20, 26] on the effects of dissociation on oxidation rates of molybdenum, tungsten, graphite, and related refractory materials over a wide range of environmental conditions, as well as insight into the important role aerodynamic factors can play in actual practice.[15, 19] This being the final report under Contract AF 49(638)1195, these data and their implications will be reviewed in Section II, which follows. Chronological lists of publications,unpublished reports, and oral presentations resulting from this research program are given in Section III.

Owing to the fruitfulness of the techniques developed,[12-14, 16-20, 26] and the fundamental and practical importance of the kinetics of this class of heterogeneous reactions, the present program is to be extended under Contract AF 49(638)-1637.

II. TECHNICAL ACCOMPLISHMENTS

Under the present program an apparatus and experimental technique have been developed which allow the kinetics of attack by both unstable and stable species to be studied under "diffusion-free" conditions, even for heterogeneous reactions which are successful upon each collision. By exploiting this technique, we have generated the first available data on the true kinetics of the high-temperature attack of molybdenum,[12, 14] tungsten,[14] graphite[17, 18] boron, and iridium surfaces by oxygen and chlorine[20] atoms.* These data, their interpretation, and some implications are reviewed below.

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*Work on the attack of molybdenum by hydroxyl radicals has also been initiated, and is discussed in Section II. H.

A. Experimental Technique

We have demonstrated that the true kinetics of the attack of refractory materials by gaseous free radicals can be obtained by combining microwave discharge fast-flow low-pressure techniques with electrical resistance heating of reacting filaments.[12,14,16,20,26] Briefly, our apparatus consists of a part Vycor-part Pyrex vacuum flow system coupled to a 25 liter/sec mechanical pump. Metered noble gas/oxidizer mixtures are passed through a ~450 Mc/sec, 125-W microwave discharge cavity, downstream of which the gas encounters an electrically heated filament fed by a regulated dc power supply (cf. Fig. 1). Simultaneous with current measurement, 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 by altering the current in accord with an optical pyrometer output, thereby allowing the decrease in filament diameter caused by the reaction to be related to the increase in electrical resistance. The absolute value of the surface temperature is determined from either the known resistance-temperature relation for the specimen or directly from the pyrometer reading, as corrected using the emittance-temperature relation for the specimen. O-atom concentrations in the vicinity of the filament are obtained using the NO_2 light titration technique. Cl-atom concentrations are determined calorimetrically.[26] In all cases, external diffusion as well as thermal accommodation limitations* were ruled out on the basis of the absence of flow rate and carrier gas effects on the observed reaction rates.

B. Kinetics of the Attack of Molybdenum by Atomic Oxygen

Figure 2 summarizes our experimental results for the temperature dependence of the oxidation probability of polycrystalline molybdenum[12,14] subjected to atomic or molecular oxygen at partial pressures representative of those encountered by lifting re-entry vehicles in the Earth's atmosphere. The quantity ε, which measures the probability† that a molybdenum atom will be removed from the solid for each oxidizer collision, does not reveal simple Arrhenius (constant activation energy) behavior, and is seen to be considerably different--depending upon whether the oxidizer is monatomic or diatomic oxygen. At about 1200°K, ε for O atoms is greater than for O_2 by one hundred-fold. In contrast to the reaction probability for O_2, the O-atom reaction probability has been found to be independent of oxygen partial pressure.‡

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[*] encountered if the surface temperature differs appreciably from the translational temperature of gas molecules one mean free path away from the surface.

[†] calculated using the Hertz-Knudsen equation evaluated at the filament surface temperature.

[‡] For the O_2-data shown (Fig. 2) $p_{O_2} = 3.0 \times 10^{-2}$ Torr. For the O-atom data $p_O = 1.0 \times 10^{-2}$ Torr.

