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THE RATE OF OXIDATION OF THE BASAL AND PRISMATIC SURFACES OF
PYROLYTIC GRAPHITE IN THE TRANSITION REGIME BETWEEN CHEMICAL
AND DIFFUSIONAL CONTROL

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Abstract

Reaction rates of oxygen with the basal and prism faces of pyrolytic graphite have been measured using a rotating disk contactor. Temperatures ranged from 1100 to 2000°K and oxygen concentrations from 0.05% to 1% in helium and argon at atmospheric pressure were employed. The intrinsic rate of the surface reaction and the magnitude of the mass transfer coefficients attainable from the rotating disk placed most of the experiments in the transition regime between the limits of chemical and diffusional control of the overall process. Surface chemical rate constants were extracted from the data with the aid of the theory of rotating disk mass transfer. Kinetic expressions for the oxidation of the basal and prism planes were obtained. The rate expression of Strickland-Constable fell in between the rates determined here for the basal and prism orientations.

1. Introduction

For some time, the role of gas phase mass transfer in limiting the rate of reaction of oxygen with graphite has been appreciated but has not been treated quantitatively in evaluating kinetic data. A very complete review of the coupling of surface reactions with reactant-product transport to and from the surface has been prepared by Rosner.¹ In the case of graphite oxidation, three general philosophies have been adopted to permit boundary layer mass transfer of reactant oxygen to the surface to be disentangled from overall rate measurements.

(1) Inasmuch as the gas diffusivity varies inversely as the total pressure, transport limitations can be eliminated by removing inert carrier gases from the system and restricting oxygen pressures to ~ 1 torr.^{2,3}

(2) The mass transfer contribution to the reaction rate in atmospheric pressure gases can be reduced by employing a flow system which insures a high boundary layer mass transfer rate at the reactant surface. (More precisely, the transition from surface control to diffusional control is pushed to higher temperatures). The high speed jet technique of Strickland-Constable and coworkers is an example of this approach.^{4,5}

(3) Whether or not explicit precautions to prevent diffusional control of the reaction have been taken, a number of tests have been employed to detect the presence of transport resistance. The dependence of the overall rate upon gas flow velocity and the nature of the inert gas mixed with

the oxygen have been used as indicators of diffusion limitations.^{2,4-6} If no such experimental tests have been conducted, the presence or absence of transport resistances has been inferred by order-of-magnitude estimates of the mass transfer rate⁷ or by examining the temperature dependence of the apparent activation energy of the reaction. In contrast to the usually rather strong temperature dependence of most heterogeneous gas-solid reactions, gas phase mass transfer coefficients are weakly (if at all) temperature dependent. Consequently, the onset of diffusion control is usually signalled by a reduction in the apparent activation energy as the temperature is increased. As pointed out by Rosner and Allendorf,⁸ this criterion cannot be applied to the graphite-oxygen reaction because the surface reaction also passes through a maximum at approximately the same temperature where diffusional limitations in common flow systems become significant. Maahs⁹ has reviewed the interplay between mass transport of oxygen to the graphite surface and the rate of the surface reaction.

One object of the present study was to investigate the reaction of oxygen and pyrolytic graphite in a flow system which permitted quantitative evaluation of the mass transfer component of the total resistance. The flow geometry chosen consists of a disk of the reactant solid rotating in a quiescent atmosphere of the reactant gas. The hydrodynamics of the rotating disk flow system are well-known (it is one of the few exact solutions of the Navier-Stokes equations¹⁰). Since the

velocity field in the vicinity of the reacting surface is known, the mass transfer rate can be calculated from first principles by solving the diffusion-convection equation. Such a solution contains no adjustable parameters; the mass transfer coefficient is determined once the disk rotational speed and the gas diffusivity are specified. The accuracy of the predicted mass (or heat) transfer coefficients for a rotating disk have been verified experimentally many times, so that overall rate measurements in the transition regime between surface chemical and transport control can be purged of diffusion effects. The use of the rotating disk as a tool in gas-solid reaction studies permits reliable surface kinetics to be obtained even when, by all of the measures cited in (3) above, mass transport and surface reaction provide resistances of comparable magnitude. The maximum temperature at which kinetic data can be extracted from overall rate measurements occurs when ~90% of the resistance is due to gas phase diffusion. At higher temperatures, the precision of the surface rate information obtained from the data becomes poor.

The rotating disk is a relatively simple experimental device. It has previously been utilized to study the iodine-germanium reaction¹¹ and the oxidation of molybdenum,¹² both of which are subject to substantial diffusion control at temperatures attainable in the experiment.

The rotating disk possesses two convenient features not available in other quantitatively describable flow systems

(e.g., the flat plate or stagnation point flow). First, the gas boundary layer is generated by moving the solid, which is simpler (if the reactant gas is to be purified or preheated) and cheaper (unless the reactant gas is air) than moving large quantities of gas past the stationary solid surface. Second, the mass transfer rate (and hence the surface reaction) is independent of radial position on the disk surface (or, the surface is said to be "uniformly accessible"). Thus, disks of any size can be used and simple weight loss measurements suffice to fix the rate of reaction.

The second objective of our study was to determine the difference in the reactivity of the basal and edge faces of pyrolytic graphite towards oxygen. The basal face consists of the hexagonal network of carbon atoms in the plane perpendicular to the "c" axis of the graphite structure. Surfaces exposing this face can be obtained by cleaving pyrolytic graphite blocks or simply by utilizing the surface of the as-fabricated material which was parallel to the deposition substrate.

Cutting a plane surface parallel to the "c" axis (i.e., perpendicular to the "a" direction) does not produce a unique crystallographic surface. Instead, one obtains a mixture of the "zig zag" faces consisting of the peaks and valleys of the basal plane hexagons and "armchair" faces composed of the sides of the hexagons.¹³ This mixture is commonly referred to as the edge or prismatic face of graphite.

It has been shown by many workers (e.g., ref. 2) that the

basal planes of pyrolytic graphite are much less reactive towards oxygen than is isotropic, polycrystalline graphite. The higher reactivity of the latter material is often attributed to the exposed prismatic surfaces of the sample.

A substantial number of measurements of the ratio of the oxidation rates along the "a" and "c" directions have been reported.¹⁴ However, these were determined by microscopically following the growth of single hexagonal etch pits in single crystal graphite natural graphite flakes which had been cleaved along a basal plane and oxidized under relatively mild conditions (temperatures below 1100°K).¹⁵ The rate of pit growth in one of the "a" directions in such experiments has little in common with the attack of an entire prismatic face under conditions of far greater carbon removal rates.

Knowledge of the rates of oxidation of these two well-defined (or at least experimentally reproducible) faces is important in interpreting the kinetics observed on specimens of pyrolytic graphite in which both surfaces are exposed. The kinetic expression commonly accepted⁹ as the most reliable estimate of the oxidation rate of pyrolytic graphite at high temperatures is the one due to Strickland-Constable and coworkers.^{4,5} In their experiments, a high speed jet of oxygen impinged upon a rod in which the basal planes were parallel to the original surface. As reaction proceeded, a crater was gouged out of the sample, so that the actual reaction surface was a mixture of basal and prismatic planes. The mix undoubtedly changed as

erosion proceeded.

Levy and Wong⁶ and Horton⁷ very approximately determined the relative rates of reaction of the edge and basal planes. They were able to qualitatively ascertain that the prismatic face reacted more rapidly than the basal face, and that the discrepancy increased with increasing temperature.

In the work reported here, individual rate expressions for the two faces are reported.

2. Experimental

The apparatus shown in Fig. 1 is similar to that described in reference 12. A variable speed hysteresis synchronous motor rotates a tantalum shaft mounted on water-cooled bearings. A boron nitride holder is screwed to the end of the shaft. The holder contains a circular hole 1 cm in diameter and 0.5 cm deep to receive the graphite specimens. The entire assembly is enclosed in a quartz reaction chamber so as to expose the disk surface to a controlled flow of oxygen-argon or oxygen-helium mixtures. The flow rates are large enough to prevent back-mixing of the oxygen-depleted gas spun off the disk with the feed gas, but small enough to prevent stagnation point-type flow from overwhelming the desired rotating disk flow patterns. The flow guide in Fig. 1 serves to generate the desired approach velocity of the gas to the disk (~ 30 cm/sec) over an area just a bit larger than the area of the reacting sample. This feature conserves gas. By way of comparison, the jet technique of

reference 5 required gas velocities of $\sim 10,000$ cm/sec at the specimen surface.

All experiments were conducted at a rotational speed of 9600 rpm, where forced convection dominates over natural convection but the flow is still laminar.¹² The disk is heated by a high frequency induction heater.

