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Publication Date
1969-11-01
MEASUREMENT OF THE KINETICS OF OXIDATION OF MOLYBDENUM
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John L. Schofill, Jr.
(Ph.D Thesis)

November 1969

AEC Contract No. W-7405-eng-48

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MEASUREMENT OF THE KINETICS OF OXIDATION OF MOLYBDENUM BY MEANS OF THE REACTING, ROTATING DISK TECHNIQUE

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ABSTRACT

A rotating disk system has been developed to study heterogeneous chemical reactions subject to gas phase diffusion limitations. The system has been operated at temperatures up to 2000°K and disk speeds up to 15,000 rpm to investigate the reaction of oxygen and molybdenum. The independence of reaction or diffusion on radial position in the rotating disk system permitted kinetic data to be obtained from simple weight loss measurements as a function of disk temperature, oxygen partial pressure, and disk speed.

Because of the availability of an exact solution of the diffusion-convection equation for the rotating disk, the diffusional contribution to the overall rate can be accurately assessed when both diffusion and surface reaction offer resistances of comparable magnitude.

The surface process was shown to be consistent with the overall reaction \( \text{Mo}(s) + \text{O}_2(g) \rightarrow \text{MoO}_3(g) \). The order of this reaction with respect to oxygen partial pressures from 0.002 to 0.05 atm at one atmosphere total pressure was found to be 1.00±0.03 and the activation energy of the reaction was determined as 40±0.3 kcal/mole. Both figures apply to the temperature range 1100-1500°K. At temperatures above ~1650°K, the overall rate of corrosion was temperature independent, and predicted by rotating disk theory to within 15%.
The results of this study have demonstrated the importance of studying heterogeneous reactions at atmospheric pressure and high temperature in a flow system for which accurate prediction of diffusional limitations is possible. The rotating disk is an eminently satisfactory tool for such theoretical and experimental studies.
I. INTRODUCTION

A. Diffusion-Influenced Oxidation of Molybdenum

The overall kinetics of the reaction, \( A(s) + B(g) = C \), may be subjected to one of three types of diffusional limitations. The most common occurs when the product \( C \) is a solid which progressively coats the surface as the reaction proceeds and introduces a slow, solid-phase diffusional resistance. If the reactant surface is porous, reactant gas \( B \) may encounter a Knudsen diffusion resistance in transferring from the outer surface to the interior of the solid. The third type of diffusional resistance may be involved when the reactant \( A \) is non-porous and the product \( C \) is gaseous at the reactant temperature. High chemical conversion rates may reduce the concentration of \( B \) at the phase boundary to the point at which the convective transfer of reactant and product through the hydrodynamic boundary layer controls the overall reaction rate. The present research examines the third type of diffusional resistance.

High temperature reactions in which a gas and a solid combine to yield a gaseous product have important practical implications. The reaction of uranium tetrafluoride with fluorine to produce volatile uranium hexafluoride at approximately 900°K is a basic step in the preparation of uranium for the gaseous diffusion plants. Chemical vapor deposition processes, such as the deposition of titanium from the tetraiodide with release of gaseous iodine, exhibit regimes of gas diffusional resistance. Deposition reactions are the reverse of those in which a solid surface is consumed.

Perhaps the most important example of this class of heterogeneous reactions is the oxidation of the refractory metals, which are of prime importance in high temperature gas cooled reactors and in rocket and aircraft engines. Molybdenum is being considered as a possible fuel.
element cladding material for the liquid metal fast breeder reactor (LMFBR). Molybdenum, tungsten, tantalum, and niobium all form oxides whose melting and boiling points are below those of the metal itself. Molybdenum trioxide, for example, melts at about 1070°K, and boils at approximately 1428°K, whereas the melting point of the metal is 2893°K. In the temperature range between 1428°K and 2893°K, oxidation of the solid surface yields a gaseous product which offers no protective coating to prevent further oxidation. In the temperature range, 1070°-1428°K, depending on system conditions, the liquid molybdenum trioxide may volatilize as fast as it is formed again leaving the molybdenum surface unprotected.

Low pressure, "diffusion-free" studies of the oxidation of molybdenum have been carried out by Rosner and Allendorf and Berkowitz-Mattuck et al. Previous measurements of molybdenum oxidation under conditions in which convective diffusion definitely influenced the reaction kinetics were done by Schryer and Modisette and Gulbransen et al. These four papers, the results of which are compared with those of the present research in Chapter V, and are briefly outlined below. Other studies of this reaction include those of Semel, an early report by North American Aviation, and a study of oxidation in the Mo-Si system by Berkowitz.

Rosner and Allendorf measured molybdenum oxidation under "diffusion-free" conditions in pure oxygen at 3×10^{-2} Torr. An electrically heated molybdenum filament was oxidized; the filament was maintained at constant temperature during reaction by altering filament current in accordance with an optical pyrometer output. The oxidation of molybdenum by atomic oxygen also was studied by passing the incoming oxygen stream through a microwave discharge prior to contacting the filament. It was found that oxygen atom attack was first order in the range, 2×10^{-3} ≤ p_0 ≤ 5×10^{-2},
with an activation energy of about 6 kcal/mole; \( O_2 \) attack was not first
order\(^\text{2}\) and exhibited an activation energy of 26 kcal/mole. The oxidation
probability for atomic oxygen attack (see Chapter V) was one to three
orders of magnitude greater than for \( O_2 \) attack over the temperature range
studied, 1050°-1500°K.

Another low pressure, "diffusion-free" study was reported by Berkowitz-
Mattuck et al\(^\text{4}\) a stream of molecular oxygen was directed against a hot
sheet of molybdenum. The gaseous products were identified by a mass
spectrometer before any gas-phase collisions could take place. The
pressure range studied was \( 0.6\times10^{-3} \leq p_{O_2} \leq 8.7\times10^{-3} \) Torr; the tem-
perature range, 1490°-2130°K. Maxima were found to exist in the overall
reaction rate; for example, with \( p_{O_2} = 0.6\times10^{-3} \) Torr, a maximum rate of
oxidation occurred at about 1900°K, and higher oxygen pressure shifted
the maximum to a higher temperature. At an oxygen pressure of \( 1.1\times10^{-3} \)
Torr, the principal reaction product was \( MoO_3 \) at temperatures up to about
1700°K; at higher temperatures, \( MoO_2 \) became dominant.

Schryer and Modisette\(^\text{12}\) studied molybdenum oxidation under conditions
of strong diffusional influence: molybdenum reacting with air (and a
He-\( O_2 \) mixture with same percentage oxygen) at atmospheric pressure and in
the temperature range, 1080°K-1650°K. Molybdenum specimens approximately
1/2"x1" were cut from 0.01" molybdenum sheet and suspended by a platinum
wire from a balance into a furnace. The weight loss of the specimen was
monitored as a function of time during the run. It was found that the
apparent activation energy of the reaction depended anomalously on tem-
perature and the flow velocity; proof of diffusional influence was obtained
when helium-oxygen was substituted for air: the oxidation rate versus
temperature curves for the two mixtures were parallel, but the helium
oxygen data were higher by about a factor of 1.4. Schryer and Modisette
performed a simple, flat-plate model calculation to account for diffusional effects, and succeeded in removing the activation energy anomalies (even with their very rough calculation) to arrive at a mean activation energy for the reaction of 21 kcal/gmole. Schryer and Modisette thus proved conclusively that diffusion effects are important in molybdenum oxidation at pressures near 1 atm.

The most comprehensive study of molybdenum oxidation in the literature is that of Gulbransen et al., which covers the temperature range, 823°-1975°K, using pure oxygen between 5 and 76 Torr. Small molybdenum rods were suspended from a balance into a furnace. Both weight change and oxygen consumption were measured, and it was shown that, at 1273°K, the reaction stoichiometry was 1-1/2 moles oxygen consumed for each mole of molybdenum reacted -- another indication that the principal reaction product in the range of interest of the present research is molybdenum trioxide.

Gulbransen et al. found that molybdenum suffered a net weight gain (due to formation of adherent oxide scale) non-linearly in time at 823°K and at 873°K. At 923°K, the molybdenum specimen suffered a weight loss non-linearly in time; at 973°K, the weight loss had become very rapid and nearly linear in time. At temperatures above 1073°K (the melting point of molybdenum trioxide), the weight loss was linear in time and "catastrophically" large. In the temperature range, 1170°-1870°K, at an oxygen pressure of 76 Torr, and for a molybdenum specimen of 1.215 cm² surface area, the reaction rate was linear in time and practically independent of temperature, indicating that the regime of complete diffusion control (for this particular specimen) began at approximately 1170°K. For smaller specimens, it was found that the diffusion-limited regime began at higher temperatures (for example, at about 1430°K for a sample of 0.304 cm² surface area).
Gulbransen et al made no attempt to treat theoretically the effect of convective diffusion. The assumption was made that, for specimens of given surface area, the "diffusion-limited" regime began at a temperature at which an Arrhenius plot of the reaction rate versus reciprocal temperature departed from linearity; data taken below this temperature were assumed to reflect true surface reaction kinetics. This assumption is subject to some question (see Chapter V), particularly because of the anomalous values of reaction order with respect to oxygen pressure that were obtained.

B. Importance of Diffusional Limitations

Rosner\textsuperscript{23,24,25} has shown theoretically that convective diffusion intrudes upon the kinetics of surface reactions. The activation energy and order of the reaction are falsified if diffusional effects are not properly accounted for in analyzing kinetic data. Walsh et al.\textsuperscript{35} have experimentally overcome diffusional limitations in the tungsten-oxygen system by employing a stagnation flow geometry in which a high speed jet of reactant gas impinges upon the sample. The very high gas flow velocities were attained by using a low pressure gas (<11 Torr). However, the mass transfer coefficients could only be estimated from a correlation, in which effects such as interfacial velocity due to the reaction and variable properties due to the large gas-solid temperature difference cannot be accommodated.

Carlton and Oxley\textsuperscript{36} studied the decomposition of nickel tetracarbonyl on wires in a cross flow geometry. The overall reaction rate in this system was also shown to be affected by both diffusional and surface reaction. Again, empirical correlations were needed to extract surface kinetic data from overall rate measurements. The existence of a gas phase diffusional resistance in high-temperature oxidation of molybdenum
in air at atmospheric pressure has been demonstrated experimentally by Schryer and Modissette,\textsuperscript{12} and by Gulbransen et al.\textsuperscript{13}

The aim of the present research is to measure the kinetics of oxidation of molybdenum at temperatures above 1070°K, using low concentrations of oxygen in inert gas at a total pressure of one atmosphere and employing a reaction system for which the contribution of convective diffusion may be calculated by theoretical methods. Thus the true oxidation kinetics of molybdenum can be measured under conditions in which diffusional effects are known to play an important role in determining the overall reaction rate.

The overall oxidation rate of molybdenum is governed by the rate constant for the chemical step occurring at the surface and the resistance to oxygen and metal oxide diffusion in the gas boundary layer adjacent to the surface. The chemical step is primarily a function of temperature, while the diffusional step is dependent on flow geometry, gas flow rate, and the transport properties of the gas (primarily the diffusion coefficient).

The relative magnitude of the chemical and diffusional rates is a strong function of temperature. The former usually follows an Arrhenius-type curve, implying an exponential behavior in inverse absolute temperature. As will be shown in Chapter II, the rate of the diffusional step is very nearly temperature-independent for the gaseous media used in the present study (oxygen diffusing through either argon or helium).