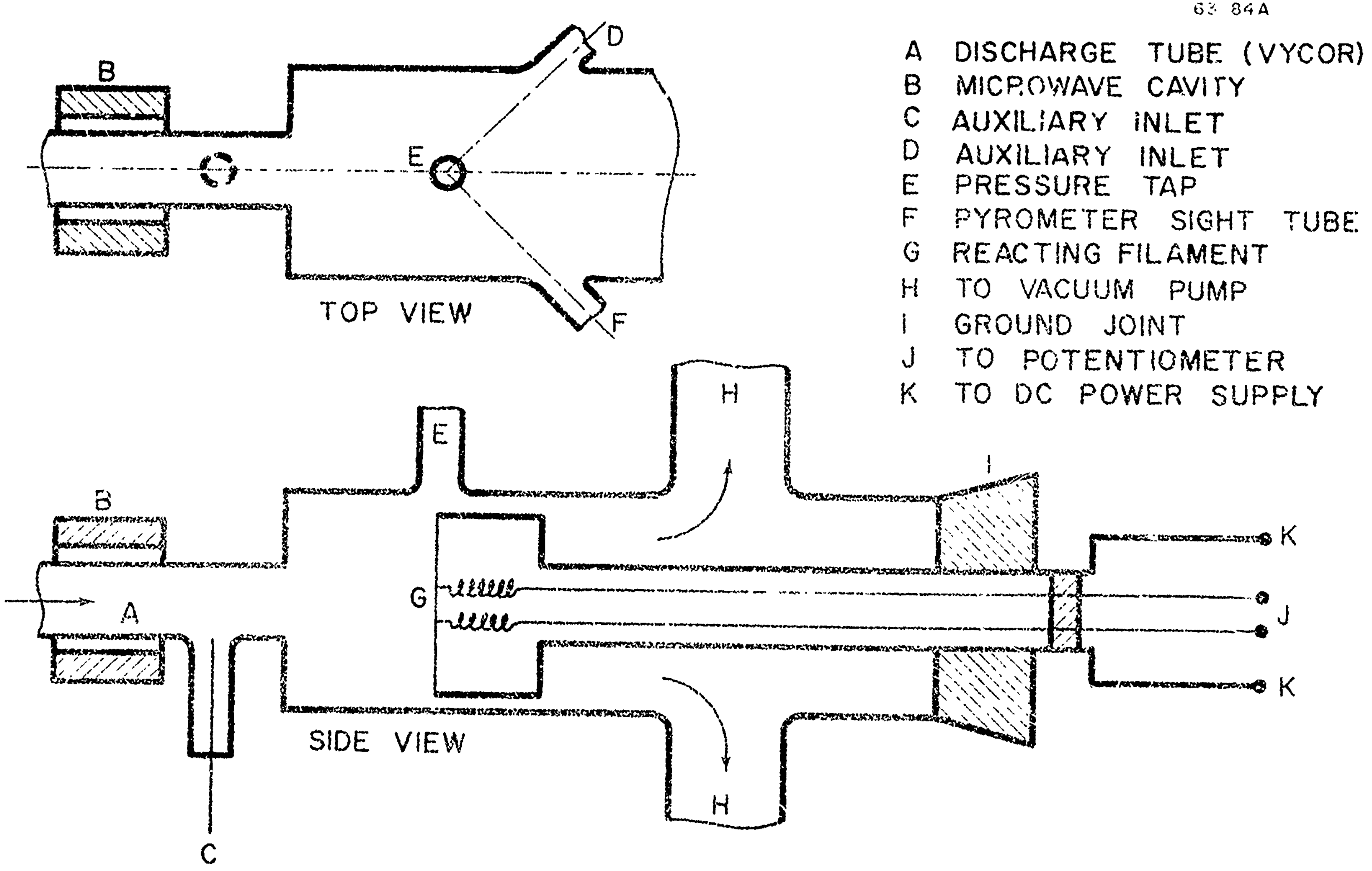

FIG. 1 FILAMENT OXIDATION APPARATUS

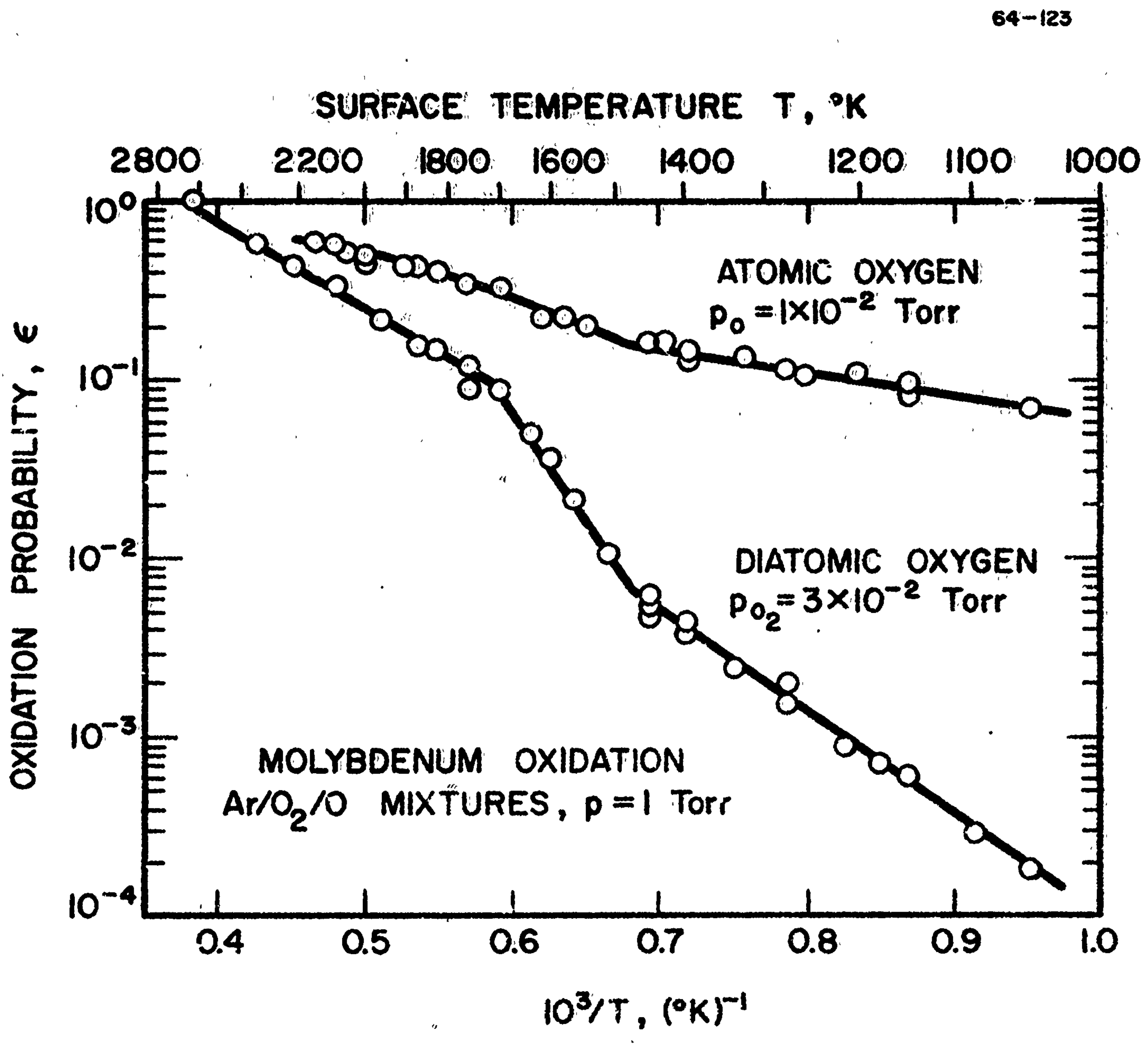

FIG. 2 OXIDATION PROBABILITIES FOR THE ATTACK OF MOLYBDENUM BY ATOMIC AND DIATOMIC OXYGEN

These data, discussed in greater detail in Refs. 12 to 14, are the first available comparing the rates of O-atom and O_2 attack of molybdenum at elevated temperatures. They indicate, in the surface temperature range of interest for aerospace applications, that the presence of O atoms in the re-entry environment will greatly increase the oxidation rate of exposed molybdenum surfaces.

In rationalizing the oxygen atom attack data, the observed large absolute values of ϵ, reduced activation energy (compared with the O_2 case), and first-order kinetics (ϵ independent of p_O) led us to postulate[12,14] that the enhanced oxidation probability exhibited by O atoms is due to direct attack of chemisorbed species by O atoms from the gas phase (a Rideal-type mechanism) rather than merely increased adatom coverage associated with an increased sticking probability. As will be seen, it is likely that this mechanism is important, if not dominant, for most of the reactions studied herein. One interesting consequence of this postulate is that a relatively simple relation should exist between the atom oxidation probability (ϵ) and recombination probability (γ) on the same surface. Whether or not this relation is experimentally found to hold, the ϵ data included herein allow upper bounds to be set on the recombination probability for each of the atom/surface reactions considered.

C. Kinetics of the Attack of Tungsten by Atomic Oxygen

Figure 3 summarizes our experimental results for the temperature dependence of the oxidation probability of tungsten[14] subjected to atomic or molecular oxygen at partial pressures[*] representative of those encountered by lifting re-entry vehicles in the Earth's atmosphere. The quantity ϵ, which here measures the probability that a tungsten atom will be removed from the solid for each oxidizer collision, is seen to be considerably different--depending on whether the oxidizer is monatomic or diatomic oxygen. At surface temperatures of interest in lifting re-entry vehicle operation ($\sim 2000^{\circ}K$), tungsten atom removal per O-atom strike is more than five times higher than in the corresponding O_2 case. Again, in contrast to the reaction probability for O_2, the O-atom reaction probability was found to be independent of oxygen partial pressure.[14] Comparing the results displayed in Figs. 2 and 3 we find that, while tungsten is much more oxidation-resistant than molybdenum in diatomic oxygen (at any given surface temperature), in atomic oxygen both metals oxidize at comparable rates.