Surface temperatures are measured by the optical pyrometer, prism and window combination depicted at the top of Fig. 1. Because of the highly anisotropic thermal and electrical properties of pyrolytic graphite, temperature measurements made by sighting on a black body hole drilled in the sample were found to be unreliable (heat from the rf field of the induction heater was not generated uniformly in the sample). In addition to window and prism corrections, brightness temperatures were converted to surface temperatures by using emissivities at 0.65 microns of 0.65 for the basal plane and 0.75 for the edge planes.¹⁶

Fig. 2 shows an exploded view of the method of mounting specimens with basal plane reaction surfaces. The disks with basal planes parallel to the surface fit into a polycrystalline graphite ring which was then slipped into the boron nitride holder. The rf field of the induction heater deposited energy predominantly in the graphite rather than the boron nitride. Consequently, the graphite ring was $\sim 300^\circ\text{C}$ hotter than the holder during operation, and because of thermal expansion, a ring which fit loosely at ambient temperature was held tightly

in the holder at operating temperature. The basal plane disk and the ring were held together by a small tungsten pin. This arrangement prevented the disk from flying out of the holder while spinning.

The purpose of the polycrystalline graphite ring between the specimen and the holder was to reduce oxidation of the edge of the specimen, part of which consisted of exposed prism planes. Without the ring, attack of the edge of the disk contributed most of the weight loss. During operation with the ring, the inner surface of the ring oxidized instead of the outside surface of the specimen with which the ring was in contact. This device permitted measurement of basal plane surface kinetics to be made up to oxygen concentrations of $\sim 0.5\%$. For higher oxygen contents, the ring arrangement of Fig. 2 no longer prevented severe edge attack.

Experiments with disks with prism plane surfaces did not have the edge reaction problem described above because the reactivity of the edge was less than or comparable to that of the top surface. However, the anisotropic properties of pyrolytic graphite caused a problem in uniform disk heating. The thermal conductivity parallel to the basal planes is very good, but the conductivity perpendicular to the basal planes it is poor. Upon heating a prism plane specimen directly by induction, a small strip along the direction of the basal planes in the center of the disk was hotter than the rest of the surface. When the disk was held in a polycrystalline graphite ring

(as in Fig. 2), the center strip was considerably colder than the rest of the disk surface. As a compromise, the elliptically shaped disk heater shown in Fig. 3 was utilized. With the basal planes of the prism face specimen oriented parallel to the major axis of the elliptical disk heater, uniform temperature distribution was achieved (approximately 10% of the surface area of the disk was $\sim 20^{\circ}\text{C}$ hotter than the rest). The disk specimen was slipped into a hole in the heater and held in position by a tungsten pin. The disk-disk heater combination was fit into the boron nitride holder.

All experiments were performed on pyrolytic graphite obtained from the Union Carbide Company. The density of the material was 2.17 gms/cm^3 (96% of theoretical density). Neutron activation analysis of the material revealed less than 1 ppm of metallic impurities, sodium being the most abundant. Reference 17 gives additional properties of the pyrolytic graphite used in this study.

The surfaces of the specimen were polished with 6 micron diamond polishing compound, washed in acetone, weighed and mounted in the appropriate polycrystalline graphite heater (the ring for basal plane orientation and the elliptical piece for prism plane orientation).

The reactant gas consisted of commercial mixtures of oxygen in either argon or helium. Oxygen concentrations (analyses provided by the supplier) ranged from 0.05% to 1%. The experiments were conducted at a total gas pressure of 1 atm.

The water vapor and other condensible impurities in the gas were removed by a liquid nitrogen cold trap.

To begin an experiment, the disk assembly was enclosed in the quartz reaction chamber and pure argon flow was started. The disk was brought to a rotational speed of 9600 rpm. The induction heater was turned on and the disk temperature was adjusted to the desired value. After the temperature had stabilized, the argon flow was turned off and a fast flush of reactant gas was introduced. Upon completion of the fast flush, the reactant gas flow was reduced to the normal rate. The run was terminated by shutting off the reactant gas flow and simultaneously fast flushing the system with pure argon. The disk was weighed after the experiment to determine weight loss. Each experiment lasted from 5 to 30 min. Since the weight loss was found to be linear with respect to the duration of the run, oxidation rates were deduced from a single experiment.

3. Surface Morphology Changes on Oxidation

Basal Plane Figure 4 shows the condition of the basal plane surface after light oxidation (4a) and extensive attack (4b). The original polished specimen is not shown, since photomicrographs under similar magnification showed no structural features of note. Oxidation of the basal plane produced nearly circular etch pits rather than the hexagonal pits invariably observed in the low temperature oxidation of cleaved natural crystals.¹⁵ The diameter of the circular pits

in Fig. 4a was always larger than their depth. The size and density of pits increased with extent of oxidation. Ultimately, the pits coalesced, new pits began growing in old ones, and a state of "equilibrium roughness" appeared to have been attained. The rate of oxidation followed this evolution of surface morphology. The rate of an initially polished sample increased with time for a fixed temperature and oxygen pressure (this effect was measured by determining the weight loss for a succession of equal-time runs using the same disk). The effect of carbon burnoff on the rate (in the chemically controlled region) is shown in Fig. 5. When the surface attained equilibrium roughness, the oxidation rate stabilized. Weight loss measurements subsequently were reproducible to within 10%. All rate measurements for basal plane specimens refer to equilibrium surfaces.

Prism Plane Figure 6 shows a photomicrograph of a polished prism plane disk. The dark spots in Fig. 6a may represent small cavities in the specimen (these were not visible in similar polished basal plane specimens, however). Fig. 6b shows a stereo pair of scanning electron micrographs of an oxidized prism plane surface. These surfaces did not respond to oxidation by producing etch pits. Rather, the surface developed ridges and valleys along the direction of the basal planes (which are perpendicular to the oxidation surface). Most of the ridges shown in Fig. 6b are $\sim 5000\text{\AA}$ apart. This distance may represent the height that the growth cones attained

during the deposition process before new cones nucleate on top of the old ones. There is one very large canyon running from lower left to upper right in Fig. 6b. The depth of this groove is approximately the same as its width. Contrary to the basal plane surfaces, the oxidation rate was not dependent upon the extent of surface roughening. No surface stabilization was needed and all rate measurements were reproducible to within 5%.

4. Results

The reaction rates are plotted in Arrhenius fashion for a reactant gas consisting of 0.052% oxygen in helium in Fig. 7. Figures 8-11 show the rates for four mixtures of oxygen in argon. The total pressure in all experiments was 1 atm. The data for both the prism and basal planes approach plateaus at high temperature. For reasons which will be discussed later, we believe that the asymptotes attained in the prism plane measurements represents complete control of the reaction by transport of oxygen through the gas boundary on the disk. These limiting prism plane rates have been labelled \dot{m}_{DC} , where the subscript DC stands for "diffusion control".

The reaction rates on basal plane specimens also approach a limiting value at high temperatures. However, this limit is ~40% lower than the corresponding limit attained by the prism plane samples. Inasmuch as the diffusion-limited rate is independent of the nature of the reaction surface or the

surface chemical kinetics, we conclude that the plateau attained by the basal plane data is a characteristic of the surface reaction and is not due to diffusion control.

The points on any one of the Arrhenium plots do not represent experiments conducted at constant surface partial pressure of oxygen, even though the bulk oxygen concentration was fixed for the entire series of runs. As the temperature of the experiment is increased and the reaction rate increases correspondingly, the surface becomes progressively more starved of oxygen, until at the highest temperatures, the oxygen partial pressure at the surface is zero.* In order to isolate the surface chemical kinetics from such plots, we must calculate the partial pressure of oxygen at the disk surface for each experiment. This is accomplished by utilizing the theory of mass transfer on a rotating disk.

The rate of oxygen transport to the disk surface may be written as:

$$N = k_g (p_\infty - p_o) \quad (1)$$

* Strictly speaking, the reaction attains local chemical equilibrium at the gas-solid surface. The free energy change for the reaction $2C(s) + O_2(g) = 2CO(g)$ is large and negative at the temperatures used in the experiments reported here. Hence, the equilibrium partial pressure of oxygen at the surface is very small and may be taken as zero for the purpose of computing diffusion rates.

where

N = mass transfer flux, gm moles oxygen/cm²-sec

k_g = mass transfer coefficient, gm moles/cm²-sec-atm

p_∞, p_o = partial pressures of oxygen in the bulk gas and at the surface, respectively, atm.

Since the mass transport and surface reaction processes occur in series, the flux of oxygen through the boundary layer is related to the measured rate of reaction by:

$$\dot{m} = 2M_C N \quad (2)$$

where

\dot{m} = gms carbon removed/cm²-sec

M_C = atomic weight of carbon.

The factor of two on the right of Eq(2) assumes that one molecule of oxygen removes two atoms of carbon, or that carbon monoxide is the sole reaction product. Had CO₂ been the sole product, the factor of two would be replaced by unity. The references cited earlier all agree that CO is the dominant, if not the sole reaction product at the temperatures at which the present experiments were conducted. Thermochemically, the equilibrium $CO(g) + \frac{1}{2}O_2(g) = CO_2(g)$ is far to the left even though the oxygen partial pressure at the disk surface is reduced to very small values by approach to (or perhaps

attainment of) equilibrium of the reaction $C(s) + \frac{1}{2}O_2(g) = CO(g)$.