One method of isolating the chemical step is to operate at temperatures sufficiently low so that diffusional resistance is negligible; this method, however suffers from two defects. First, at temperatures low enough to render the overall process chemically controlled, the
reaction product may not be gaseous. Such might be the case for molybdenum oxidation below 1428°K, if conditions were such that liquid oxide product could not volatilize fast enough after it was formed. Secondly extrapolation of chemical rate constants measured at low temperatures to higher temperatures is often questionable, because the reaction mechanism at the surface may be significantly different at the higher temperatures. A better procedure is to conduct experiments in a temperature region of interest in a system where hydrodynamic properties are known. This technique requires a system in which the diffusional resistance can be made reasonably small at will (usually by increasing the gas flow velocity).
C. Choice of the Rotating Disk Flow System

The basic theoretical and experimental problem is the determination of the chemical conversion contribution to the overall reaction kinetics under conditions of simultaneous chemical reaction and diffusional resistance of equal order of magnitude. The gas phase continuity, momentum, diffusion-convection, and energy equations must be solved simultaneously, subject to boundary conditions reflecting the stoichiometry of the surface reaction, the finite chemical rate at the surface, and the heat release due to reaction at the surface. In general this requires solution of at least six coupled, non-linear partial differential equations (three momentum, one overall continuity, the energy equation, and one diffusion equation if volatile product concentration is small enough not to interfere with diffusion of oxygen through inert diluent). Due to the chemical reaction at the solid-gas interface, the boundary conditions are non-linear. To render the theoretical problem tractable, even for machine computation, this set of equations must be reducible to ordinary differential equations.

This last requirement eliminates the flat plate as a suitable experimental flow geometry, because the non-linear boundary conditions do not allow the standard flat plate similarity transformation to be applied. Since the flat plate boundary layer thickness is dependent on the distance from the leading edge of the plate, the reaction rate will be dependent on position on the reacting surface; in addition, at high gas flow velocities, isothermality is difficult to approach for the flat-plate (stationary surface) geometry.

The number of flow systems for which the equations of change may be reduced to ordinary differential equations is small; of these, the
rotating disk in a quiescent fluid appears to be most satisfactory from both a theoretical and an experimental standpoint. In 1921, von Karman\textsuperscript{32} devised the variable transformation which reduces the continuity and momentum equations for the rotating disk system to ordinary differential equations; and in 1934, Cochran\textsuperscript{32} obtained a numerical solution to this set. Recently, Sparrow and Gregg\textsuperscript{6,7} and Millsaps and Pohlhausen\textsuperscript{34} have solved the associated energy and diffusion equations. The solution of the momentum equations for the rotating disk represents one of the rare complete solutions of the full Navier-Stokes equations, and although the solutions describe a boundary layer flow, such an assumption is not required beforehand. The heat and mass transfer coefficients for the rotating disk geometry are independent of radial positions, and the concentration and temperature profiles are functions of axial position only. In short, the surface of the rotating disk is uniformly accessible to mass transfer (and hence chemical reaction) and heat transfer; the diffusion-controlled reaction rate is independent of position on the disk surface. This has the important consequence that the non-linear boundary conditions can be accommodated into the set of ordinary differential conservation equations without altering the essential one-dimensionality of the solutions.

Additional theoretical considerations which arise in the case of chemical reaction at a rotating disk surface are the influence of non-zero interfacial velocity (due to the reaction) on the velocity profiles, and the temperature- and composition-induced transport property changes through the (non-isothermal) boundary layer. The former problem has been investigated by Sparrow and Gregg\textsuperscript{7} and Clander\textsuperscript{15}; and the latter has been investigated for gases by Omberg\textsuperscript{19}. That the laminar flow solution of the rotating disk equations of charge actually predicts
diffusion rates from the disk (to within ±10%) has been verified experimentally by Kreith, Emanuel and Olander and Olander. It will be shown in Chapter II that the mass-transfer coefficient for diffusion through the rotating disk boundary layer is proportional to the square root of the rotational speed of the disk. This makes it possible (at least in principle) to raise the temperature at which the oxidation reaction becomes diffusion-limited to any value desired, merely by increasing the disk stirring speed. The limitation of this feature lies in the practical difficulty of constructing a high-temperature, vibration-free, rotating disk system for the rotational speed required; vibration sets in roughly with the square of the angular velocity, whereas temperature dividing diffusion-controlled and reaction-controlled regions varies as the square root of the disk speed.

D. Thermodynamics of the Molybdenum-Oxygen System

Interpretation of the kinetic data may require knowledge of the molybdenum oxide species leaving the surface after reaction and whether or not it undergoes further oxidation or polymerization as it moves through the diffusion boundary layer. Berkowitz-Mattuck and Batty and Stickney have studied molybdenum oxidation mass spectrometrically at very low oxygen pressures (1.1×10⁻³ Torr and 5.0×10⁻⁵ Torr, respectively) and have found that, even at these low pressures, molybdenum trioxide is the principal reaction product, dominating over the dioxide in the approximate temperature range, 1500°-1800°K.

Berkowitz et al. have shown that, in the absence of oxygen, the vapor in equilibrium with solid molybdenum trioxide consists mostly of (MoO₃)₃, with smaller amounts of the tetra and penta polymers. In the presence of oxygen (or any other diluent), polymerization is probably
shifted toward trimer, dimer, and monomer. Possibly an important consideration in studying the oxidation mechanism in detail would be the breakdown of the polymeric species, if they exist, as they diffuse through the boundary layer after reaction.

The vapor pressure of molybdenum metal has been studied by Vozzella et al.\textsuperscript{11} in the temperature range, 2140°-2535°K. The rate of evaporation at 2141°K was found to be about $4 \times 10^{-8} \text{ g cm}^{-2} \text{ sec}^{-1}$ (compared with $6.5 \times 10^{-5} \text{ g cm}^{-2} \text{ sec}^{-1}$ oxidation rate observed at 1700°K with 0.5% oxygen in argon), and hence evaporation of molybdenum metal during oxidation may be considered to contribute negligibly to the overall reaction rate.

Thermochemical data for the following reactions in the temperature range, 1000°-2000°K, have been obtained and are summarized by Gulbransen et al.\textsuperscript{13}. Thermodynamics of molybdenum oxide evaporation and polymerization have been investigated by, among others, Burns et al.\textsuperscript{16} and Norman and Staley.\textsuperscript{8} The reactions of primary interest in this study are:

1. $\text{Mo}(s) + \frac{3}{2} \text{O}_2(g) = \text{MoO}_3(s)$
2. $\text{Mo}(s) + \frac{3}{2} \text{O}_2(g) = \text{MoO}_3(s,l,g)$
3. $3 \text{MoO}_3(g) = (\text{MoO}_3)_3(g)$
4. $2 \text{MoO}_3(g) = (\text{MoO}_3)_2(g)$
5. $\text{MoO}_2(s) + \frac{1}{2} \text{O}_2(g) = \text{MoO}_3(s,l,g)$
6. $3 \text{MoO}_3(l) = (\text{MoO}_3)_3(g)$

The vapor pressure of molybdenum trioxide has been studied by a considerable number of investigators; the literature on that subject is reviewed in a paper by Gulbransen, Andrew and Brassart.\textsuperscript{10}

Calculations have been carried out using thermodynamic data from the above four papers in order to answer tentatively certain questions concerning behavior of the oxidizing molybdenum system. These calculations,
though based on equilibrium data, are valuable as indications of possible systemic behavior, particularly in the diffusion-controlled regime, where product oxides may linger in the boundary layer near the reacting interface long enough to approach equilibrium, or to force back-reaction. The concentrations of oxygen and oxide products at the reacting surface may be estimated by assuming steady-state and applying the results of the mass-transfer coefficient derivations of Chapter II to the known stoichiometry of the system. The conclusions reached from thermodynamic considerations may be summarized:

(a) MoO$_3$ is reduced at all temperatures in the range of interest of this study by molybdenum metal to form, at equilibrium MoO$_2$. This suggests that solid molybdenum dioxide (or some lower oxide) may be present on the disk surface during reaction. This is borne out by observation and taken into consideration in the reaction mechanism proposed and discussed in Chapter V.

(b) Assuming that the reacting surface is coated by a thin layer of MoO$_2$ and that this oxide is in equilibrium with reactant oxygen according to reaction 5 of equation (I-1) (say in the diffusion-controlled regime), it is conceivable that the equilibrium pressure of oxygen given by the thermodynamics of reaction 5 is comparable to oxygen partial pressure in the ambient gas. In this case, even if the reaction were completely diffusion-controlled, the full theoretical diffusion-controlled rate predicted in Chapter II would not be observed, due to the fact that diffusion would take place not through a partial pressure difference ($p_{\infty} - 0$), but through a difference, ($p_{\infty} - p_{\text{eq}}$).

Calculations based on the thermodynamics of reaction 5, however, indicate that the value of $p_{\text{eq}}$ is infinitesimal compared to $p_{\infty}$ under all circumstances encountered in the present research.
(c) Since molybdenum trioxide exists in liquid form between 1070°K and 1428°K, it might be asked whether liquid MoO₃ ever is present on the disk surface under reacting conditions. Calculations based on thermodynamic data of the Gulbransen review paper¹⁰ indicate that, for partial pressures of MoO₃(vap) encountered under the circumstances of the present research in the boundary layer, liquid MoO₃ cannot exist on reacting molybdenum surface at equilibrium; it is expected therefore that MoO₃ volatilizes from the surface as fast as it is formed.

(d) Rough thermochemical calculations examining dimerization and trimerization of MoO₃ after it is formed indicate that both dimer and trimer may exist in the diffusion boundary layer. Equilibrium considerations indicate that trimer may dominate at the lowest temperatures of the reaction-controlled regime; but in the temperature range of mixed reaction and diffusion, and in the diffusion-controlled regime, dimer tends to be dominant by five or ten to one. It can be shown that the effect of variable molecular weight on the transfer rate is less for monomer and dimer than for trimeric molybdenum trioxide; this result, since the variable molecular weight effect was in fact not observed in the experimental results presented in Chapter IV, also would indicate that lower polymers are favored as reaction products.
II. APPLICATION OF THE HYDRODYNAMIC, ENERGY, AND MASS TRANSFER EQUATIONS TO THE NON-ISOTHERMAL, CHEMICALLY REACTING, ROTATING DISK SYSTEM

The system to be studied in this chapter is the gaseous medium above the rotating disk, illustrated schematically in Fig. II-1a. The disk itself is heated by the field of an induction heater to a uniform temperature in the range $1000^\circ$-$2000^\circ$K. The radius of the disk is considered infinite, though the diameter of the actual disk used was only 1/2 in. Because of the small disk size, the flow is always laminar. At 15,000 rpm, the Reynolds number at the edge of the disk ($Re = r^2 \omega / v$) is never larger than $\sim 10^3$, which is much smaller than the critical value of $3 \times 10^5$ at which turbulence begins in the rotating disk system.\(^1\)

The hot rotating disk is in contact with a flow of ambient gas mixture (0.2%-7% oxygen in argon or helium) at one atmosphere total pressure. Reaction takes place between molybdenum disk and ambient oxygen, producing oxide products which are gaseous in this range of disk temperatures. Below about $1000^\circ$K, the oxidation rate is moderate, and the rate of reaction is determined almost entirely by the rate of surface oxidation of molybdenum. But as the temperature of the disk is increased, the oxidation rate at the surface increases, depleting the oxygen available near the disk surface for reaction. A concentration gradient, or diffusion boundary layer, is established between ambient oxygen and oxygen near the disk surface. A sketch of the concentration profile within the boundary layer or the disk is shown in Fig. II-1b.

As the temperature of the disk is further increased, the reaction becomes so vigorous that the partial pressure of oxygen near the disk surface

\(^*\) In Refs. 1, 2, and 20, the numbers following the reference number denotes the pages in the reference.
Fig. II-la. Schematic illustration of rotating disk system.