D. Kinetics of the Attack of High-Temperature Graphite by Atomic Oxygen[16-19]

Among the assumptions used by others to analyze the ablation rate of graphite in air, two are particularly suspect,[19] viz. (a) that the specific reactivity of graphite has a simple Arrhenius behavior and (b) that oxygen atoms play no role in the true kinetics of graphite oxidation. As revealed by our experiments on a commercial grade[†] of graphite (cf. Fig. 4), neither of these assumptions is justifiable. Moreover,

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[*] For the O_2 data shown (Fig. 3) $p_{O_2} = 0.7 \times 10^{-1}$ Torr. For the O atom data $p_O = 1.9 \times 10^{-2}$ Torr.

[†] Speer Carbon Co, Grade 580.

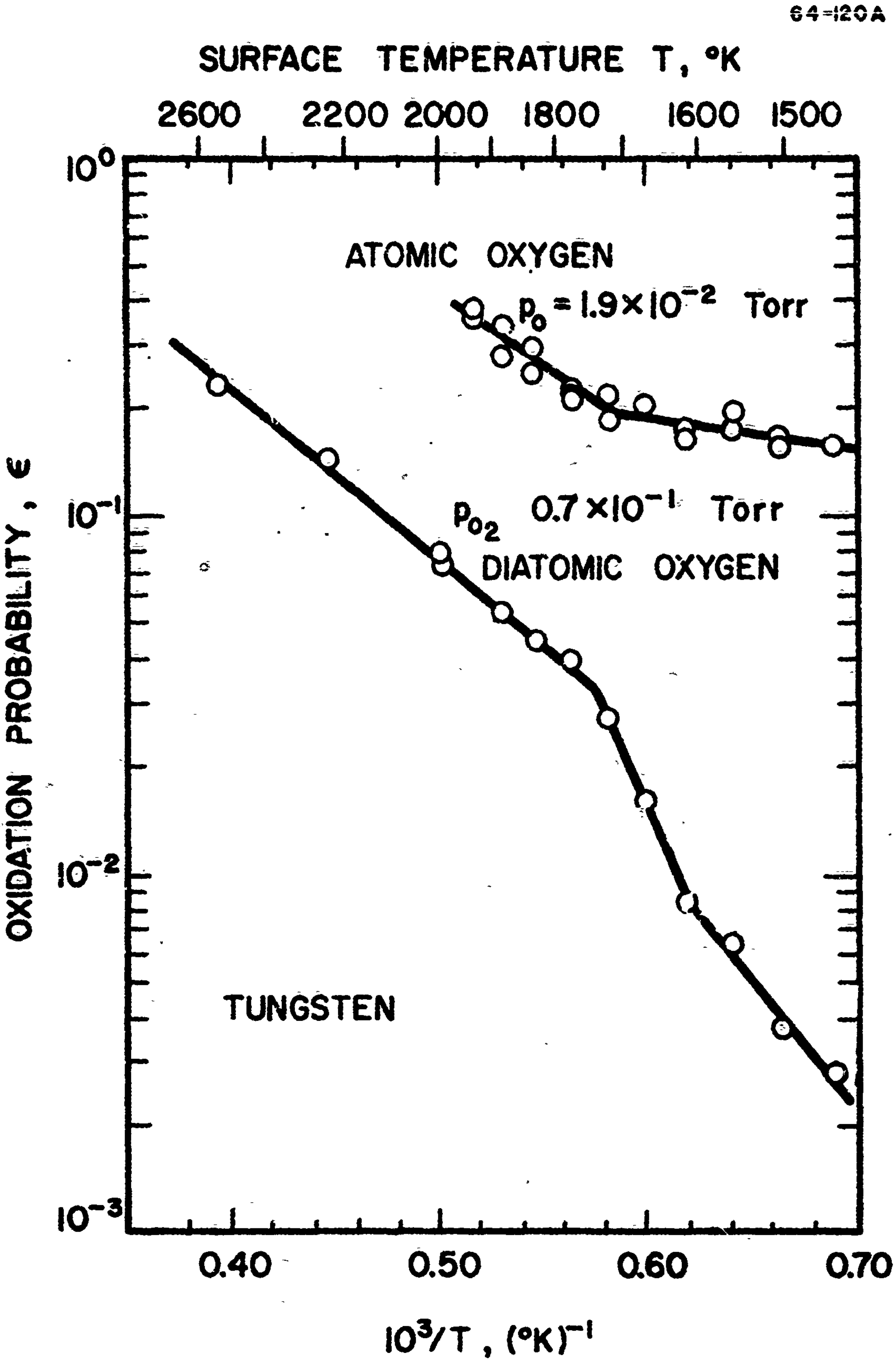

FIG. 3 OXIDATION PROBABILITIES FOR THE ATTACK OF TUNGSTEN BY ATOMIC AND DIATOMIC OXYGEN

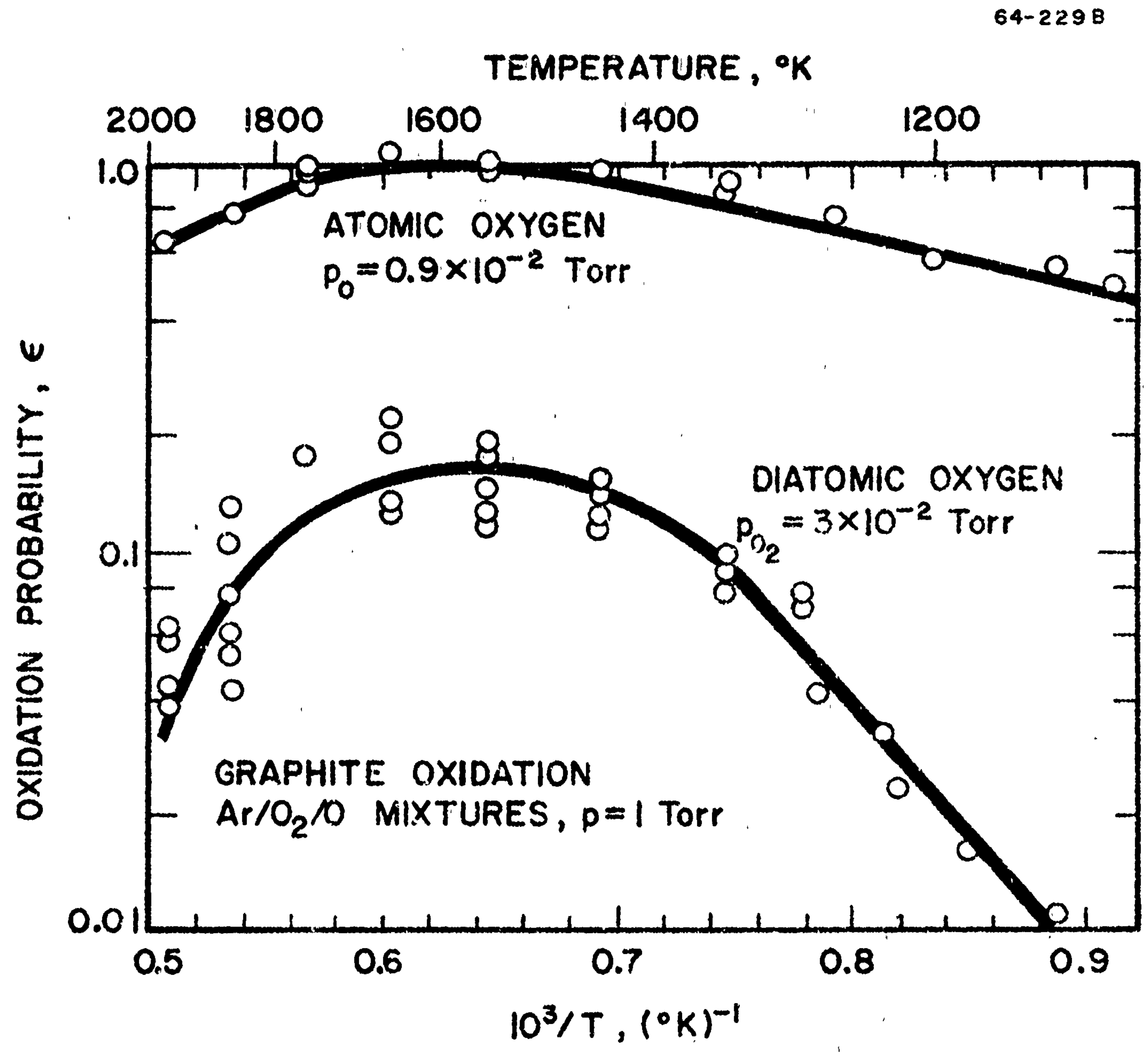

FIG. 4 OXIDATION PROBABILITIES FOR THE ATTACK OF GRAPHITE BY ATOMIC AND DIATOMIC OXYGEN

it can be shown that the effects of relaxing these assumptions are apt to be especially large for the case of lifting re-entry vehicles from Earth orbit.[20]

Figure 4 summarizes our results for the temperature dependence* of the oxidation probability, ε, defined here as the ratio of the flux of carbon atoms (regardless of their chemical state of aggregation) away from the surface to the collision flux of O or O_2 with the surface. The following features are noteworthy: 1. O-atom strikes are significantly more effective than O_2 in removing carbon atoms from the lattice. The O-atom reaction appears to occur with essentially unit probability over a temperature interval of more than 100°. 2. neither reaction probability displays simple Arrhenius behavior, and each exhibits a maximum in the temperature interval shown. 3. whereas the oxidation by O_2 exhibited complex departures from simple power law kinetics, the O atom reaction has been found to be first order (i. e., ε is independent of oxygen atom partial pressure), 4. our data below 1400°K (which includes an experiment at 380°K) confirm the low activation energy (~ 6.8 Kcal/mole) of the O atom attack mechanism. The implications of these experimental results are discussed in Refs. 16, 17, 19, and 20.

It has frequently been reported that pyrolytic graphite displays improved oxidation resistance over ordinary graphite.[21] In Ref. 19 we pointed out that the improvement, while expected, might not be so great in a dissociated oxygen environment. To check this a set of experiments was carried out during the last semi-annual period of the present program on pyrolytic graphite specimens produced by in situ pyrolysis of enthane on electrically heated 5 mil diam. tungsten wires. Preliminary oxidation data† using these specimens‡ do, in fact, reveal that the improvement in oxidation resistance in atomic oxygen is not as great as§ the observed improvement in diatomic oxygen. Thus, the error committed in neglecting the contribution of O atoms to the oxidation rate of pyrolytic graphite in lifting re-entry vehicle situations[20] will probably exceed that for the corresponding case of commerical graphite oxidation.

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[*] in this case, surface temperature was inferred directly from the filament brightness temperature using the emittance-temperature relation for this material.[16-19]