In the region of complete diffusion control, $p_o = 0$ and Eqs(1) and (2) become:

$$\dot{m}_{DC} = 2M_C k_g p_\infty \quad (3)$$

According to the theory of convective diffusion on a rotating disk, the mass transfer coefficient is given by:^{11,12}

$$k_g = \left[\frac{1}{RT_o} \left(\frac{\Omega D_o}{2\pi} \right)^{1/2} \right] \left[\left(\frac{D_o}{D_f} \right)^{1/2} \frac{T_f}{T_o} \right] \quad (4)$$

where:

R = gas constant, cm^3 -atm/gm mole- $^\circ K$

T_o = surface temperature, $^\circ K$

T_f = film temperature, equal to $\frac{1}{2}(T_o + T_\infty)$, $^\circ K$

D_o, D_f = diffusion coefficients of oxygen in the inert diluent gas at the surface and film temperatures, respectively, cm^2 -sec.

The first bracketed term on the right of Eq(4) is the mass transfer coefficient for an isothermal boundary layer at temperature T_o . The last bracketed term approximately corrects for the effect of property variations due to the steep temperature gradients in the boundary layer (in our experiments, the gas was not preheated to the disk temperature).

It may be seen from Eq(4) that if the diffusion coefficient

varies as the square of the absolute temperature, k_g is completely independent of both disk temperature and bulk gas temperature. According to estimates based upon kinetic theory¹⁸ the diffusion coefficients of oxygen in argon and helium vary as the 1.67 and 1.79 powers of the temperature, respectively. These exponents are sufficiently close to two that with negligible error we may consider the mass transfer coefficient to be temperature independent. This is the only feature of rotating disk mass transfer theory which is needed to deduce surface chemical rates from the data in Figs. 7-11. If k_g in Eq(3) (which pertains to high temperatures) is equal to k_g in Eq(1) (when applied to experiments in the transition regime), then this parameter may be eliminated from Eqs(1)-(3) and the surface partial pressure of oxygen written as:

$$p_o = p_\infty (1 - \dot{m}/\dot{m}_{DC}) \quad (5)$$

The three quantities on the right of Eq(5) are determined in the course of the experiments (\dot{m}_{DC} is taken from the horizontal lines, which were fit by eye, on the Arrhenius plots of Figs. 7-11).

Armed with the surface temperature and surface oxygen partial pressure corresponding to each measured reaction rate, kinetic expressions which purport to represent the true surface chemical reaction can be fit to the data.

We have fit the reaction rate data, in the form of $\dot{m}(p_o, T_o)$,

to the kinetic expression resulting from the two-site model originally proposed by Blyholder et al¹⁹ and subsequently modified by Nagle and Strickland-Constable⁴ to include thermal conversion of one type of site to the other. The rate expression is:⁵

$$\dot{m} = M_c \left\{ \frac{k_A k_B p_o^2}{(1 + k_z p_o)(k_T + k_B p_o)} + \frac{k_T k_B p_o}{k_T + k_B p_o} \right\} \quad (6)$$

The eight parameters in the four rate constants in Eq(6) which were obtained by Strickland-Constable and coworkers are:

$$\begin{aligned} k_A &= 20 \exp(-30,000/RT_o) \\ k_B &= 4.46 \times 10^{-3} \exp(-15,200/RT_o) \\ k_T &= 1.51 \times 10^{-5} \exp(-97,000/RT_o) \\ k_z &= 21.3 \exp(4,100/RT_o) \end{aligned} \quad (7)$$

We have appended subscript "o" to the oxygen pressure and temperature symbols in Eqs(6) and (7) to emphasize that these variables refer to surface conditions. It is clear that our data cannot be represented by the single set of rate constants of Eq(7), since the rates of reaction for the two orientations of pyrolytic graphite were found to be distinctly different.

We have fit the basal plane data points from Figs. 7-9 to Eq(6) and determined the following set of constants:

$$\begin{aligned}
 k_A &= 15 \exp(-25,000/RT_0) \\
 k_B &= 4.46 \times 10^{-3} \exp(-15,200/RT_0) \\
 k_T &= 1.51 \times 10^{-5} \exp(-100,000/RT_0) \\
 k_z &= 10,000
 \end{aligned}
 \tag{8}$$

The rate law described by Eqs(6) and (8) is valid for temperatures from 1100° to 1800°K and surface oxygen pressures from 5×10^{-4} to 2×10^{-3} atm.

Since the temperature range over which we have reasonably precise kinetic data (i.e., not obscured by diffusional resistances) is rather small, not all of the constants in the kinetic expression were changed from Strickland-Constable's values in obtaining the best fit. Moreover, our measurements on the basal plane at low oxygen concentrations are in good agreement with the original Strickland-Constable rate expression (see dashed lines in Figs. 7 and 8), so that the constants are only slightly different from the original set. The set of constants in Eq(8) is by no means the only combination that could fit our data. However, as shown by the solid lines through the basal plane points of Figs. 7-9, the fitting is satisfactory. Equally acceptable agreement is obtained with either argon or helium diluents. The kinetic expression misses all but the lowest temperature data points at 0.5% oxygen in argon (Fig. 10). At these high oxygen concentration and high temperatures, the edge attack was observed to be very severe, and the measured rates were larger than one would expect if reaction was restricted

to the basal plane disk surface. Edge attack precluded any reliable basal plane measurements with 1.0% oxygen in argon.

The prism plane data do not show enough structure (i.e., levelling off before the diffusion control plateau) to warrant an eight parameter fit. These data were fit to the following simplified form of Eq(6):

$$\dot{m} = M_c \left[\frac{k_A p_o}{1 + k_z p_o} \right] \quad (9)$$

which is equivalent to neglecting the B sites in the Strickland-Constable model. The rate constants obtained from the prism plane data of Figs. 7-11 are:

$$\begin{aligned} k_A &= 2.5 \times 10^4 \exp(-44,300/RT_o) \\ k_z &= 4.9 \times 10^4 \exp(12,200/RT_o) \end{aligned} \quad (10)$$

The kinetic expression of Eqs(9) and (10) is based upon measurements from 1100° to 1550°K and surface oxygen pressures from $\sim 5 \times 10^{-5}$ to 10^{-2} atm. The upper temperature limit corresponds to the temperature at which diffusion contributed $\sim 90\%$ of the overall resistance. The lower pressure limit corresponds to the estimated surface oxygen pressure when the specimen is exposed to a gas containing 0.05% oxygen at 1550°K. The solid lines through the prism plane data points on Figs. 7-11 show the agreement between the simplified rate expression and experimental rates.

Very little mechanistic information can be obtained from the magnitudes of the pre-exponential factors or the activation energies in the empirical rate laws (ours or Strickland-Constable's). The constant k_A , for example, is supposed to represent the rate of dissociative chemisorption of molecular oxygen on A sites. Since it is quite unlikely that this elementary step is confronted by an energy barrier of 25-40 kcal/mole, the activation energy of k_A probably reflects an intermediate step involving transition of chemisorbed oxygen atoms to adsorbed carbon monoxide molecules, which may be highly activated. Such a step is not explicitly considered in the Strickland-Constable model.

The predictions of the original Strickland-Constable rate expression is also graphed in Figs. 7-11 for comparison with the rate expressions derived in the present study. In plotting the Strickland-Constable rate, p_o in Eq(6) was obtained from Eq(5), in which \dot{m}_{DC} was taken from the asymptotes shown in Figs. 7-11. Determination of \dot{m} as a function of T_o for a fixed bulk oxygen pressure must be done by trial and error. The Strickland-Constable rate expression agrees with the basal plane data and our best fit curve at the lowest oxygen pressure. However, as the bulk oxygen concentration is increased, the Strickland-Constable curve drifts towards the prism plane results. Such behavior is not difficult to rationalize, inasmuch as higher oxygen pressures mean higher reaction rates and consequently, larger craters in the Strickland-Constable

experiments. The inner surface of the craters where reaction occurred in Strickland-Constable's apparatus undoubtedly contained a mixture of prism and basal planes (since the surface was curved), with the proportion of prism planes increasing as the crater deepened. As a result one would expect that the more rapid oxidation accompanying large oxygen pressures to reflect reaction on a surface which was more prism-like than the less distorted surfaces subjected to milder oxidation conditions.

The differences between the three kinetic expressions may best be illustrated if the variable oxygen pressure aspect implicit in the curves of Figs. 7-11 is eliminated. To accomplish this, we have plotted the pure surface kinetic controlled rates given by Eqs(6)-(10) for two constant values of p_o in Fig. 12.

The ratio of oxidation rates of the prism and basal planes is a function of both oxygen pressure and temperature, as shown in Table 1. The reaction rate on the basal plane is nearly zero order in oxygen pressure over most of the temperature range investigated. The prism plane reaction exhibits an effective order decreasing from 0.6 at 1100°K to 0.25 at 1500°K. The rate expression due to Strickland-Constable falls between the basal and prism plane rates, lying closer to the basal plane rate at low oxygen pressures but approaching the prism plane rate at high oxygen pressures.