- $\Omega$ = angular velocity of rotation of disk
- $\mathbf{V}$ = vector velocity at any point in fluid medium

at $z=0$: $T = T_0 = T_{\text{disk}}$, $v_0 = r\Omega$ (no-slip condition)
- $u_0 = w_0 = 0$

at $z=\infty$: $T = T_\infty$
- $P_{O_2}^\infty = P_{L\infty}$ = partial pressure of oxygen in inlet gas
- $u_\infty = v_\infty = 0$; $w_\infty$ is finite (disk rotation pulls fluid downward)
Fig. II-lb. Schematic illustration of diffusion of oxygen and oxide products through concentration gradients set up due to reaction at the disk surface.
finally is reduced to a negligible fraction of ambient concentration—and the oxidation rate of the molybdenum disk depends entirely on the rate at which oxygen can diffuse through the boundary layer to reach the disk surface. The purpose of this chapter is to calculate analytically the mass transfer rate of oxygen to the disk, as a function of the transport properties of the gaseous medium, the disk temperature, and the rotational speed of the disk.

The system in the case of this study is further complicated by the fact that, due to the high disk temperatures involved, isothermality is not easily attainable. The inlet gas mixture was heated to about 580°K before reacting the reaction chamber by passage through a preheating furnace. It is therefore necessary that we consider diffusion through a highly non-isothermal boundary layer. It is a most fortunate property of the hydrodynamic equations for the rotating disk system that, if the product of gas viscosity and density is considered constant with temperature, a very good, approximate solution to these equations is readily obtained.

The equations governing the reacting, rotating disk system described above will now be derived, using basically the same approach taken by von Karman and Schlichting. Modifications of this procedure necessary to reduce the equations of change with variable properties to a form identical to those of an isothermal system have been worked out by Omberg.

A. Momentum and Overall Continuity Equations

As seen from Fig. II-la, the system is best treated in cylindrical coordinates. The velocity vector \( \mathbf{V} \) at any point in the fluid has components:

\[
V = (V_r, V_\theta, V_z) = (u, v, w)
\]  

The most convenient starting point for this application is the equations of change in the form presented in Bird. The continuity equation for overall conservation of mass in the gas medium is:

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{V}) = 0
\]
The form of this equation makes it clear that matters may be simplified greatly by making two assumptions immediately:

ASSUMPTION 1: The reaction, flow, and diffusion processes are taking place at steady-state; that is, all time partial derivatives are set equal to zero.

ASSUMPTION 2: The reaction, diffusion, and flow processes are symmetric about the z-axis; that is, all derivatives with respect to \( \theta \) vanish.

Using these assumptions, the continuity equation reduces to

\[
\frac{1}{r} \frac{\partial}{\partial r} (\rho u) + \frac{\partial}{\partial z} (\rho w) = 0 \tag{II-3}
\]

Assumption 1 is a demand that the reaction reach steady-state in a time interval short compared to the length of a reaction run. This will be justified experimentally in Section IV, where results will show that the rate of oxidation is independent of the length of run, within experimental error. This assumption can also be justified on theoretical grounds by applying the results of Olander's calculations\(^\text{26}\) to the gaseous medium of this study.

Assumption 2 is easier to justify. The disk is rotating in the field of the induction heater at an angular velocity between 4800 rpm and 15,000 rpm (usually at 9600 rpm). The stirring motor is synchronous, of very constant speed. Any temperature (and hence reaction-rate) variations angularly would quickly be smoothed out by the rapid rotation.

Assumptions 1 and 2 will be applied from this point on, to the equations even before they are written down in the text, to save space. Making use of them, we may write the equations for conservation of momentum in the three coordinate directions:\(^\text{2,85}\)
The form of these equations suggests further assumptions:

ASSUMPTION 3: Gravity acts in the negative-z direction; that is, the vector \( \mathbf{g} = (g_x, g_y, g_z) = (0, 0, -g) \).

ASSUMPTION 4: The total gas pressure, \( p = p(z) \) only, and

\[
\frac{\partial p(z)}{\partial z} = -\rho \ g
\]

The third assumption merely requires that the disk face vertically upward. Assumption 4 is an excellent approximation, because the rotation of the disk under the conditions of this investigation alters the pressure of the gas from a purely hydrostatic variation by less than one part in \( 10^6 \).

Assumptions 3 and 4 together make the first term in parentheses to the right of the equal sign vanish in each of Eqs. (II-4a), (II-4b), and (II-4c). Further, Eq. (II-4c) itself may now be disregarded. As shown by Schlichting, this equation determines the pressure variation through the boundary layer caused by rotation of the disk, and is hence redundant in the present analysis, because of Assumption 4.

Making further use of Assumption 2, we may write the relevant components of the stress tensor \( \tau \) for a Newtonian fluid as follows:
We are now in a position to make the next major assumption:

**ASSUMPTION 5**: All fluid properties, density, viscosity, conductivity, and diffusivity, are dependent only on \( z \), and not on \( r \).

Assuming that the properties are independent of \( r \) is essentially a similarity transformation, since the fluid properties are quite nearly dependent on temperature alone. Therefore a correlative assumption is:

**ASSUMPTION 5a**: \( T = \text{temperature at any point in the fluid} \)
\( T = T(z) \) only

Assumption 5a is regarded as a similarity transformation because it is based on the fact that the disk is uniformly heated and the inlet gas is well-mixed. Since temperature is therefore not dependent on \( r \) at \( z = 0 \) or \( z = \infty \), temperature is assumed not to depend on \( r \) at intermediate values of \( z \). This assumption, and the other similarity transformations first used by Von Karmann, and which will appear soon in this discussion, are rather difficult to justify a priori. The strongest argument in their defense is that the similarity transformations enable us to obtain a relatively simple solution to these very
complex equations of change, and this solution also satisfies the appropriate boundary conditions, and agrees very well with experimental observations.

Substituting Eq. (II-5) into Eqs. (II-4a) and (II-4b), and making use of Assumption 5 with respect to the fluid viscosity, we obtain:

\[
\rho \left( u \frac{\partial u}{\partial r} + w \frac{\partial u}{\partial z} - \frac{v^2}{r} \right) - \frac{\partial}{\partial z} \left[ \mu \left( \frac{\partial w}{\partial r} \right) + \left( \frac{\partial u}{\partial z} \right) \mu \right] = \mu \left[ \frac{4}{3} \frac{\partial^2 u}{\partial r^2} + \frac{4}{3} \frac{1}{r} \frac{\partial u}{\partial r} - \frac{2}{3} \frac{\partial u}{\partial z} \frac{\partial r}{\partial r} - \frac{4}{3} \frac{u}{r^2} \right] \tag{II-4d}
\]

\[
\rho \left( u \frac{\partial v}{\partial r} + uv + w \frac{\partial v}{\partial z} \right) = \mu \left[ \frac{\partial^2 v}{\partial r^2} + \frac{1}{r} \frac{\partial v}{\partial r} - \frac{v}{r^2} \right] + \frac{\partial}{\partial z} \left( \mu \frac{\partial v}{\partial z} \right) \tag{II-4e}
\]

Despite the fact that in the non-isothermal rotating disk system under consideration the temperature difference between disk and ambient gas may be several hundred degrees, the effect of natural convection will be disregarded. A calculation based on standard correlations shows that, under the conditions of this research, forced convection heat transfer dominates over natural convection transfer. Experimental results presented in Section IV show that, if disk rotational speed is sufficiently high, the mass transfer rate is proportional to the square root of the rotational speed (showing dominance of forced convection transfer), which justifies:

ASSUMPTION 6a: The effect of natural convection is to be neglected in this derivation.

It is now appropriate to apply the Von Karman similarity transformations in the form: \[1, 85, 19\]
ASSUMPTION 6: The velocity components are of the form

\[ u = \rho F(\xi) \]
\[ v = \rho G(\xi) \]
\[ w = \sqrt{n} v_\infty H_1(\xi) \]

where \( \xi = \sqrt{n}/v_\infty \)

Substituting the similarity transformations into Eqs. (II-3, 4a, 4b):

\[ 2F + \frac{1}{\rho} \frac{d}{d\xi} (\rho H_1) = 0 \]  
\[ F^2 + F'H_1 - G^2 = \frac{1}{\rho} \frac{d}{d\xi} \left( \frac{\mu_0}{\mu_\infty} F' \right) \]  
\[ 2FG + \mu_0 G' = \frac{1}{\rho} \frac{d}{d\xi} \left( \frac{\mu_0}{\mu_\infty} G' \right) \]

B. The Diffusion-Convection Equation

The equation of mass conservation for species \( i \) (diffusion equation) expressed in its most convenient form is:

\[ 0 = -\nabla \cdot (\rho_i V + j_i) + r_i ; \quad i = 1, 2, 3 \]

The gas medium must now be considered a multicomponent, diffusing system. The reaction taking place at the disk surface may be written as:

\[ \text{Mo (s)} + (3/2) \text{O}_2(g) = (1/n) (\text{MoO}_3)_n \]

The exact nature of the reaction product, and how it reacts and decomposes while diffusing through the boundary layer, causes some difficulty in solving the energy equation, but does not (fortunately) make much difference in solving the diffusion equation; since the concentration of oxygen (and therefore, oxide products) is low (5% at most, diluted
by argon or helium), the diffusion process may be considered to be essentially binary. That is,

ASSUMPTION 7: The effect of multicomponent diffusion will be neglected. Oxygen, or oxide product, diffusing through the boundary layer will be considered to behave as though diffusing through pure inert gas.

It is estimated that the effect of neglecting multicomponent diffusion is an error on the order of about 2% at worst, if the reaction product is trimeric molybdenum trioxide.

ASSUMPTION 8: The gaseous medium above the disk behaves as a mixture of ideal gases.

The term, \( r_i \), in Eq. (II-7) refers to the reaction rate of species \( i \) as it diffuses through the boundary layer.\(^2\) It may be set equal to zero if we assume:

ASSUMPTION 9: Chemical reaction occurs entirely at the disk surface; oxygen does not further react with any of the oxide products in the boundary layer; and the oxide products do not react, decompose, or change form while diffusing away from the disk.

This restriction is based upon the supposition that the molybdenum leaves the surface in its most highly oxidized form (i.e., as MoO\(_3\)). Consequently, oxidation to a higher valence state of the metal is impossible. Since in diffusing from the disk surface to the bulk gas the oxide product encounters increasing oxygen partial pressures, reduction of MoO\(_3\) to a lower oxide is also ruled out. The only homogeneous reaction in which the oxide product could take part is polymerization, which would affect its rate of transport only by altering the diffusion coefficient of the product species; because the system is dilute in both reactant oxygen and product oxide, polymerization of the latter would not affect the rate of oxygen transport to the surface.

Since the rate of oxide removal from the disk surface is a function
only of the oxygen transport rate to the surface and the stoichiometry of the reaction, variation in product oxide diffusivity must be offset by compensating changes in the product oxide driving force (i.e., its concentration in the gas at the disk surface). This will directly affect the overall rate only if the product oxide reduces the surface chemical reaction by back reaction (see Chap. V for a more quantitative discussion of this point).

The mass flux of component \( i \) with respect to the mass-average velocity, \( j_i \), is given by Bird as:

\[
j_i = j_{i,x} + \text{diffusion due to pressure gradient} + \text{thermal diffusion}
\]

(BII-9)

Because of Assumption 4, pressure diffusion is negligible. The effect of thermal diffusion is, due to the steep temperature gradient through the boundary layer, finite but small. This effect is discussed in reference 19, but for the sake of this treatment, we make

ASSUMPTION 12: The effect of thermal diffusion is negligible.