[†] In this case and that of pyrolytic boron described below reaction rates were computed from diameter changes as measured using a microscope.

[‡] Deposition conditions were: p = 32 Torr, ethane mole fraction = 0.10, substrate brightness temperature = 1920°K.

[§] At 1440°K the improvement ratio in atomic oxygen was found to be about 1/3 of that observed in diatomic oxygen.

E. Kinetics of the Attack of Boron by Atomic Oxygen

In view of current Air Force interest in boron-containing fuels, resins, and reinforcements, a series of experiments on the oxidation rate of vitreous 4 mil diam. boron filaments[*] in atomic oxygen was carried out during the final semi-annual period.[†] Two features appear noteworthy in the preliminary results obtained thus far (cf. Fig. 5): (a) the O-atom oxidation probability exceeds that for O_2 by a factor of about 50, and (b) the observed activation energies appear similar and close to that (77 kcal/mole) reported in earlier studies of the $B(s) + O_2(g)$ reaction[22] at higher surface temperatures. This result, which constitutes the largest apparent activation energy yet observed for the attack of a solid by an atomic oxidizer, bears further investigation.

F. Kinetics of the Attack of Iridium by Atomic Oxygen

Quite apart from theoretical interest[6, 23, 24] in refractory noble metals, their importance (particularly iridium) has suddenly increased in view of their possible use as protective coatings on oxidation-prone refractory substrate materials. For example, a program has been underway to evaluate iridium as a protective coating on graphite in re-entry vehicle applications.[25] For such applications it is clear that the net ablation rate of the protective film must be accurately predicted, based on available data. Experimental oxidation rates have been reported for iridium in O_2-containing gases but, despite the fact that atomic oxygen can be present in the shock layer of re-entry vehicles in concentrations up to 34.7 mole percent,[†] no data have been reported for reaction in partially dissociated oxygen. Therefore, during the last semi-annual period of the present program, a series of measurements on iridium filaments[‡] was made using the techniques outlined earlier. Perhaps the most striking new feature observed was the highly nonlinear diameter-time curves in an argon/oxygen stream originally containing 2 mole % O_2. When this gas mixture is partially dissociated (using the microwave discharge), the rate of oxidation suddenly increases but then gradually decelerates toward an asymptotic value (which still exceeds the corresponding rate for O_2 by a factor of 2.75). When the filament temperature is changed (e.g., from 1770°K to 1970°K), the curvilinear portion of the d-t trace is found to remain

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[*] surface temperature was inferred from the filament brightness temperature using an assumed emittance of 0.72. In all cases, the pressure level was 1 Torr. Reaction order experiments and tests for the absence of flow rate effects have not yet been made for this reaction.

[†] Engelhard Industries, Newark, N.J.

[‡] This upper limit corresponds to the realizable case of complete oxygen dissociation in the absence of appreciable nitrogen dissociation.