5. Diffusion-Limited Oxidation

The final aspect of the data interpretation which needs explanation is the justification for referring to the high temperature plateaus attained by the rates on the prism planes as diffusion controlled rates. The theoretical diffusion controlled rate is given by Eqs(3) and (4). Table 2 shows a comparison of the experimental values of \dot{m}_{DC} obtained from Figs. 7-11 with the calculated values. The latter were computed for a bulk gas temperature of 300°K and a surface temperature of 1650°K for helium and 1500°K for argon (the choice of these temperatures has a very minor effect on the calculated mass transfer coefficients). The diffusion coefficients were estimated by the methods described in reference 18.

The experimental diffusion controlled rate is approximately twice as large with helium diluent as with argon diluent, in very good agreement with theory (this ratio is essentially equal to the square root of the ratio of the diffusion coefficients of oxygen in helium and argon). The theoretical rates are on the average 30% smaller than the measured rates at high temperatures. Part of this discrepancy is undoubtedly due to edge effects, which in previous rotating disk studies has accounted for a ~15% systematic error.^{11,12} The remaining 15% discrepancy in the present experiments may be due to one or more of the following causes: (1) larger than normal edge effects because of the somewhat smaller disks used in the present experiments compared to the disks used in previous studies; (2) larger than

normal temperature non-uniformities over the surface were encountered here because of the difficulty in heating pyrolytic graphite. This non-isothermality may have induced a small amount of natural convection mass transfer which would have added to the forced convection component given by Eq(4); (3) the gas analyses provided by the supplier of the gas mixtures may have been too low. We cannot determine which (if any) of these possibilities is the most likely source of the lack of perfect agreement between experimental and predicted diffusion controlled rates, but in any case, the residual gap between theory and experiment ($\sim 15\%$) is quite small.

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Table 1. Ratio of Oxidation Rates of the Prism and Basal Planes

$T_o, ^\circ K$ p_o, atm	1100	1500
10^{-3}	2.5	18
10^{-2}	10	29

Table 2. Diffusion Controlled Rates

oxygen concentration, %	$2M_C k_g = \dot{m}_{DC} / P_\infty, gm/atm-cm^2-sec \times 10^3$	
	experimental	theory
	<u>Helium</u>	
0.052	10.3	7.4
	<u>Argon</u>	
0.1	5.0	
0.2	5.4	
0.5	6.4	3.9
1.0	5.6	

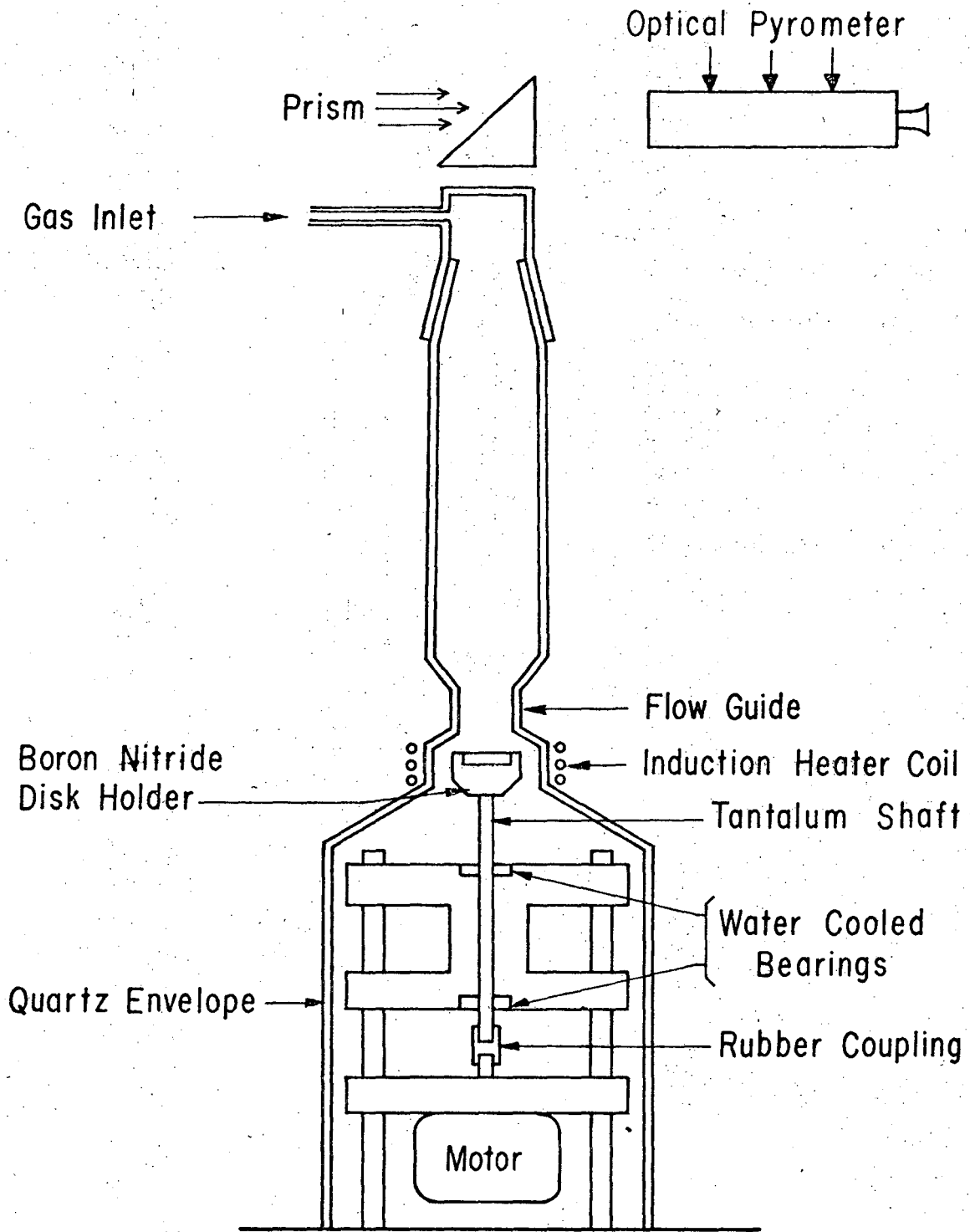
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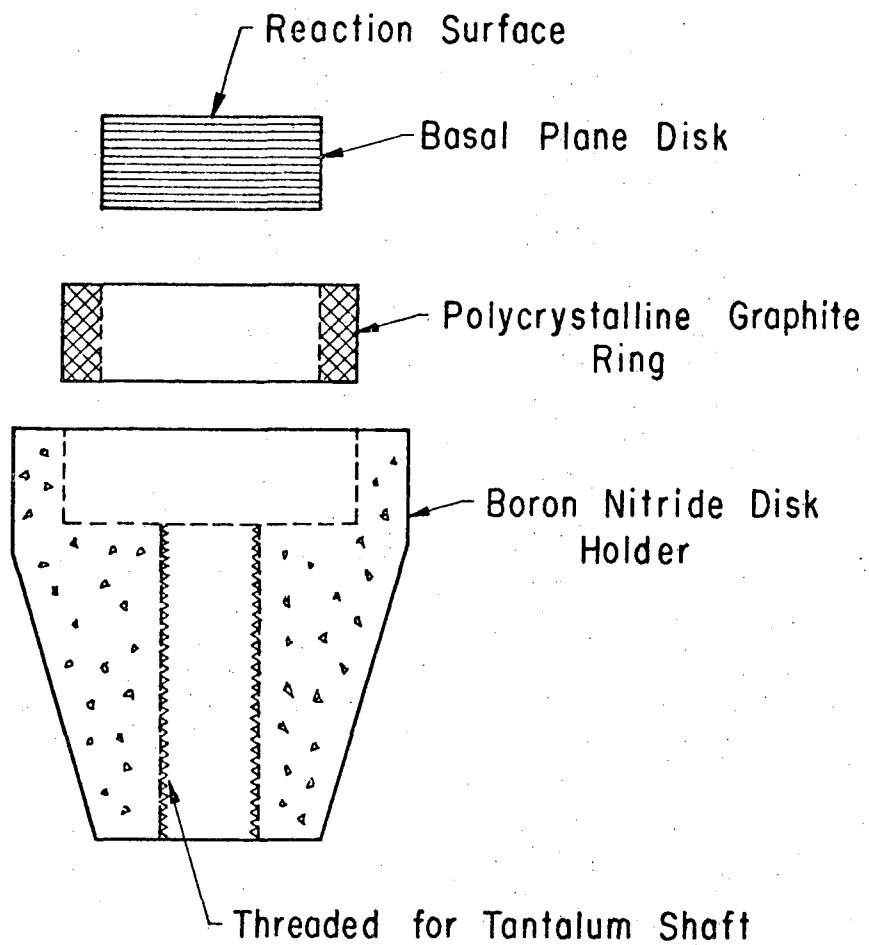
FIGURE CAPTIONS

1. Schematic of the rotating disk apparatus.
2. Disk mounting arrangement for basal plane specimens.
3. Disk mounting arrangement for prism plane specimens (the boron nitride disk holder is not shown).
4. Photomicrographs of basal plane surfaces. (a) slightly oxidized, (b) heavily oxidized.
5. Attainment of stabilized reaction rates in low temperature experiments with basal plane specimens. $T_0=1225^\circ\text{K}$, 0.5% oxygen in argon.
6. The prism plane surface. (a) as polished; (b) oxidized (stereo pair).
7. Reaction rate - 0.052% oxygen in helium.
8. Reaction rate - 0.1% oxygen in argon.
9. Reaction rate - 0.2% oxygen in argon.
10. Reaction rate - 0.5% oxygen in argon.
11. Reaction rate - 1.0% oxygen in argon.
12. Comparison of rate expressions for constant oxygen surface pressures.