What is now left of \( j_i \) is \( j_{i,x} \) -- the mass flux of component \( i \) due to the concentration gradient of species \( i \) at any point in the fluid. In particular, we want to known the rate of diffusion of oxygen (component 1) through the boundary layer to the disk. Because of Assumptions 7 and 8, the oxygen diffuses through a boundary layer composed essentially of pure argon (or helium), and the gas mixture is ideal. The mass flux for this case of ideal, binary, non-thermal diffusion is:

\[
j_{i,x} = -\frac{c}{\rho} M_1 M_2 D_{12} \nabla x_1
\]

(II-10)

where \( c \) is the total concentration, moles per unit volume, at any point in the fluid, \( M_1 \) the molecular weight of species \( i \), and \( x_1 \) the mole fraction of oxygen at any point above the disk. \( D_{12} \) is the diffusivity of oxygen in the inert gas (argon or helium), and is a function essentially
of temperature only; the binary diffusion coefficient is practically independent of oxygen concentration.

The next simplification makes use of the well-known, experimentally verified, fact that the rotating disk presents a uniformly accessible surface for chemical reaction. That is to say, given the fact that the disk is heated to a temperature uniform across its diameter, reaction or diffusion rates are independent of position on the disk surface.

Uniform accessibility on a rotating disk is a consequence of the uniform thicknesses of both the hydrodynamic and diffusion boundary layers on such a surface. Since the reaction rate depends on the mole fraction, \( x_1 \), of oxygen at the disk surface \((z=0)\), it follows that \( x_1 \), and therefore \( x_3 \) are also independent of \( r \) and \( \theta \) at \( z=0 \).

The above discussion tempts us to make a similarity transformation similar to the one made for the gas temperature in Assumption 5a, and this is

**ASSUMPTION 13:** The disk surface is uniformly accessible to oxidation. The mole fractions of oxygen and oxide products in the boundary layer are functionally dependent on the \( z \)-coordinate only.

However, it is quite clear that the above discussion ignores the attack of oxygen at the edge of the disk, which generally is slightly higher than the rate of attack on the rest of the disk. (The bottom of the disk is in intimate contact with the disk holder and suffers no attack from the gas phase.) Edge attack can be taken care of by an assumption we will need later anyway:

**ASSUMPTION 14:** The rotating disk is infinite in extent, and rotates concentrically about the \( z \)-axis at a uniform angular velocity.

That theoretical results obtained from the analytically tractable infinite disk are directly applicable to the finite disk which must be used in
Experimental work is another attractive feature of the rotating disk system. The reason for this fortunate situation is the direction of bulk flow in the boundary layer on the disk. The flow in the boundary layer is radially outward, which means that alteration of the surface boundary condition at a particular radial location can be transmitted to the inner portions of the disk only by diffusion against the convective flow, which is very inefficient. Consequently, the effect of the finite disk is felt only at radial positions approximately one boundary layer thickness in from the edge.

Making use of Assumptions 1, 2, 3, 5, 5a, 6, 9, and 13, the insertion of Eq. (II-10) into (II-7) produces after some simplification, and the use of the overall continuity Eq. (II-6a), the dimensionless equation for diffusion of oxygen:

$$\rho H_1(\xi) \frac{d \omega_1}{d \xi} = \frac{1}{\nu_0} \frac{d}{d \xi} \left( \rho D_{12} \frac{d \omega_1}{d \xi} \right) \quad (II-11)$$

In Eq. (II-11), $x_1$ has been converted to $\omega_1$, the mass fraction of oxygen. Mass fraction, like mole fraction, is dependent only on the dimensionless axial coordinate $\xi$, and is defined:

$$\omega_1 = \frac{\rho_1(\xi)}{\rho(\xi)} = \frac{x_1(\xi) M_1}{x_1 M_1 + x_2 M_2 + x_3 M_3} = \omega_1(\xi) \quad (II-12)$$
C. The Energy Equation

Next in line is the energy equation. It should be noted at this point that the temperature distribution and energy flux across the boundary layer is of very much interest to this analysis; ultimately, we are interested in obtaining the mass flux. The energy equation is given for the sake of completeness, and to illustrate that, in approximate form, the energy equation resembles the diffusion equation,

\[ \rho c_p H \frac{d\phi_T}{d\xi} = \frac{d}{d\xi} \left( \frac{k}{\mu_{\infty}} \frac{d\phi_T}{d\xi} \right) \]  

(II-13)

where

\[ \phi_T(\xi) = \frac{T(\xi) - T_\infty}{T_0 - T_\infty} \]

D. Dimensionless Form of the Conservation Equations

A new set of variables necessary to make the next simplification are defined:

\[ d\eta = \frac{\rho}{\rho_{\infty}} \frac{d\xi}{D_{12}} \]

\[ Sc = \frac{\nu}{D_{12}} \] (Schmidt number)

\[ \lambda = \frac{\rho u}{\rho_{\infty} \mu_{\infty}} \]

\[ Pr = \frac{\mu c_p}{k} \] (Prandtl number)

Using these new variables in Eqs. (II-6a-c), (II-11) and (II-13):

\[ 2F + \frac{d}{d\eta} \left( \frac{\rho}{\rho_{\infty}} H_1 \right) = 0 \]  

(II-15a)

\[ F^2 - G^2 + \left( \frac{\rho}{\rho_{\infty}} H_1 \right) \frac{dF}{d\eta} = \frac{d}{d\eta} \left( \lambda \frac{dF}{d\eta} \right) \]  

(II-15b)

\[ 2FG + \left( \frac{\rho}{\rho_{\infty}} H_1 \right) \frac{dG}{d\eta} = \frac{d}{d\eta} \left( \lambda \frac{dG}{d\eta} \right) \]  

(II-15c)
These equations will simplify greatly if \( \text{Pr}, \text{Sc}, \text{c}_p \) and \( \text{c}_p \) are treated as constants. These parameters will be evaluated at some mean temperature between \( T_0 \) (the disk temperature) and \( T_\infty \) (ambient gas temperature, about 580°K). It is simplest to take the mean temperature to be \( T_f \), the film temperature, where

\[
T_f = \frac{1}{2} (T_0 + T_\infty)
\]

The final results are relatively insensitive to the choice of the mean temperature.

Between 580°K and 1900°K, the density of the gas mixture (taking 2% oxygen in 98% argon as an example) decreases by more than a factor of three and viscosity decreases by more than a factor of two, but the function \( \text{c}_p \) suffers a net decrease of only \( 3\% \). It is therefore a much better approximation to consider \( \text{c}_p \) constant in the boundary layer, and to evaluate it at the film temperature, than to assume that the gas is isothermal, with properties evaluated at some mean temperature. Furthermore, it will be shown that the diffusion-controlled reaction rate varies inversely with \( (\text{c}_p/\text{Sc})^{1/2} \), which increases by only 23% between 580°K and 1900°K.

Prandtl and Schmidt numbers for a mixture of 2% oxygen in argon vary by less than 2% in this temperature range. For helium diluent, Prandtl number is very nearly constant at 0.64 between 580° and 1900°K, but the Schmidt number decreases by about 20% through the boundary layer.
Prandtl and Schmidt numbers for these two gas mixtures are tabulated as a function of temperature in Appendix A.

ASSUMPTION 15: For the purpose of solving Eqs. (II-15), Prandtl number, Schmidt number, heat capacity, and the function $\lambda$ will be considered constant with temperature (and hence $\eta$), and will be replaced by their respective values at the film temperature.

Tables II-1 and II-2 list $\lambda$ and $\lambda/Sc$ as functions of temperature for the gas mixtures cited in the paragraph above. Examination of these figures reveals that the function $\lambda/Sc$ varies by about 50% over the temperature range of interest for the argon-oxygen system, but only by about 30% for the helium-oxygen mixture. The properties listed in the two tables are calculated in detail in Appendix A.

Properties (with the exception of the heat capacity) which are considered constant by Assumption 15 and evaluated at the film temperature, $T_f$, will henceforth bear the subscript, f.

Making use of Assumption 15, and letting

$$\frac{dy}{\sqrt{\lambda_f}} = \frac{d\eta}{\sqrt{\lambda_f}} = \frac{\rho}{\rho_\infty} \frac{dz}{\sqrt{\frac{\Omega}{V_\infty \lambda_f}}} \frac{\rho}{\rho_\infty}$$

$$H = \frac{1}{\sqrt{\lambda_f}} \frac{\rho}{\rho_\infty} H_1$$

$$\phi = \frac{\omega_1 - \omega_{10}}{\omega_{1\infty} - \omega_{10}}$$

the final equations are obtained from Eq. (II-15a,b,c,d,e):
Table II-1  Test of the validity of Assumption 15 for an ideal mixture of 2% oxygen in argon.

<table>
<thead>
<tr>
<th>T(°K)</th>
<th>λ = ( \frac{(μμ)(T)}{(μμ)(580°K)} )</th>
<th>( λ/Sc )</th>
</tr>
</thead>
<tbody>
<tr>
<td>580</td>
<td>1</td>
<td>1.41</td>
</tr>
<tr>
<td>1073</td>
<td>0.806</td>
<td>1.15</td>
</tr>
<tr>
<td>1300</td>
<td>0.750</td>
<td>1.07</td>
</tr>
<tr>
<td>1600</td>
<td>0.699</td>
<td>0.998</td>
</tr>
<tr>
<td>1900</td>
<td>0.662</td>
<td>0.948</td>
</tr>
</tbody>
</table>

Table II-2  Same as above, for 0.53% oxygen in helium.

<table>
<thead>
<tr>
<th>T(°K)</th>
<th>λ = ( \frac{(μμ)(T)}{(μμ)(580°K)} )</th>
<th>( λ/Sc )</th>
</tr>
</thead>
<tbody>
<tr>
<td>580</td>
<td>1</td>
<td>0.602</td>
</tr>
<tr>
<td>1073</td>
<td>0.801</td>
<td>0.527</td>
</tr>
<tr>
<td>1300</td>
<td>0.745</td>
<td>0.507</td>
</tr>
<tr>
<td>1600</td>
<td>0.691</td>
<td>0.483</td>
</tr>
<tr>
<td>1900</td>
<td>0.647</td>
<td>0.465</td>
</tr>
</tbody>
</table>
E. Boundary Conditions

Equations (II-17a,b,c) are three equations in three unknowns, F, G, and H, and together with appropriate boundary conditions determine the flow velocity profile in the three coordinate directions. These equations (II-17 a,b,c) are identical to the equations in Schlichting which were derived by von Karman for an isothermal system. The boundary conditions are also identical:

\[ y = 0; \quad F = 0; \quad G = 1; \quad H = 0 \]  
\[ y = \infty; \quad F = 0; \quad G = 0 \]

The set (BC1) is the no-slip condition at the disk surface, and follows from the definitions of F, G, and H in Assumption 6 because at \( y = z = 0 \), the radial velocity is zero, tangential velocity is \( r \omega \), and the axial velocity at the surface is zero (even for a reacting system) if the following assumption is made:

**ASSUMPTION 16**: The effect of interfacial velocity due to the reaction of the diffusing oxygen at the disk surface, is negligible. The velocity of recession of the disk is also very small compared to the fluid velocity in the axial direction.
The Eqs. (II-17 a, b, c) have been solved numerically with the boundary conditions (BC1,2), and the solutions are tabulated in Schlichting. The appropriate boundary conditions on Eqs. (II-17 d, e) are quite simple, and need no explanation:

\[
\begin{align*}
  y = 0: & \quad \phi_T = 1; \quad \phi = 0 \\
  y = \infty: & \quad \phi_T = 0; \quad \phi = 1
\end{align*}
\] (BC3) (BC4)

F. Solution of the Diffusion-Convection Equation

The diffusion-convection equation (II-17e) must be solved by numerical methods, because the function \( H \) cannot be expressed in closed form. Sparrow and Gregg have obtained a numerical solution to the energy equation (II-17d) for fluids of any Prandtl number. Their results, although unnecessarily cumbersome for the purpose of this analysis, will be used to check on the results of the approximations to follow.