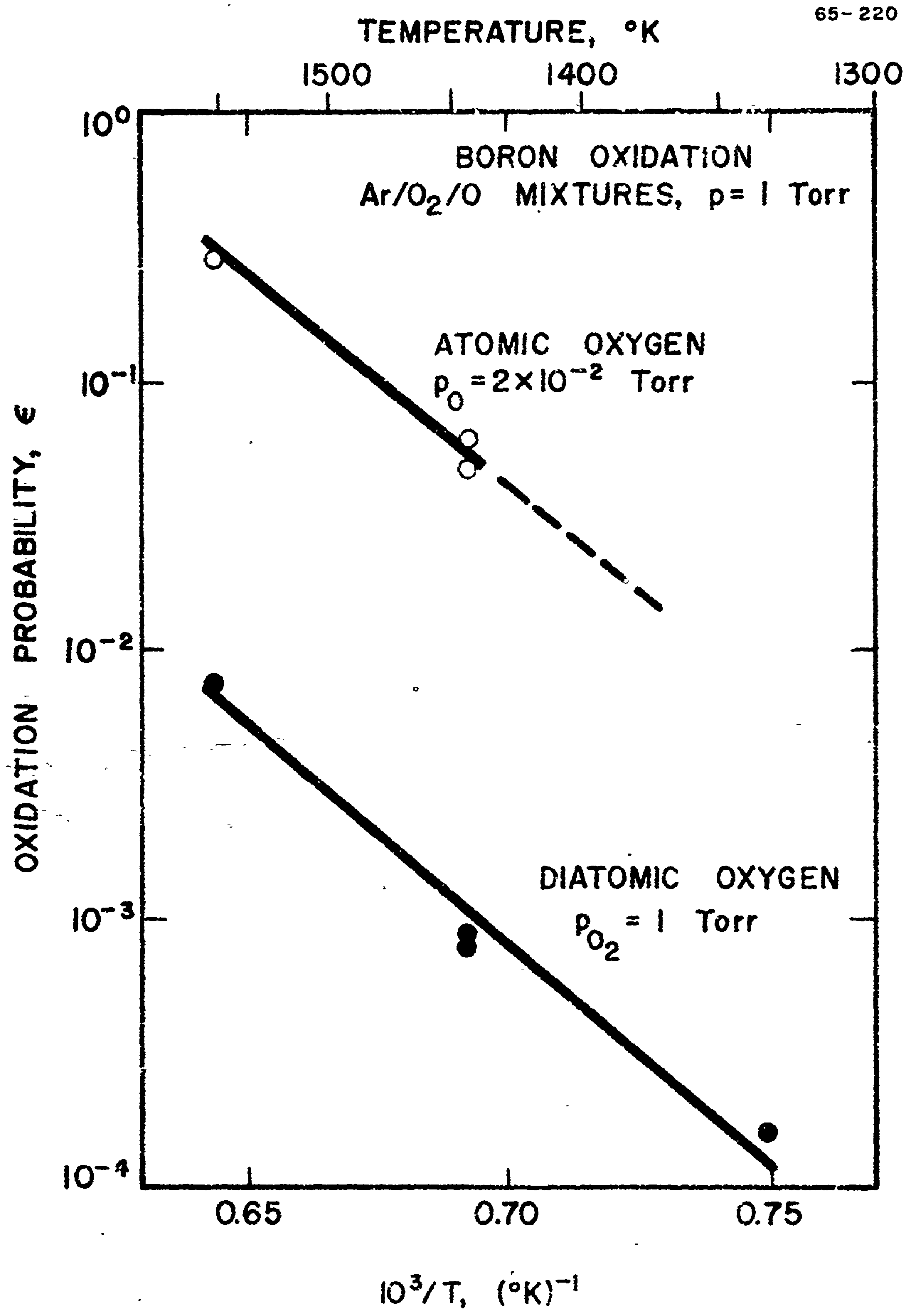

FIG. 5 OXIDATION PROBABILITIES FOR THE ATTACK OF BORON BY ATOMIC AND DIATOMIC OXYGEN

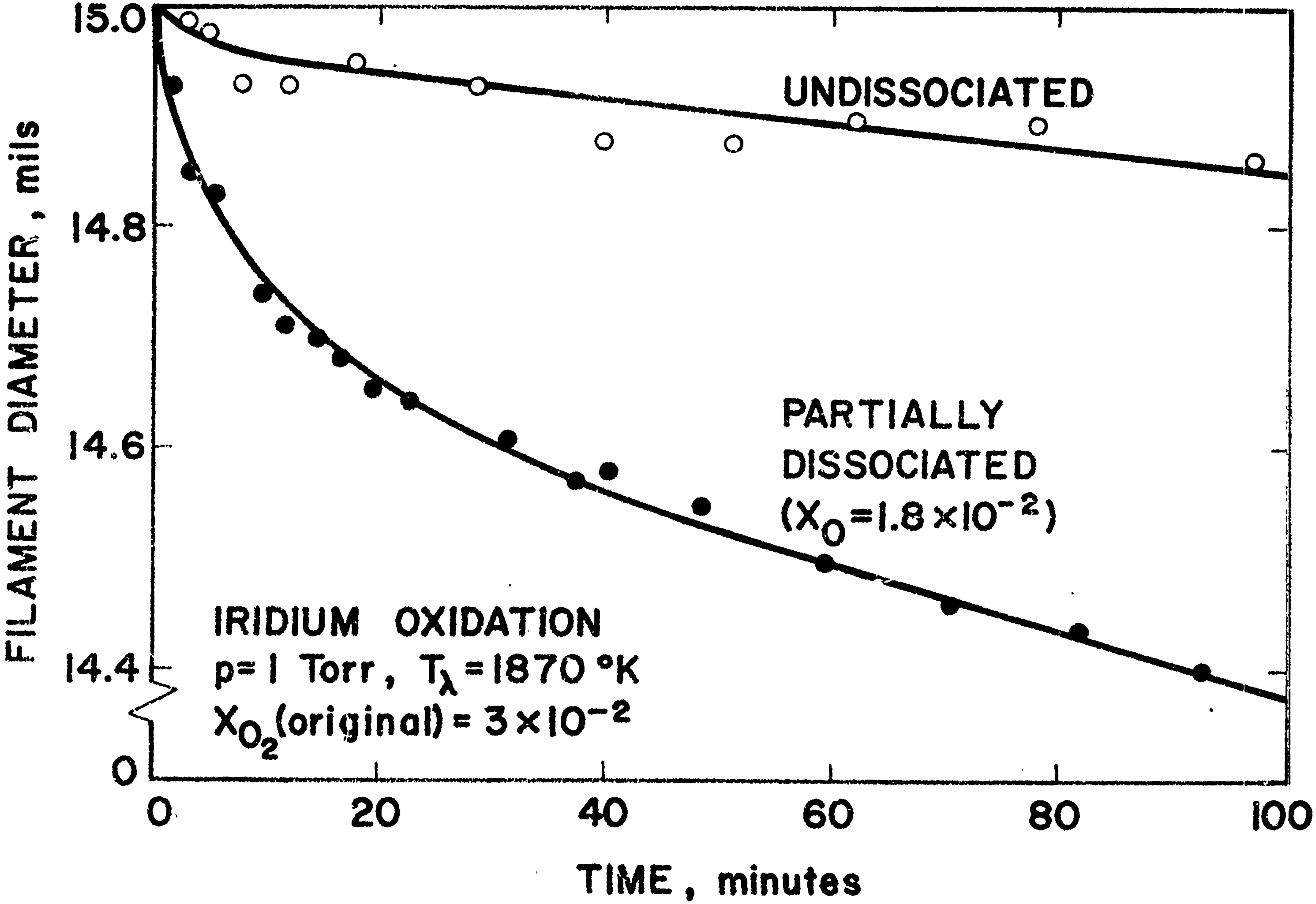

FIG. 6 DIAMETER REDUCTION OF IRIDIUM AS A FUNCTION OF TIME IN DISSOCIATED AND UNDISSOCIATED GAS MIXTURES

essentially invariant, with only the asymptotic rate reflecting the temperature change. These novel features, and the difficulty of eliminating flow rate effects on the observed reaction rates, set iridium apart from the other materials studied under the present program. Further experiments are planned to unravel the true kinetics of this reaction.