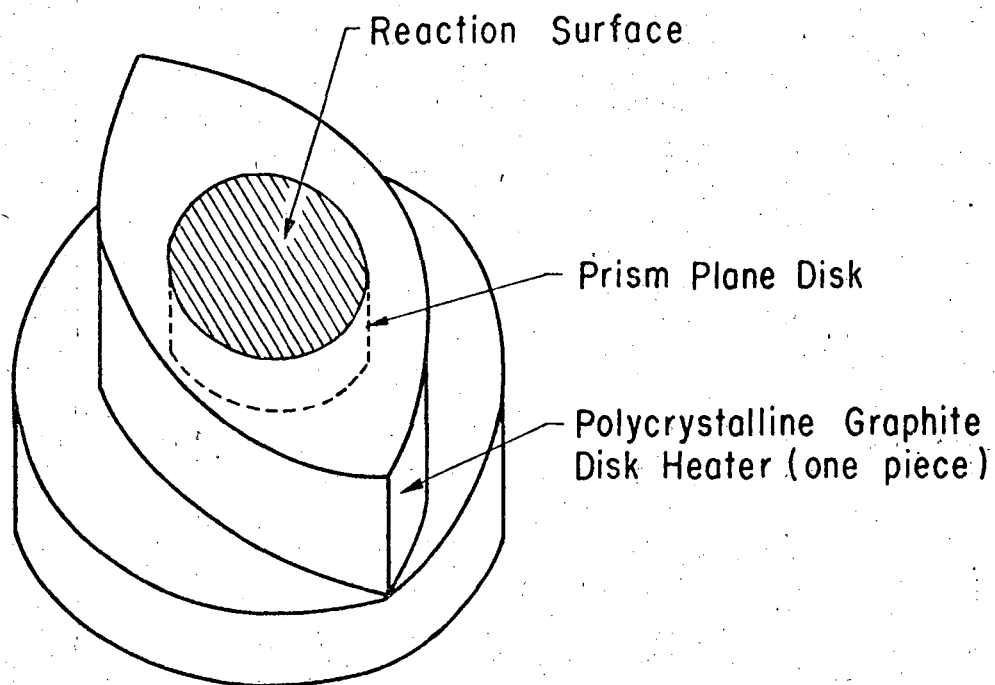
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Fig. 1.



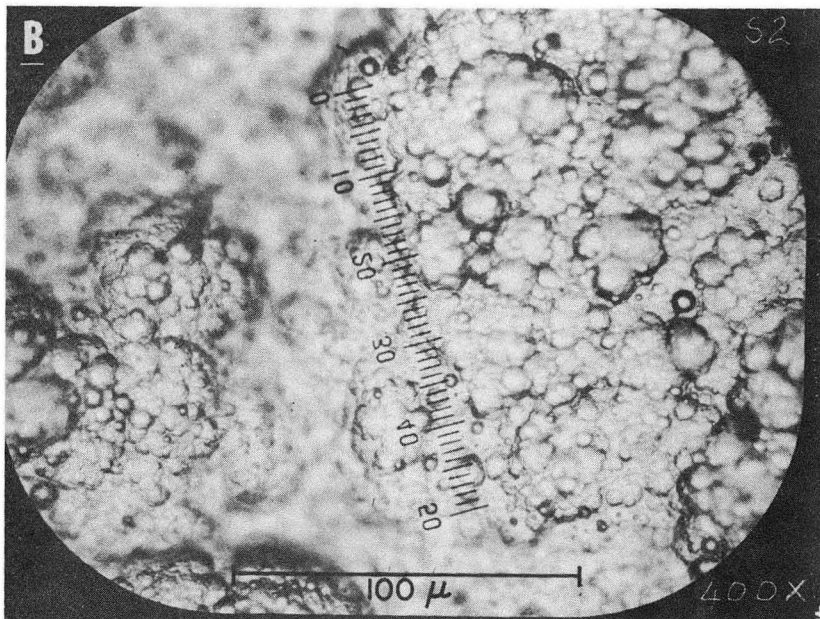
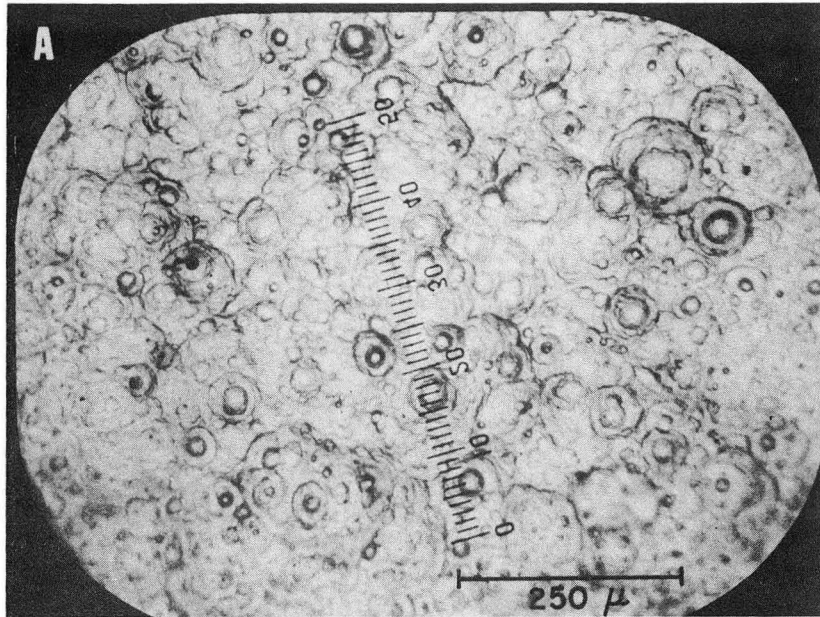
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Fig. 2.



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Fig. 3.



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Fig. 4.