Figure II-2 compares the axial velocity profile, \( \frac{H(y)}{H_\infty} \), with the exact numerical solution of the diffusion equation, \( 1-\phi(y) \), for \( Sc = 1 \). The \( 1-\phi(y) \) curve for \( Sc = 0.7 \) would lie slightly above, and the curve for \( Sc = 1.5 \), slightly below, the curve for \( Sc = 1 \); but the difference is not important for the purpose of this illustration.

It may be noted from Fig. II-2 that \( \frac{H(y)}{H_\infty} = 0.9 \) at \( y \approx 3.3 \), and that \( 1-\phi(y) = 0.1 \) at \( y \approx 3.5 \). That is, the thickness of the velocity boundary layer is approximately equal to the thickness of the concentration (diffusion) boundary layer; the boundary layer regions in which these transport processes occur overlap. Because of this overlap, the velocity profile may be approximated linearly through the concentration boundary layer, and considered constant outside (as shown by the dashed line in Fig. II-2).
Fig. II-2. Mass fraction profile $\phi(y)$ for $Sc = 1$ compared with axial velocity profile for rotating disk. Mass fraction profile (solution to Eq. II-17e with $Sc = 1$) is reproduced from Sparrow and Gregg.\textsuperscript{6} Axial velocity profile, $H(y)/H_\infty$, is from Schlichting.\textsuperscript{5}
\[
H(y) \equiv (1/3.5) H_{\infty} y \approx -0.25 y \quad 0 \leq y \leq 3.5
\]
\[
H(y) \equiv H_{\infty} = -0.886 \quad 3.5 \leq y < \infty
\] (II-18)

Since an exact solution is available, we may for the purpose of illustration obtain a seemingly very approximate solution to Eq. (II-17e) by simplifying the velocity profile, Eqs. (II-18), further:

\[
H(y) \approx -0.25 y \quad 0 \leq y < \infty
\] (II-18a)

Ultimately the quantity to be calculated is the mass flux of oxygen at the disk surface, \(J_{10}\), which determines the rate of oxidation of molybdenum in the diffusion-controlled regime. The mass flux of oxygen at any point in the boundary layer is given by Eq. (II-10), which may be reduced, in view of Assumptions 5, 5a, and 13, and using Eqs. (II-16) and converting mole fraction to mass fraction, to the form:

\[
J_{10} = J_1(0) = \rho_0 \, D_{12,0} \, \left( m_{\infty} - m_{10} \right) \, \sqrt{\frac{\nu}{\nu_\infty}} \, \frac{\rho_0}{\rho_\infty} \, \frac{d\phi}{dy} \bigg|_{y=0}
\] (II-19)

Using Eq. (II-18a) for the velocity profile in Eq. (II-17e) and solving subject to (BC3,4) yields:

\[
\left. \frac{d\phi}{dy} \right|_{y=0} = \sqrt{\frac{Sc_f}{2\pi}} \quad \text{(approximate solution)}
\] (II-20)

The exact value of this gradient, as a function of \(Sc_f\), has been computed numerically, and the results are shown in Fig. II-3. Equation (II-20) is plotted in Fig. II-3 for comparison. The approximate solution is higher than the exact solution by only about 1% at \(Sc_f = 0.7\);
Fig. II-3. Dimensionless gradient of oxygen mass fraction at the disk surface. The solid curve is the numerical solution to Eq. II-17e taken from Sparrow and Gregg. The dashed line shows the approximate solution based on the velocity profile of Eq. II-18a.
for this reason, Eq. (II-20) will be used in the mass flux expression, Eq. (II-19), which takes the form:

\[ j_{10} = \rho_0 D_{12,0} (\omega_{1,\infty} - \omega_{1,0}) \sqrt{\frac{\Omega}{\lambda f_\infty}} \sqrt{\frac{\rho_0}{\rho_\infty}} \sqrt{\frac{3c_f}{2\pi}} \]  

(II-21)

= mass flux of oxygen due to diffusion to the disk through the mass fraction difference, \((\omega_{1,\infty} - \omega_{1,0})\)

Again, subscripts 1 and 2 denote oxygen and argon (or helium) respectively, subscript \(f\) means "evaluated at the film temperature," subscripts 0 and \(\infty\) mean "at the disk surface" and "at ambient conditions," respectively.

1. Reaction-Limited Regime

The form of Eq. (II-21) allows for two possible limiting cases: the previously-discussed regions of reaction- and diffusion-control of the overall oxidation-diffusion process. The important factor is the difference, \((\omega_{1,\infty} - \omega_{1,0})\). This difference depends on the relative rates of surface reaction and diffusion process. If the reaction rate at the disk surface is "low" (compared to the maximum rate of diffusion possible at a given temperature), then \(\omega_{1,\infty} - \omega_{1,0}\) is small. The mass fraction of oxygen at the disk surface is only slightly less than that in the bulk gas, and the surface kinetics expression may be written (for a first-order reaction at a total pressure of 1 atm):

\[ \dot{m}_{\text{RC}} = k_R(T) x_{10} \approx k_R(T) x_{1,\infty} = k_R(T) (M_\infty / M_1) \omega_{1,\infty} \]  

(II-22)

where \( \dot{M}_\infty = x_{1,\infty} M_1 + x_{2,\infty} M_2 \)  

(II-23)

\( \dot{m}_{\text{RC}} = \text{rate of loss of mass by the disk per unit area, in the reaction-controlled regime} \)
Experimental determination of the magnitude and temperature dependence of the rate constant $k_R$ is one of the primary objectives of this study. If the oxidation experiment is carried out at a temperature low enough so that the diffusion driving force is small, then the data may yield this parameter directly.

2. **Diffusion-Limited Regime**

Increasing the temperature of the disk increases the rate of oxidation, which tends to deplete the oxygen available at the surface for reaction faster than it can be replaced by diffusion from the bulk gas. $\omega_{10}$ is lowered to a value significant below $\omega_{100}$, establishing a mass-fraction (concentration) gradient. Thus, at temperatures above the regime of clear-cut reaction-control, it is erroneous to assume that Eq. (II-22) is valid in interpreting the reaction-rate data; the observed reaction rate in this "mixed" regime is lower than the rate expected from pure surface kinetics. It should be noted, however, that the reaction and diffusion rates are equal at all temperatures, because these processes occur in series. By equating the expressions for rate of diffusion and rate of reaction at the surface, $\omega_{10}$ may be calculated—an essential requirement of data interpretation.

In the limit of higher and higher temperatures, the surface reaction becomes so rapid compared to the diffusion process that the concentration of oxygen at the disk surface approaches $\omega_{10} \ll \omega_{100}$. The reaction is now completely diffusion-controlled, with a rate given by Eq. (II-21) with $\omega_{10} = 0$:

$$m_{DC} = \frac{2}{3} \left( \frac{M_0}{M_1} \right) J_{10} = \frac{2}{3} \frac{M_0}{M_1} \rho_0 \text{D}_{12,0} \omega_{100} \left( \frac{\Omega}{\lambda_f v_\infty} \right)^{1/2} \rho_0 \rho_\infty \left( \frac{Sc_f}{2\pi} \right)^{1/2}$$

$$= \rho_0 \left( \frac{Sc_f}{2\pi} \right)^{1/2}$$

(II-24)
where \( M_{\text{Mo}} \) is the molecular weight of molybdenum, and the reaction has been assumed to be \( \text{Mo}(s) + (3/2) \text{O}_2(g) = \text{products} \).

3. Mixed Regime

Equation (II-21) may also be written as a mass-transfer coefficient times a difference in oxygen partial pressure by making use of the ideal gas law. The result is:

\[
\dot{m} = \frac{2}{3} M_{\text{Mo}} \left( \frac{\rho_0}{\rho_\infty} \right)^2 \frac{D_{12,0}}{R T_\infty} \left( \frac{\Omega \Sc_T}{2m \nu_\infty} \right)^{1/2} \left( P_\infty - P_{10} \frac{\tilde{M}}{M_0} \right)
\]  

(II-25)

The molecular weight of the gas mixture is in general a function of position in the boundary layer. Assuming a ternary mixture of oxygen, inert gas, and oxide product,

\[
\tilde{M} = M_1 x_1 + M_2 x_2 + M_3 x_3
\]  

(II-26)

The presence of the ratio, \( \tilde{M}_\infty/M_0 \) in Eq. (II.25) complicates the analysis considerably. The molecular weight of the gas varies in the boundary layer primarily because of the introduction of heavy (\( M_{\text{Mo}} = 95.95 \)) molybdenum atoms into the gas by the oxidation reaction at the disk surface. The effect of molecular weight variation should be more noticeable therefore, under conditions of relatively high reaction rates -- i.e., high oxygen concentrations. In experimental studies described in Section III, oxygen concentrations no higher than 5 mole percent were used, in an attempt to reduce the effect of variable molecular weight and other effects associated with large concentrations of oxide products in the boundary layer. Estimates of the ratio \( \tilde{M}_\infty/M_0 \) have been made.
Although this ratio may under certain circumstances differ significantly from unity, the effect at worst makes little difference in the methods used to interpret reaction-rate data. The effect of variable molecular weight is quite small for ambient gas mixtures of 2% (or less) oxygen in argon. The ratio does differ from unity by about 25% at temperatures in the "mixed" regime (around 1400°K) for the runs involving 5% oxygen in argon, and because of the low molecular weight of helium, also for those runs using 0.5% oxygen in helium.

Furthermore, the ratio \( \bar{M}_\infty / \bar{M}_0 \) will be farthest from unity precisely in that temperature region (the "mixed" regime) in which \( p_{10} \) is small with respect to \( p_{1\infty} \). An important consideration (from a practical standpoint) is the bothersome fact that, if a reliable estimation of the ratio, \( \bar{M}_\infty / \bar{M}(y) \) is to be made as a function of \( y \), then one must have detailed knowledge on the behavior of the complex molybdenum oxidation products as they diffuse, interact, polymerize, and break down in the boundary layer. These considerations strongly impel us to set the molecular weight ratio equal to unity in Eq. (II-25) which may be rearranged, using Eq. (II-14), to yield:

\[
\dot{m} = \frac{2}{3} \frac{M_M}{R T_{\infty}} \frac{\rho_0^2}{\rho_{\infty} \rho_f} \left( \frac{\alpha}{2\pi} \right)^{1/2} \frac{D_{12,0}}{\sqrt{D_{12,f}}} (p_{1\infty} - p_{10}) \tag{II-27}
\]

Equation (II-27) shows that the rate of diffusion is independent of the viscosity of the gas mixture, which is a direct consequence of the linear velocity profile of Eq. (II-18a). The ideal gas law states that the density of the gas mixture at any point is proportional to the molecular weight of the mixture at that point, and inversely proportional to the temperature, which allows (II-27) to be written as:
The factor \( g_{vp} \) is the mass-transfer coefficient for reaction of molybdenum with oxygen in the diffusion-controlled or "mixed" regimes (if the molecular weight of the gas mixture is considered constant through the boundary layer). Examination of \( g_{vp} \) reveals that the diffusion rate is not only independent of gas viscosity, but also is insensitive to the value of \( T_\infty \) -- which means that it is not necessary to measure very accurately the temperature of the ambient gas as it leaves the pre-heating furnace. The factor \( \bar{M} \) is the molecular weight of the gas mixture at some "mean" point in the boundary layer; since the molecular weight varies through the boundary layer by at most 25\% (and for low concentrations and low temperatures, much less), the molecular weight ratio in Eqs. (II-28) and (II-29) will be taken to be unity.