G. Kinetics of the Attack of Molybdenum by Atomic Chlorine

Owing to the presence of halogen atoms in the exhaust gases of high-performance rocket motors, we initiated studies of their reactions with refractory materials commonly used as rocket nozzle inserts. Figure 7 summarizes the major results of our molybdenum chlorination experiments[20, 26] carried out in the surface temperature range from 400 to 1530°K. As before, ε is a dimensionless reaction probability, defined here as the average number of molybdenum atoms removed from the filament per Cl or Cl_2 strike. The chlorine atom concentration (cited in Fig. 7 and used in the data reduction) is that inferred from the output of a calorimetric nickel (catalytic) detector[27] similar in concept to that used by Ogryzlo[28] and co-workers. Of special interest here are: (a) the remarkable temperature dependence of the Cl-atom attack, giving rise to impressive reaction probabilities ($>10^{-2}$) even at nearly room temperature, and (b) the significantly lower reaction probability for the Cl_2 molecule attack over the entire temperature range investigated. Again, the attack by the atomic species is apparently a first-order process (for which ε is independent of Cl atom partial pressure), since the chlorination rate was found to be linear in the calorimetric detector output.[20, 26] For purposes of comparison with these results, and also with those of McKinley and Shuler,[29] several experiments were also carried out on the chlorination of nickel. We found that: (a) in marked contrast to the behavior of molybdenum, dissociation does not appreciably affect the nickel chlorination rate, and (b) the high probability observed[26] for the attack of nickel by $Cl_2(g)$ agrees well with that reported in Ref. 29. The nickel/atomic chlorine reaction thus has the distinction of being the only atom/surface oxidation reaction yet studied for which the observed oxidation rates are not appreciably faster than in the corresponding case of attack by stable diatomic molecules (O_2, Cl_2). Some implications of these observations with regard to dissociative adsorption probabilities and binding energies on nickel and molybdenum surfaces are discussed in Ref. 26.

H. The Hydroxyl Radical as an Oxidizer

Water vapor is the principal oxidizing agent in many solid propellant and radiation-cooled liquid rocket engine applications. Since it is known that hydroxyl radicals are more than ten times as abundant as O atoms in equilibrium partially dissociated water vapor, it is of interest to consider the oxidation kinetics for OH attack of refractory materials. We have initiated such studies[20] using the experimental techniques described in Section II. A. Two different gaseous environments have been used: The first consists simply of the dissociated products of a microwave discharge through argon-diluted water vapor. The second (and more satisfactory in many ways) environment is the gas mixture produced when $NO_2(g)$ is added to the products of a microwave discharge through argon-diluted hydrogen. In this case we make use of the extremely rapid reaction[30]

$$H + NO_2 \rightarrow OH + NO \qquad (1)$$

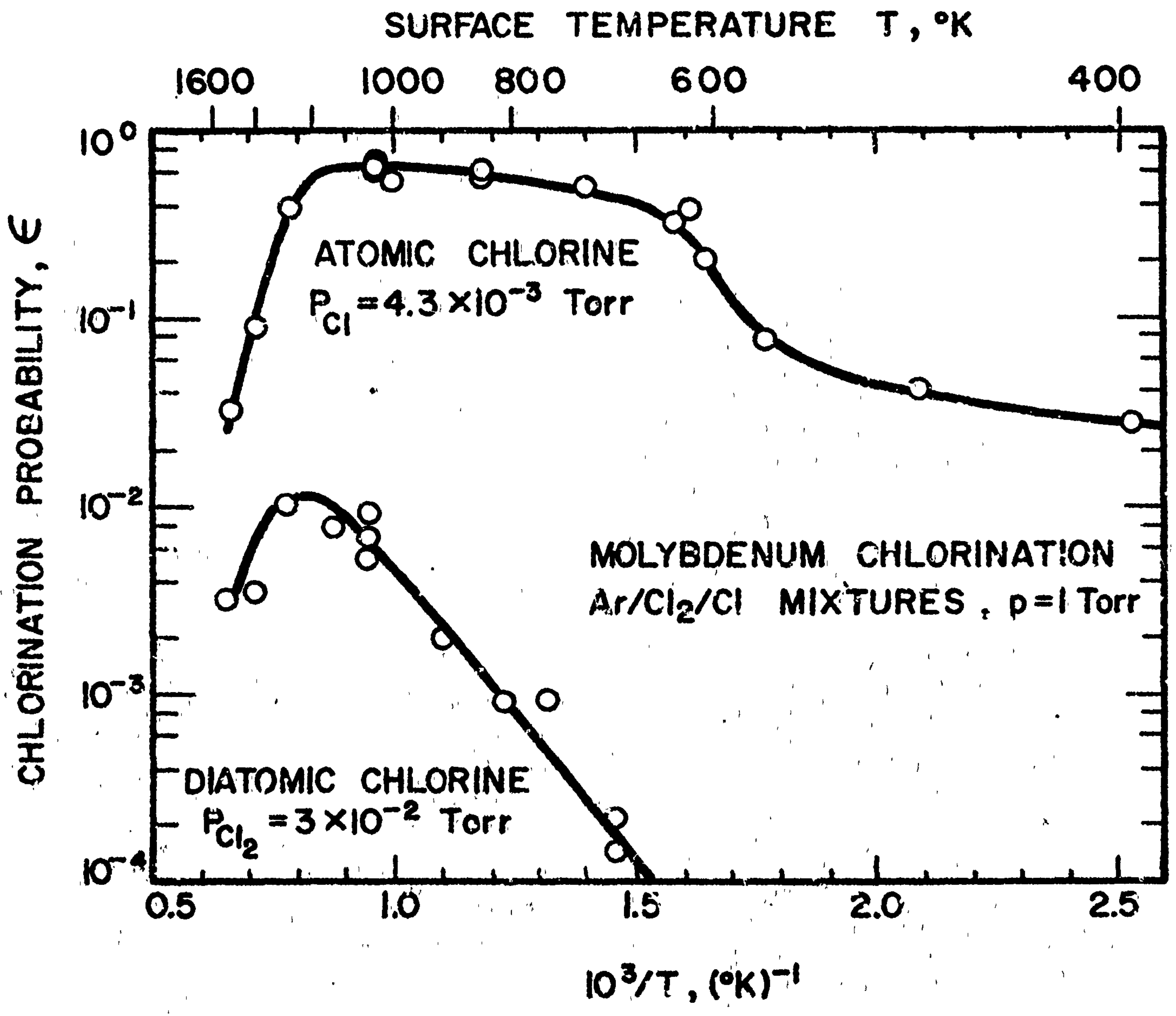

FIG. 7 CHLORINATION PROBABILITIES FOR THE ATTACK OF MOLYBDENUM BY ATOMIC AND DIATOMIC CHLORINE

which produces one hydroxyl radical for each NO_2 molecule consumed. Using either method, to extract the kinetics of OH attack of any particular surface, it is necessary to also study the kinetic effects of the other gases present in the environment (e.g., $H_2O(g)$, $H(g)$).