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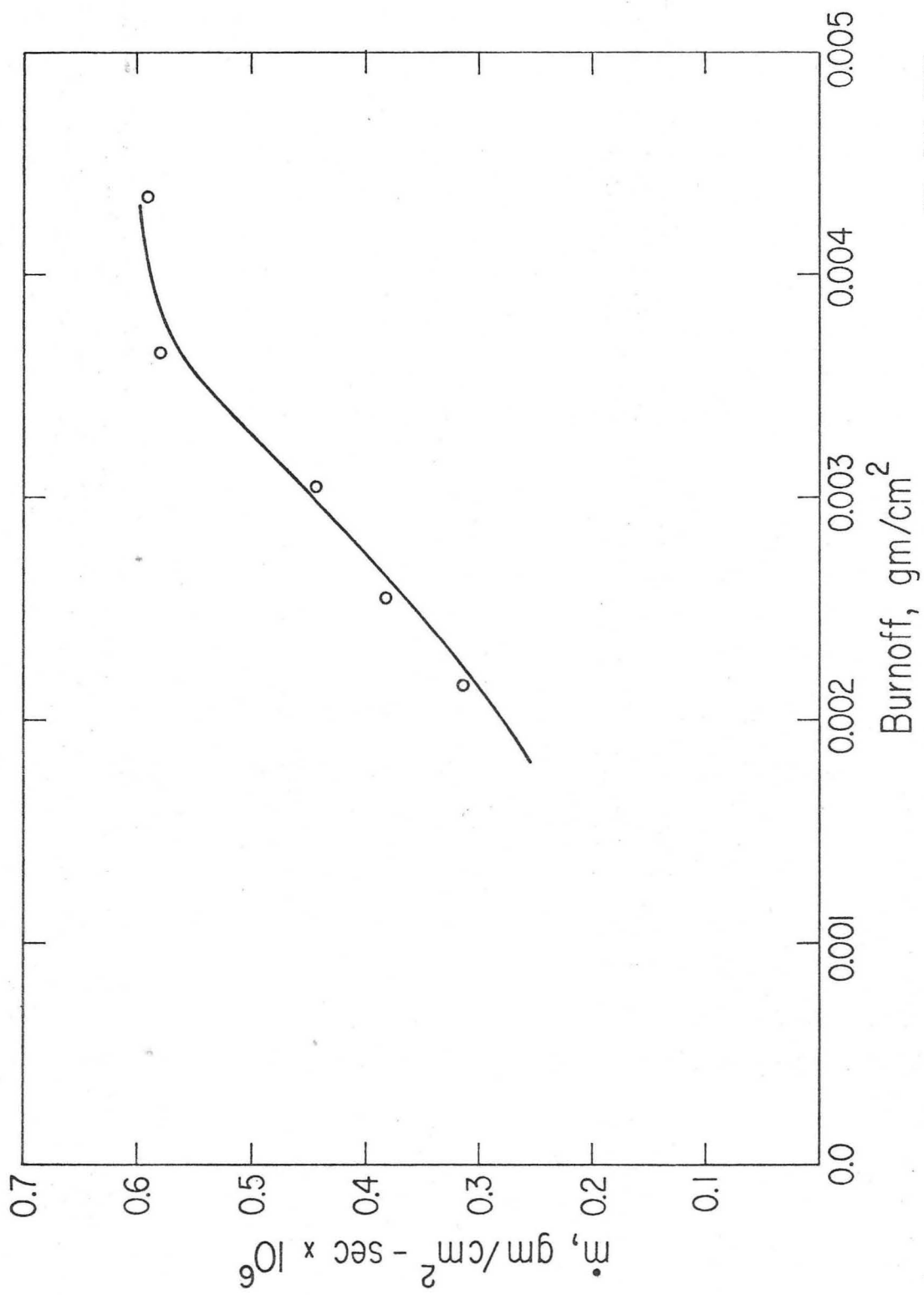
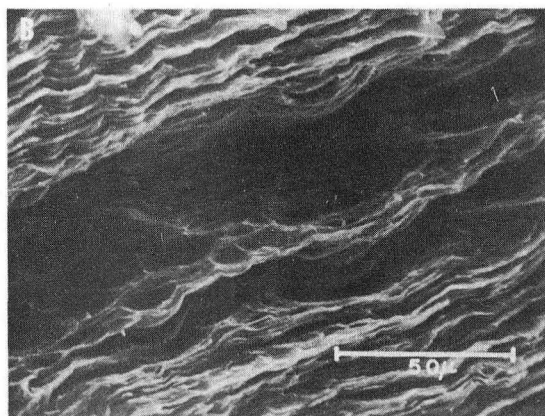
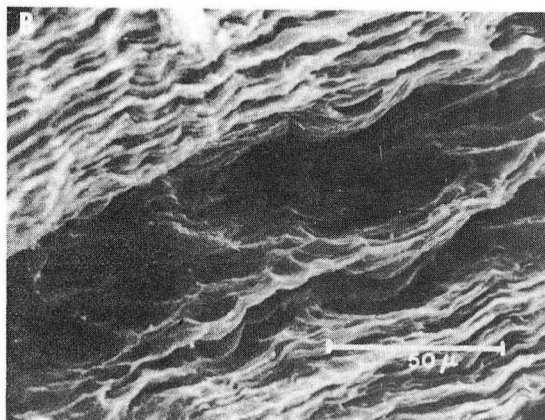
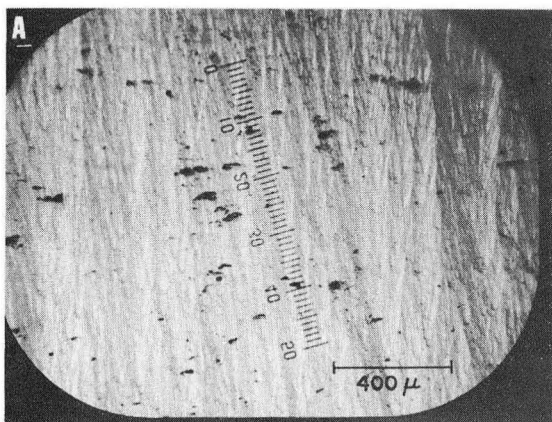
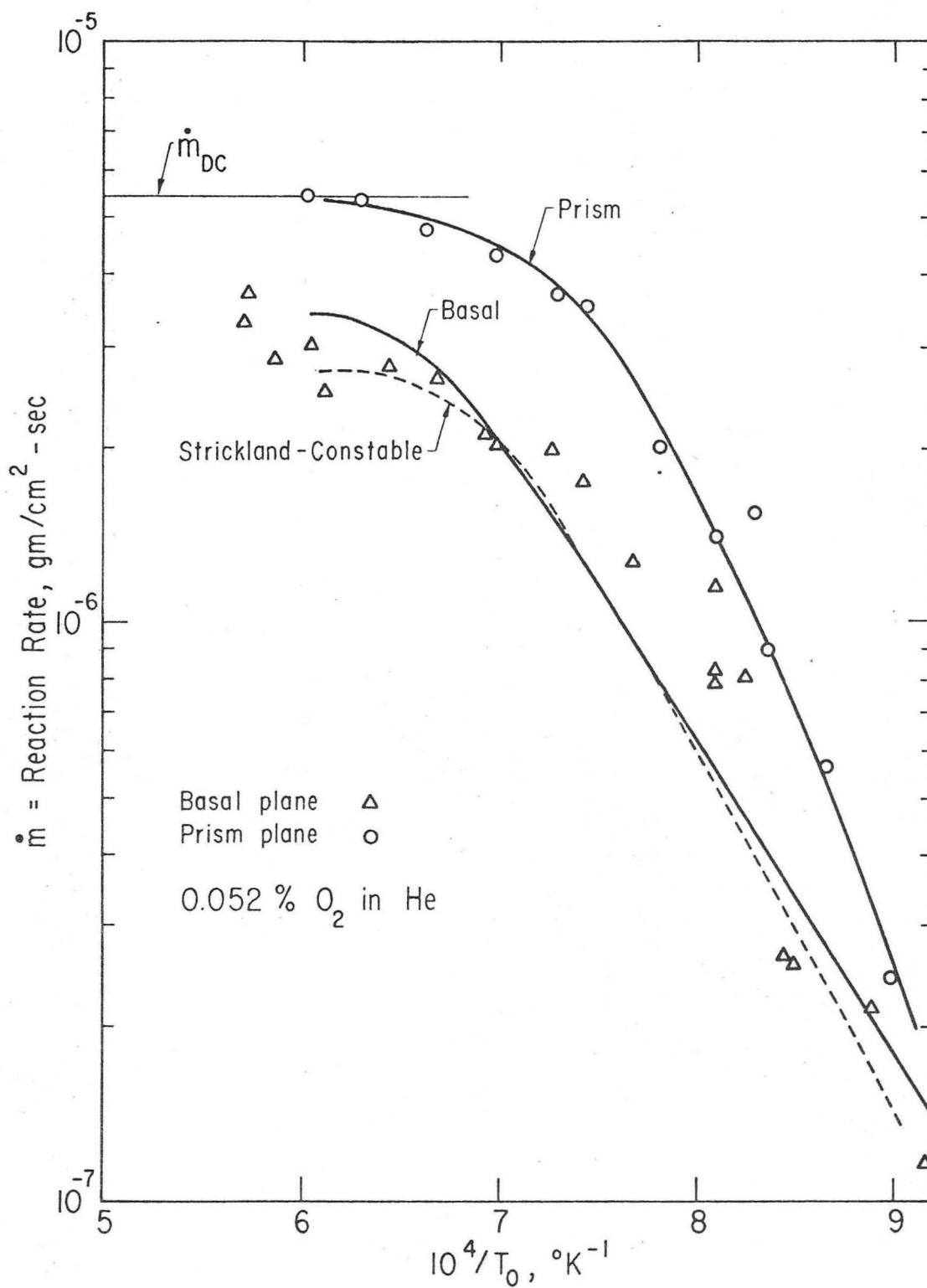


Fig. 5.



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Fig. 6.



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Fig. 7.