4. **Effect of Non-Isothermality on the Diffusion-Controlled Rate**

For the case of the rotating disk system, the effect of variable properties may easily be separated out from the other factors in the expression for the mass-transfer coefficient, Eq. (II-30). Suppose that the system is isothermal at \( T_0 \); then \( T_f = T_0 \), and Eq. (II-30) becomes:

\[
\dot{m} = \frac{2}{3} \left( \frac{\Omega}{2\pi} \right)^{1/2} \frac{D_{12,0}}{\sqrt{D_{12,f}}} \left[ \frac{T_f}{T_0} \right] \left[ \frac{M_0}{\bar{M}} \right] \left( p_\infty - p_0 \right)
\]  

(II-28)

\[
\dot{m}_{DC} = g_{vp} \left[ \frac{\bar{M}}{\bar{M}_f} \right] \left( \frac{\Omega}{2\pi} \right)^{1/2} \left( \frac{T_f}{T_0} \right) \left( p_\infty \right)
\]

(II-29)

\[
g_{vp} = \frac{2}{3} \frac{M_0}{\bar{M}_f} \left( \frac{\Omega}{2\pi} \right)^{1/2} \frac{D_{12,0}}{\sqrt{D_{12,f}}} \left( \frac{T_f}{T_0} \right)
\]

(II-30)
This relation is analogous to the diffusion-limited rate expression derived by Olander for the germanium-iodine reaction. The effect of temperature-induced physical property variations on the rate is given by:

\[ \alpha_{vp} = g_{vp}/g_{iso} = \left( \frac{D_{12},_0}{D_{12},f} \right)^{1/2} \left( \frac{T_f}{T_0} \right) \]  

(II-32)

Note that if \( D_{12} \) varies as \( T^2 \), the effect of non-isothermality disappears.

Tables II-3 and II-4 list values of \( g_{vp} \) as a function of \( T_0 \) for mixtures of 2% oxygen in argon and 0.5% oxygen in helium, with \( T_\infty = 580^\circ K \), using diffusivity values resulting from the calculations in Appendix A. In both tables, \( \Omega \) is taken to be 9600 rpm.

A most important conclusion may be drawn from examination of Tables II-3 and II-4. In the case of argon-oxygen, the mass transfer coefficient decreases by about 13% between 1073° and 1900°K, and for helium-oxygen, the decrease is only about 9%. Therefore it is reasonable to assume that the mass-transfer coefficient is constant with temperature for the purpose of data interpretation, and this will be done in Section IV. This assumption makes it possible to calculate a mass-transfer coefficient based on experimentally determined values of the diffusion-controlled reaction rate, and this experimental mass-transfer coefficient should be, like its theoretical counterpart \( g_{vp} \), practically independent of temperature.

Another interesting question to ask at this point is whether an inaccuracy in measurement of \( T_\infty \) will cause a great error in the theoretical value of \( g_{vp} \). Suppose it is assumed that the value of \( T_\infty \) is actually 150° K lower than 580°K, or \( T_\infty = 430^\circ K \), or 157°C. Let \( T_0 = 1900^\circ K \), and
Table II-3  $g_{vp}$ as a function of disk temperature, $T_0$, for a mixture of 2 mole percent oxygen in argon above a disk rotating at 9600 rpm, with $T_\infty = 580^\circ$K.

<table>
<thead>
<tr>
<th>$T_0$ (°K)</th>
<th>$D_{12,0}$ (cm$^2$/sec)</th>
<th>$g_{vp}$ (g/cm$^2$-atm-sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1073</td>
<td>1.71</td>
<td>$1.15 \times 10^{-2}$</td>
</tr>
<tr>
<td>1300</td>
<td>2.34</td>
<td>1.10</td>
</tr>
<tr>
<td>1600</td>
<td>3.30</td>
<td>1.05</td>
</tr>
<tr>
<td>1900</td>
<td>4.43</td>
<td>1.02</td>
</tr>
</tbody>
</table>

Table II-4  $g_{vp}$ as a function of $T_0$ for a mixture of 0.53 mole percent oxygen in helium, with $\Omega = 9600$ rpm, $T_\infty = 580^\circ$K.

<table>
<thead>
<tr>
<th>$T_0$ (°K)</th>
<th>$D_{12,0}$ (cm$^2$/sec)</th>
<th>$g_{vp}$ (g/cm$^2$-atm-sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1073</td>
<td>6.33</td>
<td>$2.25 \times 10^{-2}$</td>
</tr>
<tr>
<td>1300</td>
<td>8.92</td>
<td>2.19</td>
</tr>
<tr>
<td>1600</td>
<td>12.9</td>
<td>2.12</td>
</tr>
<tr>
<td>1900</td>
<td>17.5</td>
<td>2.07</td>
</tr>
</tbody>
</table>
-43-

\[ T_f = 1165^\circ K. \]  Then \( D_{12, 0} = 17.54 \text{ cm}^2/\text{sec} \) and \( D_{12, f} = 7.4 \text{ cm}^2/\text{sec} \), for the helium-oxygen system. Using Eq. (II-30), we find that

\[ g_{\text{vp}}(T_f = 430^\circ K) = 2.05 \times 10^{-2} \text{ g cm}^{-2} \text{ atm}^{-1} \text{ sec}^{-1} \]

Therefore an error of 150°C in measurement of the bulk temperature causes an error of less than 1% in the theoretical prediction of the diffusion-controlled reaction rate.

In Table II-5 the numerical values of \( g_{\text{vp}} \) from Tables II-3 and II-4 are used to calculate the variable property factor, defined by Eq. (II-32).

The effect of physical property changes due to temperature variation through the boundary layer retards diffusion with respect to what would be observed if the gas were preheated to the temperature of the reacting molybdenum disk. But the effect is surprisingly small—less than 7% for argon diluent, less than 5% for helium inert, even though the temperature difference through the boundary layer is, in the diffusion-controlled regime, on the order of 1000^\circ K.

It is indeed fortunate that the influence of non-isothermality on the transfer rate of the rotating disk system is so small. Large perturbations due to this effect would have rendered comparison of theoretical and experimental diffusion-controlled oxidation rates somewhat insecure. Experimentally, it is exceedingly difficult to preheat an oxygen-containing gas to the temperatures investigated here. Quartz is the only easily fabricated container material which will not react with oxygen above 1000^\circ C, but its low thermal conductivity and brittleness make construction of an efficient heat exchanger difficult.
Table II-5: Effect of variable property factor, $\alpha_{vp}$, as a function of temperature for 2% oxygen in argon and 0.53% oxygen in helium, as a function of $T_0$. $\alpha_{vp}$ is defined by Eq. (II-32).

<table>
<thead>
<tr>
<th>$T_0$ (°K)</th>
<th>$\alpha_{vp, Ar-O_2}$</th>
<th>$\alpha_{vp, He-O_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1073</td>
<td>0.953</td>
<td>0.972</td>
</tr>
<tr>
<td>1300</td>
<td>0.945</td>
<td>0.965</td>
</tr>
<tr>
<td>1600</td>
<td>0.933</td>
<td>0.956</td>
</tr>
<tr>
<td>1900</td>
<td>0.932</td>
<td>0.952</td>
</tr>
</tbody>
</table>
III. DESCRIPTION OF EXPERIMENTAL EQUIPMENT AND PROCEDURE FOR MEASUREMENT OF OXIDATION KINETICS OF MOLYBDENUM

A. Apparatus

An apparatus necessary to measure the kinetics of oxidation of molybdenum in accordance with the discussion in the preceding chapters was developed. The first system that was constructed is illustrated schematically in Fig. III-1. This system attempted to achieve isothermality* by quite strongly pre-heating the gas as it flowed toward the disk. This particular design proved impractical because it could not produce disk temperatures above 1000°C. Furthermore, certain operational techniques were not fully developed until just before the "isothermal" system was abandoned in favor of the system illustrated in Fig. III-2. It is nearly correct to say, therefore, that the system of Fig. III-2 produced all of the data reported in this study, except for some low-temperature data that have been retained to demonstrate that non-isothermal effects were not significant.

*Clouds of molybdenum oxide smoke were observed during preliminary oxidation tests involving non-rotating molybdenum samples in air. It was feared that the presence of this smoke above the disk would prohibit accurate measurement of disk surface temperature during actual oxidation runs. An unsuccessful attempt was therefore made to construct a thermocouple device to monitor continuously the temperature of the disk while rotating.

It was thought that oxide condensation could be prevented by pre-heating the inlet gas mixture to a temperature as close as possible to that of the reacting disk, thus creating quasi-isothermal conditions in the boundary layer above the disk. Hence the construction of the "isothermal" system of Fig. III-1, and the use of the pre-heating furnace in the system of Fig. III-2. Isothermality in the boundary layer would also eliminate any effect of variable properties.

In practice, the creation of smoke during oxidation did not cause difficulties in temperature measurement. This was largely because the rotation of the disk caused the gaseous products to be thrown radially outward from the disk center, and the flow guide placed close above the disk tended to act as a sink for condensation well away from the black body hole in the center of the disk. Oxide condensed heavily on the underside of the flow guide and the glass surrounding the disk holder (see Fig. III-2), but only very sparsely on the glass above the disk.
Fig. III-1. Schematic drawing of early, "isothermal," rotating disk apparatus used to obtain molybdenum oxidation rate data in the temperature range, 1100°-1300°K.
Fig. III-2. Schematic diagram of final rotating disk apparatus with pre-heating furnace, used to obtain molybdenum oxidation rate data in the temperature range, 1200°-2000°K.
In the abstract, the reacting, rotating disk system of either Fig. III-1, or III-2 consists of a variable speed motor turning a shaft to which is attached a hot, rotating disk of molybdenum contained in an appropriate holder. The disk is exposed to a flowing stream of oxygen mixed with an inert, diluent gas in a pre-determined ratio. The flow rate of the reactant gas mixture must be greater than the natural approach velocity of the fluid in the rotating disk system to prevent back mixing of the reacted gas (depleted in oxygen) and the fresh feed gas.\textsuperscript{14} The flow rates are small enough to prevent a stagnation point type flow from displacing the desired rotating disk flow characteristic on the surface.\textsuperscript{19} Some provision is made for pre-heating the gas mixture before it contacts the hot, rotating disk. The temperature of the disk must be monitored continuously and held as nearly constant as possible during an oxidation run.

Perhaps the most difficult and important of these considerations is the design and construction of a holder for the disk while it is rotating and reacting at high temperatures. The holder must protect the disk as much as possible from oxidative attack on its back and edges during the run, but must allow the disk to be easily removed for weighing after the run. Disk holders made of carbon and boron nitride were tested and rejected, the former because it appeared to react with molybdenum, and the latter because it proved difficult to fabricate boron nitride holders which could grip the disk firmly while rotating, even at room temperature.

Molybdenum disk holders solved the problems very adequately. Two designs actually used in this research are illustrated in Figs. III-3a and III-3b. Molybdenum rod stock, from which the holders were made, was found somewhat difficult but quite possible to machine. Since both disk and holder are of the same material, there is no differential thermal
Fig. III-3a. Basic, "earlier" design of disk holder, used to obtain data in the great majority of runs. This design prevented contact between tantalum shaft (and the graphite anti-oxidant lubricant) and the molybdenum disk during the run, and eliminated the need for a separate lock-nut. Disk was removed (usually without difficulty) after each run by forcing a brass screw into the smaller, threaded hole. However, this design also required a certain minimum amount of material to execute, and was hard to balance. Vibration and eccentricity problems precluded runs with disk holders of this design at speeds above 9600 rpm. The disk holder was fabricated from molybdenum rod stock.
Fig. III-3b. "Advanced" design of molybdenum disk holder, used for final data-taking runs (particularly runs with angular velocity above 9600 rpm). The threaded hole was coated with graphite prior to each run, before attaching holder to the tantalum shaft, to prevent high-temperature fusion of the two metals. In some runs, the tantalum shaft was screwed upward until it contacted the molybdenum disk; but this procedure was unsatisfactory if the disk fit was relatively loose, and in some cases, reaction was noted between the tip of the tantalum shaft and the disk. In cases where vibration was not excessive, a better procedure was to lock the disk holder to the tantalum shaft by means of a separate molybdenum lock-nut screwed onto the shaft below the disk holder.
expansion problem, nor do disk and holder react with each other, except possibly to fuse together when heated. Fortunately, fusion was observed only rarely.