For molybdenum oxidation we have found that the effectiveness of OH as an oxidizer can be appreciably impaired by the simultaneous presence of H atoms. This is illustrated in Fig. 8, which shows how the oxidation rate of molybdenum (at $T = 1395^{\circ}K$) varies with the upstream addition of $NO_2(g)$ to the products of an argon-diluted hydrogen discharge. In the left-hand (shaded) region, H atoms are present in excess, and every $NO_2(g)$ molecule added produces one hydroxl radical. In the right-hand (unshaded) region, NO_2 is present in excess, and all the H atoms have been consumed in producing OH. While the OH concentration is thus unaltered as one crosses the equivalence "point" (NO_2 flow = H-atom flow, cf. dark shaded band), the rate of molybdenum oxidation is higher in the absence of H atoms (right-hand side) than can be accounted for by the simultaneous presence of undecomposed $NO_2(g)$.*

Another interesting observation is, that when molybdenum was oxidized in an argon/water vapor mixture ($p_{H_2O} \approx 1 \times 10^{-2}$ Torr, $p \approx 1$ Torr) the reaction rates below about $1700^{\circ}K$ actually exceeded those observed when a microwave discharge was first passed through this same mixture. Additional studies of these interesting "coupling" phenomena and their important implications are planned.

I. Fluid Dynamic and Transport Effects in Heterogeneous Kinetics

True kinetic data can be combined with relatively abundant convective mass and heat transfer data to predict heterogeneous reaction rates in a wide variety of engineering configurations and environments[15, 31] (e.g., nozzle insert erosion in short-duration solid propellant rocket firings, leading edge ablation on lifting re-entry vehicles,[20] etc.). However, if one attempts to invert this process, extremely large errors can be made in deducing the true kinetics of a surface reaction from experiments in which the observed reaction rates are, in part, diffusion-controlled.[15,32] Indeed, diffusional effects have complicated or completely falsified several "kinetic" studies,[33, 35] 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. An extensive review paper[15] quantitatively describing the effects of convective diffusion in heterogeneous kinetic studies was prepared under partial support of the present contract. These concepts have been specifically applied in our published discussions of diffusional effects in available studies of the oxidation of refractory metals[13] and graphite.[19] The design of the present set of experiments represents a specific application in which the intent was to avoid diffusional complications, even for very rapid heterogeneous reactions. This has been experimentally verified in the studies of the oxidation of molybdenum,[12, 14] tungsten[14] and graphite[17, 18, 20] described above.

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*This latter conclusion follows from the data (also shown in Fig. 8) on the isolated effect of $NO_2(g)$ when the microwave discharge is not in operation.

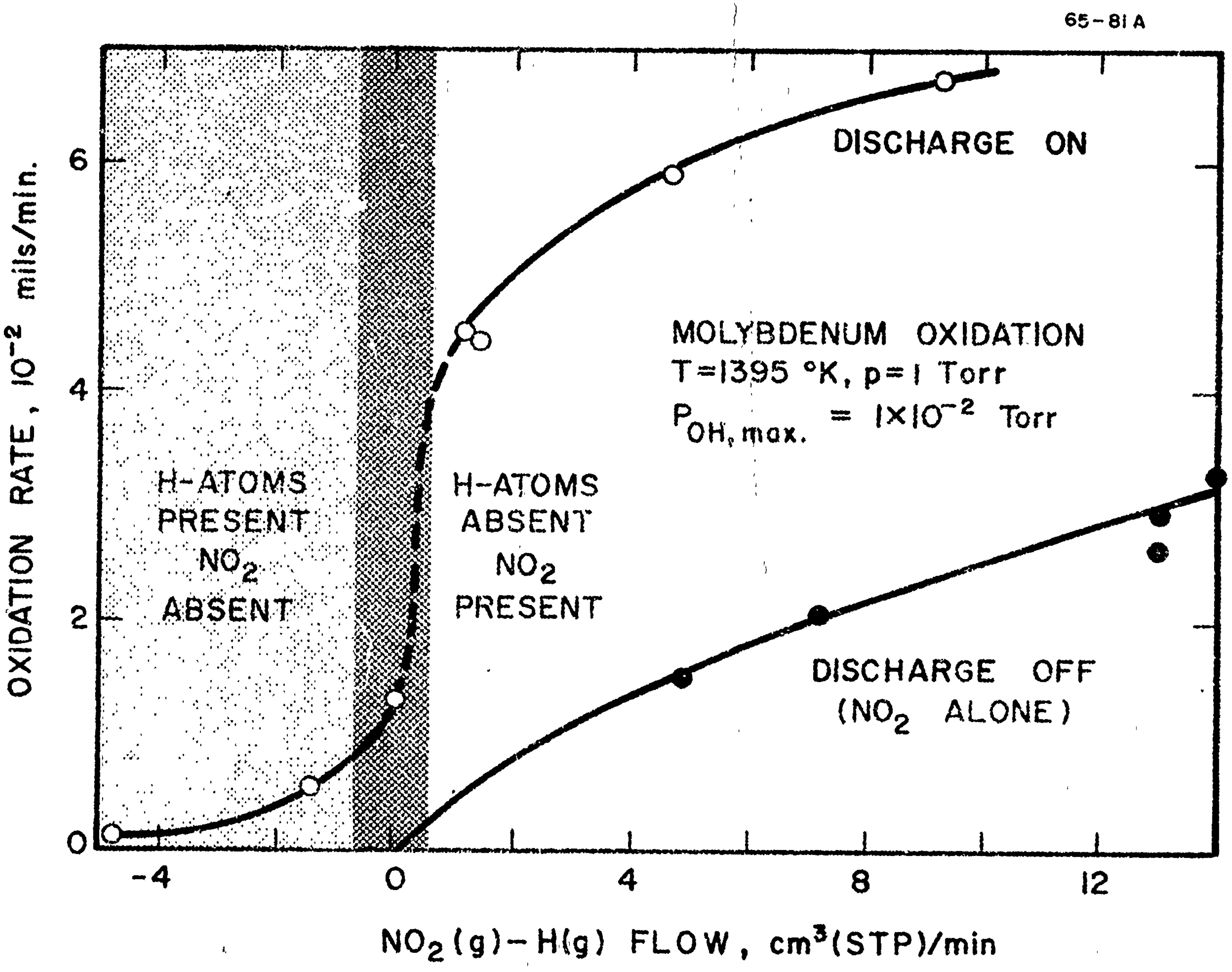

FIG. 8 MOLYBDENUM OXIDATION IN THE MIXTURE FORMED BY ADDING NO_2 TO PARTIALLY DISSOCIATED HYDROGEN

III. COMMUNICATION OF RESEARCH RESULTS

A. Chronological Publication List

Rosner, D. E. and Allendorf, H. D., "Kinetics of the Attack of Molybdenum by Dissociated Chlorine," AeroChem TP-117, July 7, 1965, J. Phys. Chem. (in press, ca. December 1965 issue).