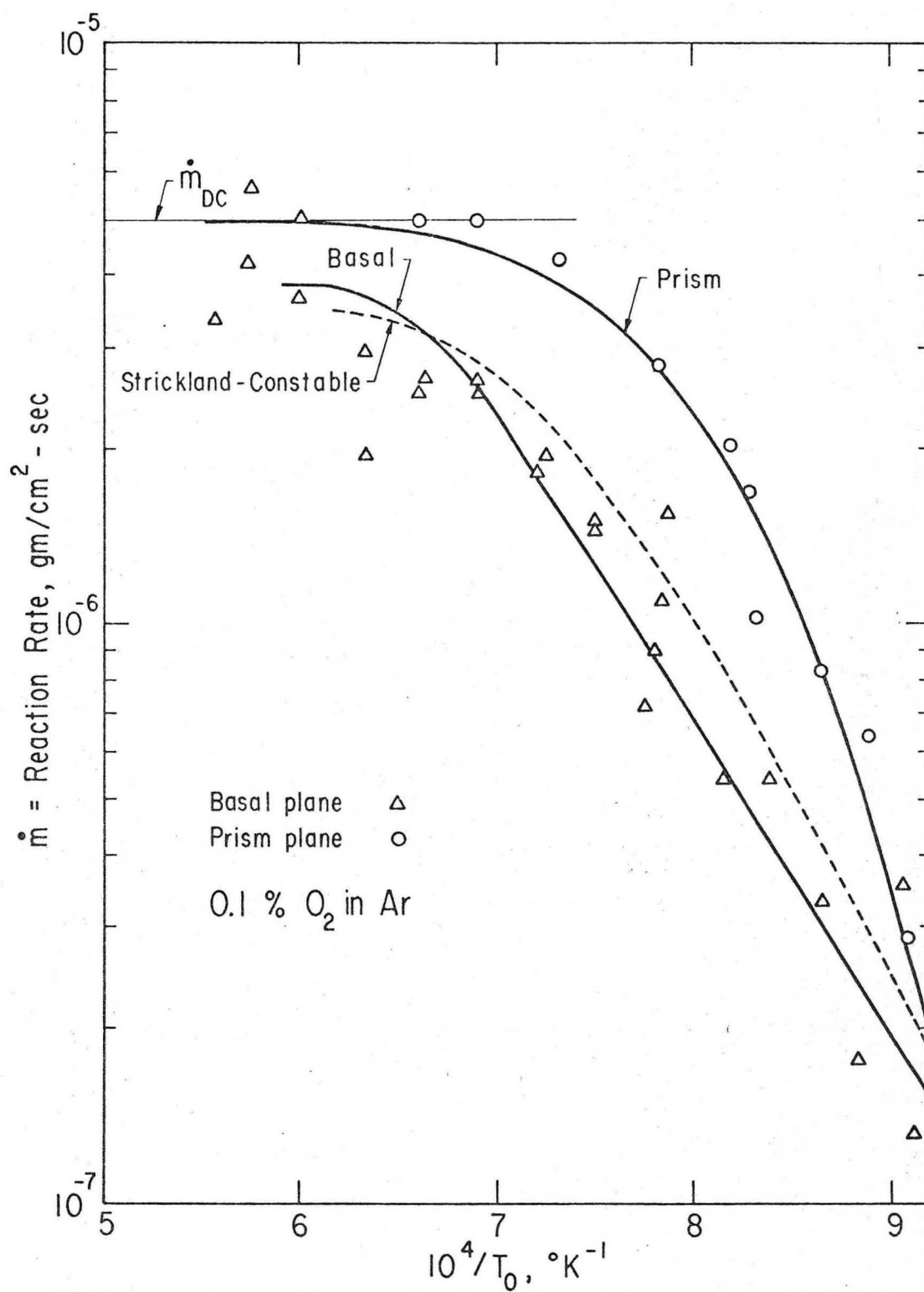
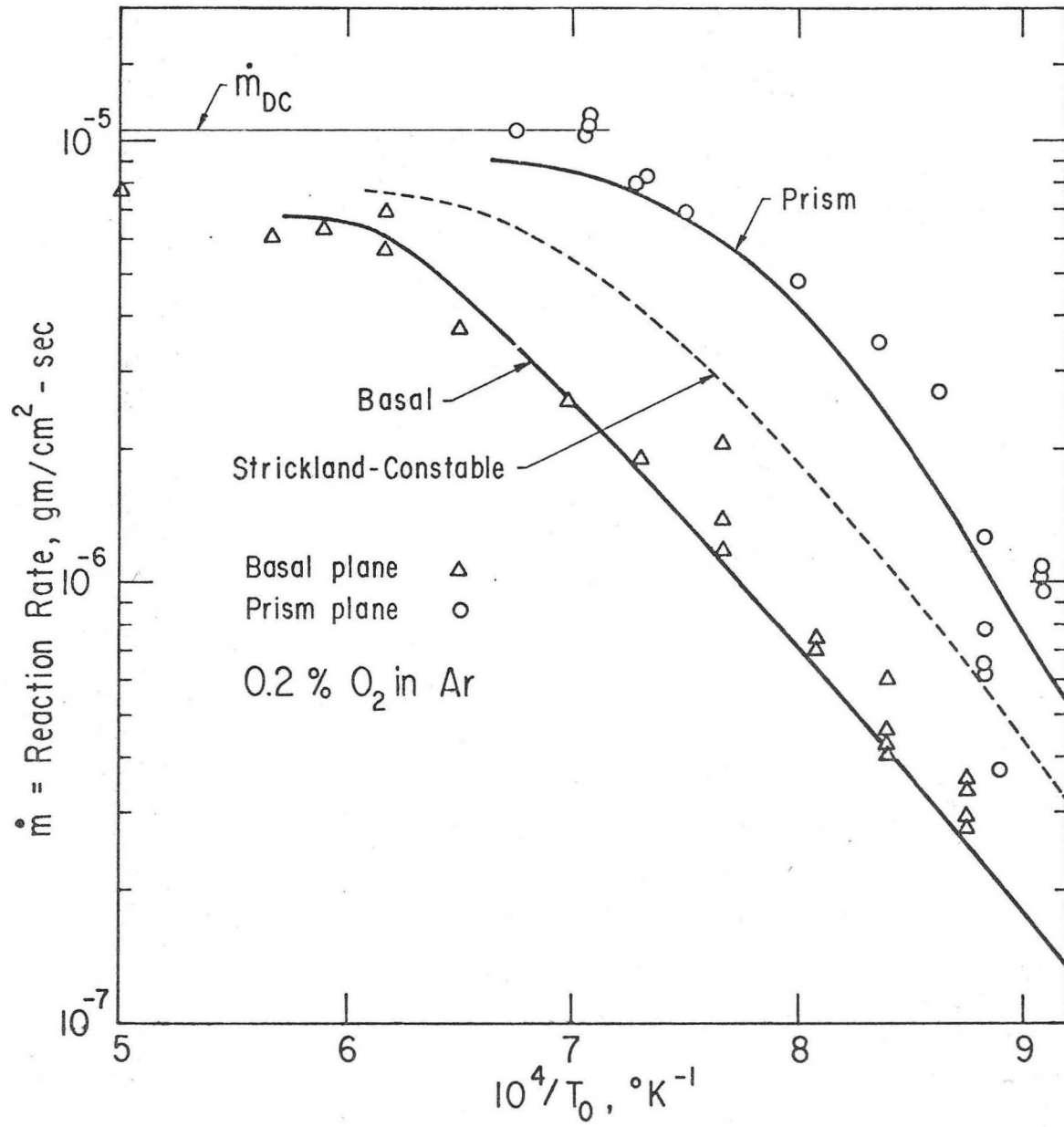
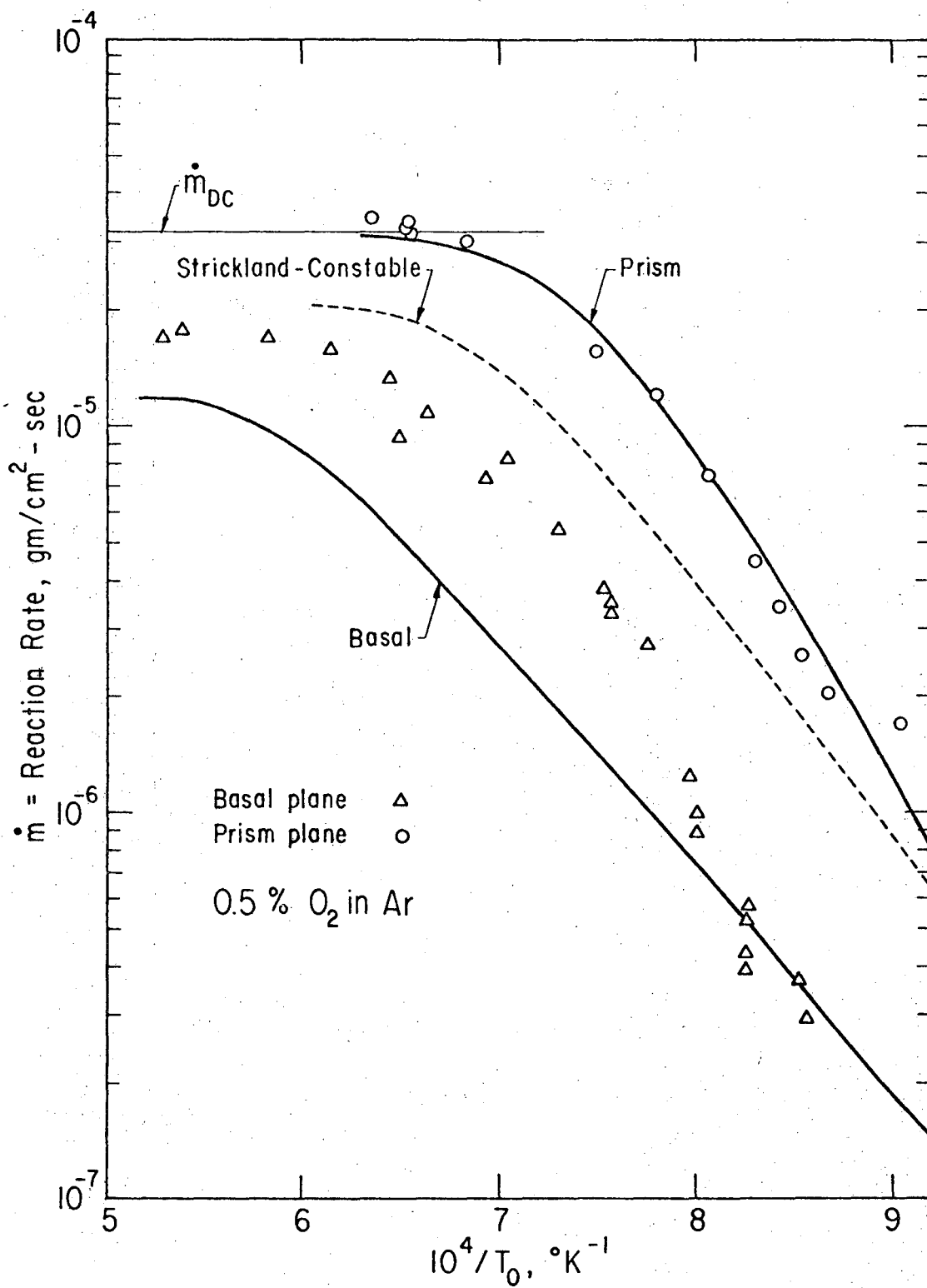


Fig. 8.