Prior to each run, the disk was weighed and force-fit into its holder. The holder was then screwed onto a shaft in a bearing-block which was rotated by means of a hysteresis synchronous motor. The shaft was made of tantalum to resist corrosion at high temperatures. Two of these centerless ground tantalum shafts were ruined in preliminary runs due to fusion of the molybdenum disk holder to the tantalum shaft at high temperatures. It was found that fusion could be prevented by covering the threads of holder and shaft with graphite powder before screwing them together. This was adopted as standard procedure prior to each run, and fusion of holder to shaft rarely occurred thereafter.

The stirring motor was two-phase, 115 VAC hysteresis synchronous motor from Globe Industries with a design rotational speed of 24,000 rpm. A control unit for this motor consisted basically of a Hewlett-Packard 200ABR audio oscillator with amplification and impedance-matching circuitry. With impedance properly matched, the frequency selected on the dial of the audio oscillator would equal the angular velocity of rotation of the shaft. Rotational speeds as low as 1000 rpm were possible with the motor-control unit, and the upper limit of rotational velocity was fixed by the resistance of the shaft and holder to vibration. In practice, an upper limit of 15,000 rpm was observed, using a shortened shaft and a disk holder design of the type shown by Fig. III-3b. The rotational velocity, once set on the audio oscillator, is very constant -- a well-known property of hysteresis synchronous motors.

The disk was heated by induction. In the early system of Fig. III-1 the pre-heating of the gas also was done by induction. The quartz chamber
which carried the gas mixture to the disk and housed the reaction was sheathed in a long, stainless steel "neck." A long coil of copper refrigeration tubing was wound from the top of this neck down to the reaction area. This tubing was then connected to the RF induction heater. When power was applied to the coil, induced currents heated the entire length (approximately 1 foot) of the neck. Temperatures on the order of 1300°C were noted by direct optical pyrometer readings on hotter sections of the neck. However, the power loss by radiation from the neck was enormous; and even at full power output from the induction heater (30 kV), it was not possible to produce disk temperatures above 1000°C.

It was concluded that the system of Fig. III-1 made inefficient use of the induction heater. At that time, the results of Section II, which show that the variable properties effect is rather small, were not yet worked out. It was thought that it would be desirable to attempt to pre-heat the gas, however inadequately, and this was done in the final system of Fig. III-2 by means of a resistance furnace which had its own, external power supply. A small induction coil (about 1-1/2 in. long) was wound and placed to concentrate heat entirely on the disk and holder, and this method of heating worked so well that disk temperatures of 1700°-1800°C could be attained using only a small percentage of the power output of the induction heater. The use of the resistance furnace for pre-heating was less successful, partly because the furnace had a highly non-uniform temperature distribution and tended to create a "hot spot" in the quartz neck, sometimes causing breakage.

In the advanced system of Fig. III-2, the temperature of the disk was determined quite critically by the power output of the induction heater. For this reason, a Honeywell Electronik 18 control unit was utilized to regulate the induction heater. This control unit had the capability (when used in combination with an appropriate temperature sensing device) of
automatically regulating the power of the induction heater so as to hold the disk temperature constant by feedback during the run. Attempts were made to regulate temperature in this way, but proved unnecessary and troublesome. It proved very satisfactory to monitor the disk temperature continuously during the run by means of the optical pyrometer. A special 10-decade potentiometer was installed to replace the manual control in the Honeywell control unit, and it was quite easy to maintain manual temperature regulation to ±5°C constancy by this visual-manual feedback alone.

The disk temperature was measured in the case of both systems by means of a Pyro Micro-Optical pyrometer, which sighted on the disk through a right angle prism. The optical pyrometer was checked for accuracy by the Meter Shop of Lawrence Radiation Laboratory, Berkeley, and a correction table was made to account for reflection and transmission loss in sighting the pyrometer through the prism and the layer of optically flat glass (see Fig. III-2). This apparent temperature loss due to indirect sighting on the disk amounted to 5°C at a disk temperature of 850°C, about 10°C at 1200°C, and 20°C at 1500°C.

The design of the molybdenum disk itself is discussed in Fig. III-3c. The "blackbody" hole, 0.016 in. to 0.030 in. in diameter, was drilled into all disks used in runs with the advanced, highly non-isothermal system of Fig. III-2. The optical pyrometer is quite a good telescope; the pyrometer filament is thin enough to "fit" visually into the area of these small, black-body holes when the pyrometer is focused on the disk from a distance of three or four feet away. There are two temperatures that the optical pyrometer can measure: (1) the apparent disk surface temperature and (2) the "black-body" temperature of the hole drilled into the disk. If the system were completely isothermal and at equilibrium, and the emissivity of the disk surface were unity these two temperatures would be the same; that is, the hole in the disk would be invisible during the run. The
disk diameter: 0.5"-0.55"

material: high-purity molybdenum metal
0.04" thick

"black-body" hole (for temperature measurement with optical pyrometer)

Fig. III-3c: Design of molybdenum disk, press-fit prior to each run into the appropriate space in the molybdenum disk holders, illustrated in Figs. III-3a and III-3b. The disk diameter varied as runs with a particular disk holder proceeded; a given disk, due to edge corrosion, could be used only 1-5 times. When a given disk was retired, the disk holder would be bored out to eliminate the oxidation effects, and a new disk custom-made to fit the larger dimension.

The diameter of the "black-body" hole, while in principle required to be as small as possible, in practice had to be made fairly large—otherwise slightly eccentric rotation of the disk made it difficult to measure temperature easily and reliably. The largest black-body hole diameter used was 0.030", or a mere 0.3% of the total disk area.

In the earliest runs (with the "isothermal" system of Fig. III-1), no black-body hole was used—a probable cause of the unreliability of the early data. Preliminary runs with the system of Fig. III-2 used a black-body hole 0.016" diam. X 0.03" deep, or 3/4-way through the disk. Due to the difficulty of drilling such holes, it finally became necessary to make the holes penetrate the entire disk thickness—and temperature measurements in the bulk of the data reported in this chapter were obtained by sighting on such holes (abbreviated BBT, or "black-body through the disk").
purpose of the hole (cavity) is to approximate black-body radiation, thereby eliminating the need for the more difficult emissivity corrections of the apparent surface temperature.

With the system of Fig. III-2 with pre-heating furnace, there is the attendant problem of temperature measurement error, due to light emitted by the furnace being reflected from the disk surface. The hottest part of the furnace is about 1300°-1400°C. If the heater were not there, the disk surface would always appear cooler than the black body hole because of its lower emissivity. With the heater, if the disk temperature is low (about 1000°C or less), it is expected that the disk surface would appear hotter than the black body hole, because of reflection. And if the disk is very hot, say about 1500°C, the disk surface will appear cooler than the black-body hole. This was observed experimentally; at low disk temperatures, the black body hole appeared 100°C-150°C cooler than the disk surface, which made pyrometer readings so difficult to measure accurately as to preclude the possibility of obtaining kinetic data with the advanced system of Fig. III-2 at temperatures below 900°C. At very high temperatures, above 1500°C, the black-body hole appeared 40°-100° hotter than the rest of the disk. A crossover effect was observed: at temperatures in the range 1150°-1350°C, the black-body hole usually was observed to be within 5°-10°C of the disk surface temperature. In some cases, the black-body hole was invisible during runs in the "crossover" range.

Temperature measurements for early runs employing the "isothermal" system of Fig. III-1, were made without the aid of a black body hole, by sighting directly on the disk surface. Since the system was considered to be roughly isothermal, this was a reasonable initial experimental procedure, but it is likely in retrospect that those early temperature readings were inaccurate. The reproducibility of data taken during those early runs was not high, but this cannot be attributed to inaccurate temperature readings alone; this was due partly to the state of evolution of disk preparation methods.
Black body holes were drilled into every disk used with the advanced, highly non-isothermal system of Fig. III-2. The earliest black-body holes were 0.016 in. in diameter, and were drilled only three-quarters through the thickness of the disk. Later, because of the difficulty of drilling such shallow holes, the holes were drilled completely through the thickness of the disk (BHT, or "black-body hole drilled through the disk"). Particularly in the case of disk holders of the design in Fig. III-3a, the effect of the BHT was to form a quite good "black-body" cavity radiator of small aperture. Assuming rapid heat conduction within the disk-holder-shaft tip system (and hence temperature uniformity), the temperatures read by the optical pyrometer sighting on the BHT should reflect true disk surface temperatures, without need of emissivity corrections.

The rotating tantalum shaft resisted oxidation quite well at high temperatures, but the threads of the shaft did suffer some corrosion damage with succeeding runs. This caused increasingly eccentric rotation of the disk. It was found necessary in later runs to enlarge the diameter of the BHT from 0.016 in. to 0.030 in. -- but even so, the BHT occupied a mere 0.36% of the surface area of a 1/2 in. diameter disk.

The earliest runs made with the system of Fig. III-1 employed disks cut from ordinary, stock molybdenum sheet from Lawrence Radiation Laboratory stores. The disks were sanded to a rough finish and washed with acetone prior to oxidation. Figure III-4a is a photomicrograph (magnified 200 times) of a typical surface area of a molybdenum disk so prepared. The surface is covered with scratches on the order of 2-1/2 microns (or less) in width, and some small pits may be noted.

Reproducibility of data taken with such disks, at least in runs using 2% and 7% oxygen in argon ("high" reaction rates), was good (within 10-20%).
Figure III-4a Photomicrograph (200X) of typical surface area of molybdenum disk after fabrication by machine shop. The disk surface has been sanded with fine emery cloth and washed with acetone. The superimposed scale measures 50 mm. At 200X, each division therefore represents 5 microns.
but it was thought that this might be improved by using high-purity molybdenum sheet as disk material. A quantity of molybdenum sheet of 99.9% purity sufficient to supply disks for all anticipated runs was purchased from Electronic Space Products, Inc. Results obtained with disks of high-purity molybdenum and concentrations of 7% oxygen in argon were reproducible within 11% in tests run, but later observations indicated that there was little difference detectable in oxidation rates between stock molybdenum and high-purity molybdenum. Nevertheless, high-purity molybdenum was used to obtain virtually all data reported in this work.

The first runs made with the "isothermal" system of Fig. III-1 at "low" reaction rates (0.5% oxygen in argon) revealed a more serious difficulty: non-uniform disk temperatures. During these runs, the disk surface appeared to be hotter by 10° or more in the center than at the edge. Inspection of the disk after oxidation revealed apparently non-uniform reaction; the disk appeared duller in tone in the center than at the edge.

This problem was solved most satisfactorily by polishing the disks prior to reaction, and this became standard procedure throughout the remainder of the study. Polishing was accomplished by means of a Buehler polishing wheel with an Automet 1900AB attachment. Special holders were made to attach the molybdenum disk/holder combination to the Automet device. The polishing wheel was covered with a double thickness of polishing cloth: an under-layer of soft AB Microcloth; topped by a tough covering of AB nylon polishing cloth. AB Metadi 15 micron diamond polishing compound was used as abrasive, lubricated with AB Metadi fluid.

The effect of polishing is seen by comparing Fig. III-4a with the photomicrographs of Fig. III-4b. Polishing tended to remove major cuts, scratches, and pits in the disk surface, producing surfaces more uniform and reproducible (especially prior to the initial reaction run) than those of unpolished
Figure III-4b Photomicrographs (200X) of two areas of the disk of Figure III-4a after polishing with diamond compound. (Note: the quality of polishing in this case was not as good as was obtained later; this was the first disk to be polished, and technique was not fully developed.)
disks. Oxidation itself also tended to smooth the disk surface, and for this reason the disks were not re-polished after each run.