Rosner, D. E. and Allendorf, H. D., "High-Temperature Oxidation of Carbon by Atomic Oxygen," AeroChem TP-110, March 1965; CARBON (in press).

Rosner, D. E. and Allendorf, H. D., "High-Temperature Kinetics of Graphite Oxidation by Dissociated Oxygen," AIAA J. 3, 1522-1523 (1965).

Rosner, D. E. and Allendorf, H. D., "Oxidation Kinetics of Graphite at Surface Temperatures Above 1000°K,"* J. Electrochem Soc. 112, 653-654 (1965).

Rosner, D. E. and Allendorf, H. D., "Kinetics of the High-Temperature Oxidation of Molybdenum by Dissociated Oxygen," J. Chem. Phys. 40, 3441-3442 (1964).

Rosner, D. E. and Allendorf, H. D., "Discussion of 'Oxidation of Molybdenum, 550°C to 1700°C,'" J. Electrochem Soc. 111, 759-761 (1964).

Rosner, D. E., "Convective Diffusion as an Intruder in Kinetics Studies of Surface-Catalyzed Reactions,"* AIAA J. 2, 593-610 (1964).

B. Reports and Documents

Rosner, D. E., AFOSR 1965 Research Inventory: Kinetic and Aerodynamic Aspects of the Oxidation of Materials by Dissociated Gases, TN-84, November 1965.

Rosner, D. E. and Allendorf, H. D., "Chemical Kinetic Aspects of the Oxidation of Materials by Partially Dissociated Gases," AeroChem TP-124, December 1965.

Rosner, D. E. and Allendorf, H. D., "Chemical Kinetic Aspects of the Ablation of Molybdenum, Tungsten, and Graphite in Partially Dissociated Oxygen," (extended abstract) AeroChem TN-80, August 1965.

Rosner, D. E. and Allendorf, H. D., "Kinetic and Aerodynamic Aspects of the Oxidation of Materials by Partially Dissociated Gases," AeroChem TN-76, May 1965.

Rosner, D. E., "AFOSR 1964 Research Inventory: Kinetic and Aerodynamic Aspects of the Oxidation of Metals by Partially Dissociated Oxygen," AeroChem TN-72, November 1964.

Rosner, D. E. and Allendorf, H. D., "Kinetic and Aerodynamic Aspects of the Oxidation of Metals by Partially Dissociated Oxygen," AeroChem TN-61, May 1964; DDC AD 438 927.

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*jointly supported by contract AF 49(638)1138.

Rosner, D.E., "Oxidation of Metals by Partially Dissociated Oxygen," AeroChem TL-161, November 1963, Quarterly Letter Report No. 4: Contract AF 49(6381195.

Rosner, D.E., "Oxidation of Metals by Partially Dissociated Oxygen," AeroChem TL-145, August 1963, Quarterly Letter Report No. 3: Contract AF 49(368)1195.

Rosner, D.E., "Oxidation of Metals by Partially Dissociated Oxygen," AeroChem TL-129, May 1963, Quarterly Letter Report No. 2: Contract AF 49(638)1195.

Rosner, D.E., "Oxidation of Metals by Partially Dissociated Oxygen," AeroChem TL-115, February 1963, Quarterly Letter Report No. 1: Contract AF 49(638)1195.

C. Oral Presentations

Rosner, D.E., "Chemical Aspects of Convective Heat Transfer and Materials Ablation,"* Paper presented at Session III of Symposium Series of Problems of Re-entry and Hypersonic Flight; AIAA, Long Island Chapter, September 21, 1965, Farmingdale, Long Island.

Rosner, D.E. and Allendorf, H.D., "Kinetic and Aerodynamic Aspects of the Attack of Refractory Materials by Dissociated Gases,"* Paper presented at the 6th AFOSR Contractor's Meeting on Chemical Kinetics of Propulsion, New York City, September 20-21, 1965.

Rosner, D.E., "Kinetic and Aerodynamic Aspects of Materials Ablation in Dissociated Gases,"* Paper presented at the Conference on Aerospace Engineering and the Ninth (AIAA) Minta Martin Lecture, Aerospace Engineering Department, University of Maryland (College Park, Md.) March 16, 1965.

Rosner, D.E., "Aerodynamic and Kinetic Aspects of Ablation in Partially Dissociated Gaseous Environments,"* Mechanical and Metallurgical Engineering Seminar, Polytechnic Inst. of Brooklyn, February 26, 1965.

Rosner, D.E. and Allendorf, H.D., "Kinetic and Aerodynamic Aspects of the Oxidation of Molybdenum and Tungsten by Partially Dissociated Oxygen," Paper presented at the 94th Annual Meeting of the AIME, Metallurgical Society: Symposium on Gas-Solid Reactions at High-Velocity Flow Conditions, Chicago, Ill., February 18, 1965.

Rosner, D.E. and Allendorf, H.D., "Kinetic and Aerodynamic Aspects of the Oxidation of Metals by Partially Dissociated Oxygen," Paper presented at the 5th AFOSR Contractor's Meeting on Chemical Kinetics of Propulsion, INTA Madrid, Spain, September 2-4, 1964.

Rosner, D.E. and Allendorf, H.D., "Kinetic and Aerodynamic Aspects of the Oxidation of Refractory Metals by Partially Dissociated Oxygen," Paper presented at the 4th AFOSR Contractor's Meeting on Chemical Kinetics of Propulsion, UCLA, Los Angeles, AFOSR 5423, DDC AD 426 541, September 5, 6 1963.

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*jointly supported by Contract AF 49(638)1138.

D. General

Rosner, D. E., "News Release on Refractory Metal Oxidation by O Atoms," AeroChem Research Laboratories, Inc., 3 June 1964; Appeared, e.g., in Materials in Design Engineering, September 1964, page 15.

IV. ACKNOWLEDGEMENTS

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"KINETIC AND AERODYNAMIC ASPECTS OF THE OXIDATION OF MATERIALS BY PARTIALLY DISSOCIATED GASES"

Final Report

Dr (PI)

Rosner, Daniel ~~E~~ A and Allendorf, H. Donald

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A synopsis is presented of the most significant results of a three-year research program carried out at this laboratory on the oxidation kinetics of refractory materials in dissociated gases. Microwave-discharge fast flow system techniques, coupled with electrical resistance heating and monitoring of the reacting specimens have been used throughtout. Experimental results are included for the attack of (a) polycrystalline molybdenum, tungsten, graphite, iridium and vitreous boron by atomic oxygen, (b) polycrystalline molybdenum and nickel by atomic chlorine, and (c) polycrystalline molybdenum by hydroxyl radicals. Reactant (O, Cl, and OH) partial pressures were of the order of 10^{-3} to 5×10^{-2} and surface temperatures were within the range 400 to 2600°K. A chronological list is provided of the seven publications and eleven reports describing these results and the underlying methods in greater detail.

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