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Fig. 9.



XBL 7112-2286

Fig. 10.

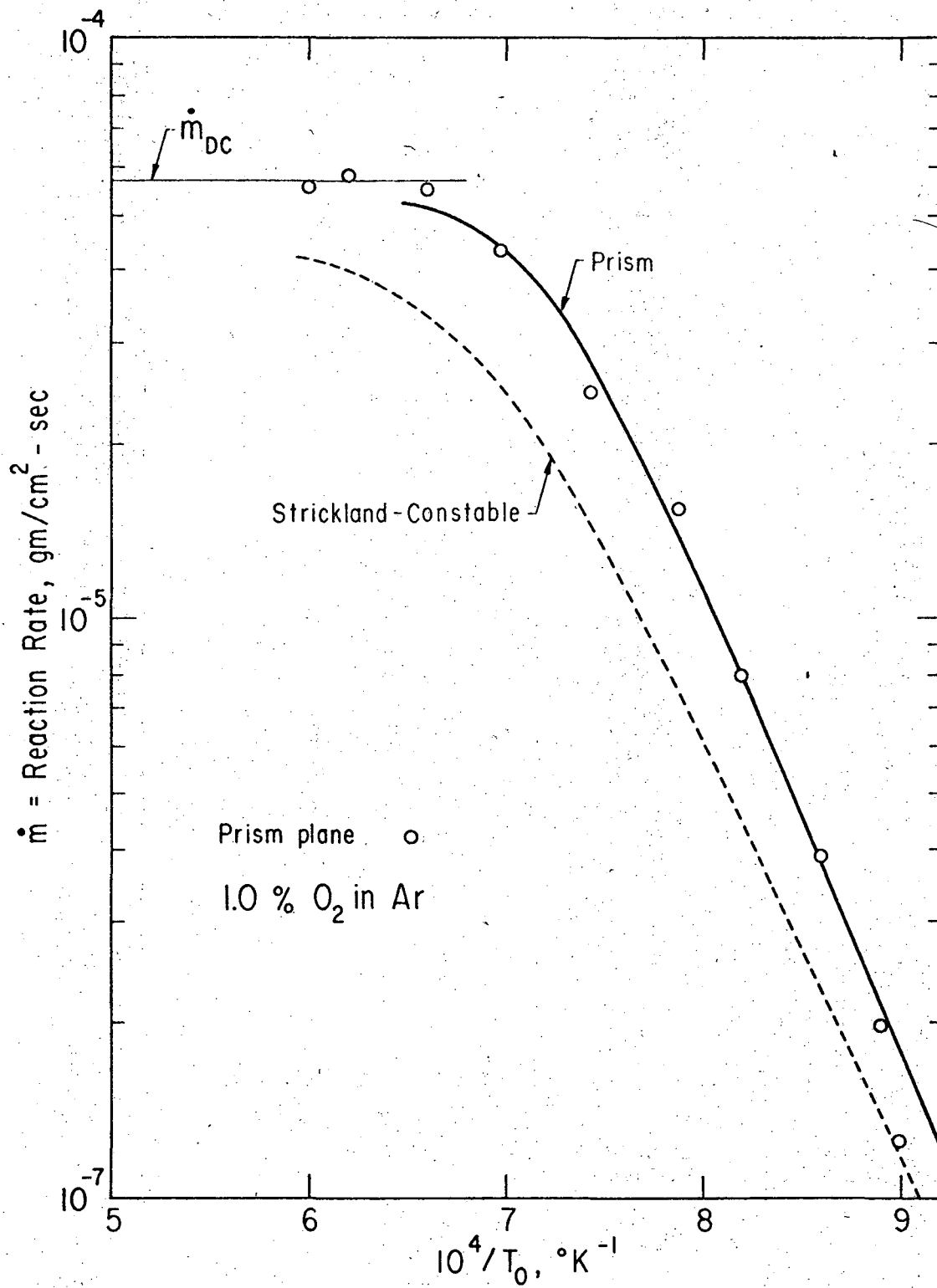
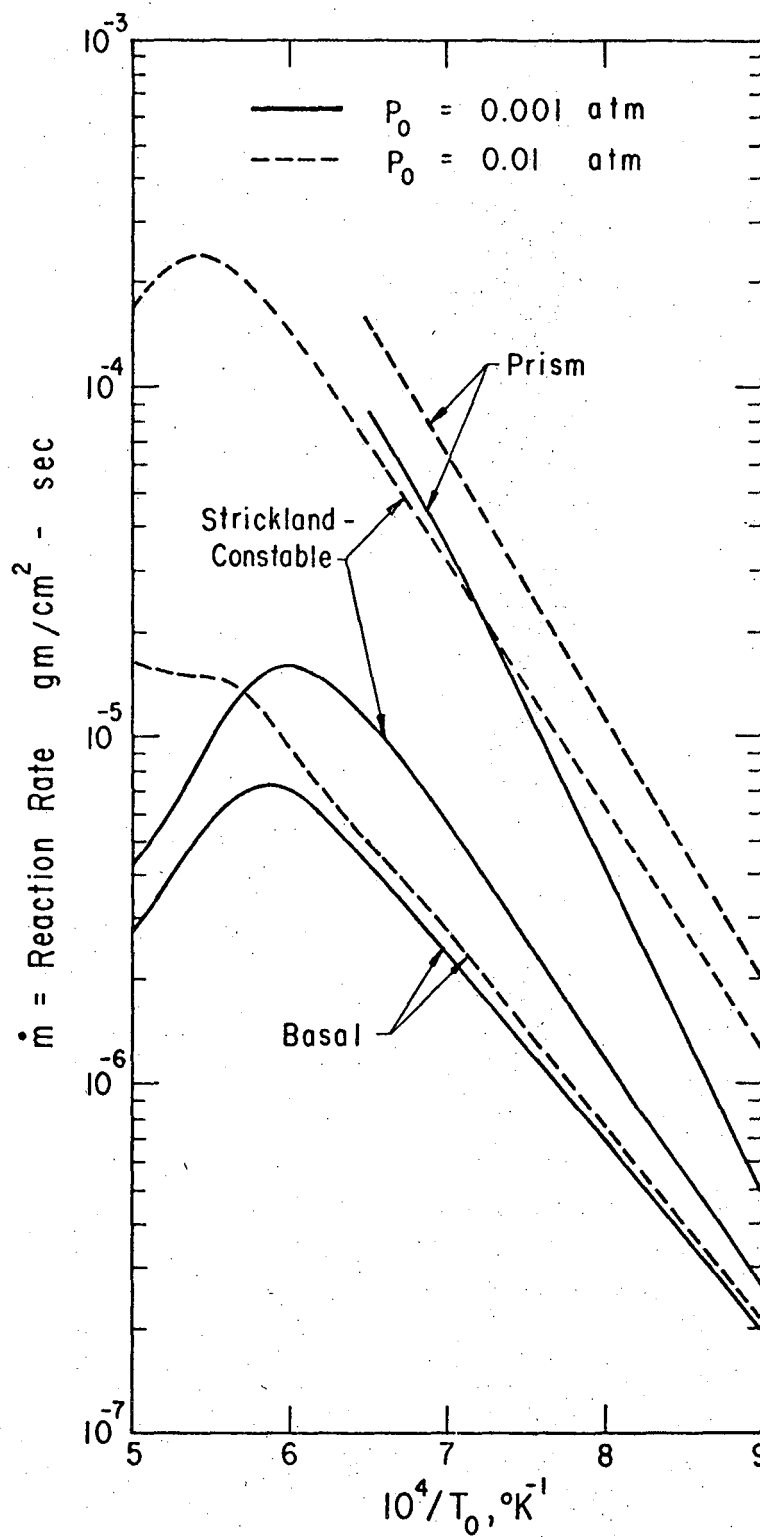


Fig. 11.



XBL 7112-2288

Fig. 12.

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