The effectiveness of polishing the disks was tested experimentally in a series of four oxidation runs using the system of Fig. III-1; two different disks were used. In all four runs the previously observed, apparent temperature non-uniformities were almost completely eliminated. The disk temperature in each case was uniform across the diameter of the disk within a degree or two. Non-uniformity of oxidative attack was greatly reduced, except for an unexplainable zone near the disk/holder interface. But even this small zone of non-uniformity was eliminated by introduction of the new, advanced system of Fig. III-2; it may be concluded therefore that the combination of the disk polishing and direct induction heating (the latter by means of the advanced system design) produced uniform heating of the disk and uniformity of oxidative attack.

The experimental observation that disk polishing appeared to eliminate or greatly reduce surface temperature non-uniformity is difficult to explain. The reason may be in part that polishing produced a condition of uniform emissivity on the disk surface which could not be obtained rapidly enough be oxidation alone at the "low" reaction rates cited above.

The series of four runs (all with 0.7% oxygen in argon, and in the temperature range, 861-868°C) were reproducible within 2% -- and indications are, in retrospect, that this spread might partially have been due to lack of black body holes in the disks for accurate temperature measurement. Introduction of disk polishing also seems to have helped to eliminate pitting of the disk, which sometimes occurred progressively during a series of runs with the same disk. This pitting sometimes occurred, for no easily discernible reason, but seldom recurred except microscopically after polished disks came into use.
It is now in order to describe in detail the general operating procedure during the actual data-gathering exercise, or "run". This will be outlined for the "advanced," non-isothermal system of Fig. III-2. The procedure for the earlier system was almost the same, except that the pre-heating furnace was not used, and the optical pyrometer did not sight upon a "black-body" hole.

B. General Operating Procedure During Oxiation Run

The fresh disk, cut to size and force fit into its holder in the machine shop, was polished with 15 micron diamond paste on the Buehler wheel for one to ten hours, depending on surface roughness. The conclusion of the polishing operation was determined by visual inspection, sometimes under the microscope. The disk was then removed from its holder by screw pressure, and both disk and holder thoroughly cleaned in acetone to remove polishing oil. The disk was fired, weighed on a precision microbalance to five significant figures, and forced back into its holder. Graphite was applied to the threads of the holder and of the tantalum shaft before the holder was screwed onto the shaft. The motor drive control unit was then turned on, and the disk surface further cleaned with acetone while rotating.

The rotation, if observed to be stable and non-eccentric, was terminated, and the entire upper assembly, consisting of quartz reaction chamber, pre-heating furnace, gas inlet tube, and prism, was put into place. Pure argon gas was introduced into the chamber through the gas inlet. The copper induction coil was attached to the induction heater, and the induction heater turned on for warm-up. Cables from the furnace power supply were attached to the pre-heating resistance furnace, and cooling water pumped through the furnace coils. The furnace was then turned on for warm-up.
While furnace and induction heater were warming up, the optical pyrometer was adjusted to sight on the black body hole in the disk, by looking downward through the prism. The motor was then turned on, proper speed checked, and fine adjustments made with the optical pyrometer.

The pre-heating furnace slowly warmed to a pre-determined steady-state current. Power from the induction heater was applied to the induction coils surrounding the rotating disk, and the disk was heated to the temperature desired and allowed to reach a steady value. This part of the run was carried out with the disk rotating in a flowing, inert argon atmosphere.

Conditions stabilized after a few minutes heating. Initial disk temperature was noted. By means of a two-way valve, the argon flow was shut off, the reactant gas (commercial pre-mixed gases of oxygen in either argon or helium), was admitted and the timing clock turned on. The flow rate of reactant gas purposely was set very high initially and kept at this high value for about the first thirty seconds of each run, so as to flush the disk instantly with oxygen; after this initial flushing, the reactant gas flow rate was turned down to a pre-determined, steady value and held constant for the duration of the run.

The temperature was monitored continuously through the optical pyrometer, and disk temperature recorded each minute or two. If any temperature change occurred after the first minute (usually the disk temperature would jump upward or down when oxygen was admitted, and reach a relatively stable value after about thirty seconds or a minute), the manual induction heater control would be used to compensate. Once experience had been acquired with operating procedure, it was possible in most cases to keep the disk temperature constant within ±5°C after the initial two or three minutes of the run. The radial temperature variation on the surface was never more than a degree or two for polished disks.
The length of the run varied between 3 and 45 minutes, depending on oxygen concentration and the pre-determined purpose of the run. The usual length was 10-20 minutes.

The run was terminated by switching off the flow of reactant gas and flushing the system with a high flow rate of a reducing gas mixture (96% helium, 4% hydrogen). In addition to removing oxygen rapidly from contact with the hot disk, the helium inert caused a rapid drop in disk temperature (since the thermal conductivity of helium is greater than that of argon) of 80°-100°C or more, thereby "cooling down" the reaction. This is of course not true with runs using oxygen diluted with helium; during quenching in those cases, the disk temperature rose by 10°-100°C, depending on the temperature of the run. This did not appear to affect the data obtained during the helium-oxygen series of runs.

The runs were quenched with helium-hydrogen mixture instead of, say, pure argon because of the reducing properties of hydrogen. Pure argon was used to quench certain trial runs; upon cooling, examination of disks used in those runs revealed that the molybdenum surfaces which had been exposed to oxidation were bluish in color -- indicating the presence of oxide products (possibly Mo$_2$O$_5$) left from the reaction. Disks from runs quenched by hydrogen-helium mixture were dull gray with an adherent, powdery, easily scratchable surface -- indicating that the surface oxide had been reduced to elemental molybdenum by reaction with hydrogen at high temperature. Thus the disk was restored essentially to its condition prior to oxidation.

In order to assure maximum oxide reduction, the disks were allowed to rotate at temperature in the helium-hydrogen mixture of 3-5 minutes after termination of each run. Temperature drop (or rise) upon quenching was noted.
After "soaking" in the reducing atmosphere under heat, the induction heater was turned off, rotation stopped, and the disk assembly, quartz chamber, and pre-heating furnace allowed to cool down. Upon cooling, the superstructure surrounding the disk was removed, and the holder unscrewed from the shaft. The disk was forced out of its holder, cleaned with acetone, and weighed.

The data point obtained from each run consists of the weight loss suffered by the disk due to oxidation, the disk area, the length of the run, and the corrected, time-averaged temperature of the disk during the run. Since it was in general possible to maintain disk temperature constancy within a narrow temperature range during the greater part of each run, the temperature of oxidation was taken to be a simple time average of the temperatures monitored and recorded during the run.
IV. PRESENTATION OF MOLYBDENUM OXIDATION-RATE DATA

The classical reaction-rate equation, to which the data of this study will be fitted, may be written:

\[ \dot{m} = k_R p_{10}^n \exp \left( -\frac{E_a}{RT_0} \right) \]  

where \( k_R \) is the temperature-independent component of the reaction-rate constant; \( p_{10} \) the partial pressure of oxygen at the disk surface during reaction; \( n \) the order of the reaction; \( R \) the gas constant; \( E_a \) the activation energy of the reaction (kcal/gram-mole); and \( \dot{m} \) the rate of reaction (weight loss) of the disk per unit (geometrical) surface area (grams/cm²·sec).

The experimental data from this study consist of measurements of \( \dot{m} \) as a function of \( T_0 \); the oxygen partial pressure in the reactant gas, \( p_{10} \); and disk rotational speed, \( \Omega \). The last two variables determine \( p_{10} \).

A. Determination of the Surface Oxygen Partial Pressure

It is clear that there is no easy method of measuring the partial pressure of oxygen at the disk surface while reaction is occurring -- unless the partial pressure at the disk surface is nearly equal to that in the bulk gas mixture (in the reaction-controlled regime). But for the special case of the rotating disk system, we may calculate \( p_{10} \) from the following considerations.

In Section II it was indicated that interpretation of reaction rate data obtained with the rotating disk system is particularly simple, because separation of reactive and diffusional effects is readily effected. Referring to Eqs. (II-37) and (II-38), setting the variable molecular weight ratio equal to unity, we may write:
In Tables II-3 and II-4 it was shown that \( g_{vp} \) for both argon- and helium diluted systems is nearly constant over the entire temperature range of interest. If was assume constant \( g_{vp} \) and solve (IV-2) and (IV-3) simultaneously for \( p_{10} \), we obtain:

\[
\hat{m}_{DC} = g_{vp}(T_{DC}) p_{1\infty}
\]  

\[
\hat{m}(T_0) = g_{vp}(T_0) (p_{1\infty} - p_{10})
\]  

Equation (IV-4) provides a means of deducing the concentration of oxygen at the disk surface during reaction from experimental data. \( \hat{m}(T_0) \) is the datum from a specific run at temperature \( T_0 \); \( \hat{m}_{DC} \) is the "diffusion-limited" reaction rate, measured at high temperatures; and \( p_{1\infty} \) is given by analysis of the reactant gas mixture.

Three separate analyses were performed on each of the five gas mixtures. The first, usually rough, analysis was performed by the supplier, Pacific Oxygen Company of Oakland (in two cases by the Matheson Company of Newark, California), before the gas cylinders were shipped. The second, a more careful re-analysis about a year later, was done by Pacific Oxygen; but the error limits listed for this second analysis were unsatisfactorily wide. The third, which could have been quite accurate, was carried out by mass spectrometer at the Lawrence Radiation Laboratory, Berkeley. This last analysis was rendered questionable by deficient preparation of the gas samples, and had to be corrected for leakage; and it was not possible to re-analyze the mixtures by mass spectrometer due to unavailability of personnel and equipment. The results of these three analyses are given in Table IV-1.
Table IV-1 Results of three separate analyses of each of the five mixed gases (oxygen diluted with argon or helium) used to obtain molybdenum reaction-rate data.

<table>
<thead>
<tr>
<th>Nominal Oxygen Concentration</th>
<th>Mole Fraction Oxygen rough analysis</th>
<th>POXCO analysis</th>
<th>mass spectrometer</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2% (in argon)</td>
<td>0.0021</td>
<td>0.002±0.0005</td>
<td>0.0018</td>
</tr>
<tr>
<td>0.5% (in argon)</td>
<td>0.006</td>
<td>0.0055±0.0005</td>
<td>0.0054</td>
</tr>
<tr>
<td>2% (in argon)</td>
<td>0.0206</td>
<td>0.021±0.0005</td>
<td>0.0190</td>
</tr>
<tr>
<td>5% (in argon)</td>
<td>0.0495</td>
<td>0.0515±0.0005</td>
<td>0.0503</td>
</tr>
<tr>
<td>0.5% (in helium)</td>
<td>0.00569</td>
<td>0.0050±0.0005</td>
<td>0.0053</td>
</tr>
</tbody>
</table>

* The mass spectrometric analyses were corrected for leakage by analyzing nitrogen content of the samples and subtracting the appropriate air/ratio of oxygen from the total oxygen content.
B. The Order of the Surface Chemical Reaction

If \( \dot{m} = \dot{m}(p_{10}, T_0) \) is considered to be a function of the independent variable, \( p_{10} \) (calculated for each point of experimental data from Eq.(IV-4) and the corrected mass spectrometric analyses of Table IV-1) and parametric in \( T_0 \), we may make a series of plots of \( \dot{m} \) versus \( p_{10} \) for various disk temperatures. The experimental data interpreted in this manner should appear linear on a log-log plot, and the lines for all temperatures should have the same slope, equal to \( n \), the order of the reaction. The five points plotted in each of Figs. IV-la-e represent oxidation rates of molybdenum obtained (at a given \( T_0 \)) with each of the five gas mixtures: (approximately) 0.2%, 0.5%, 2% and 5% oxygen in argon; and 0.5% oxygen in helium. It is noteworthy that the five oxygen-helium data points are most consistently close to the straight lines at all temperatures.

It is quite clear from Figs. IV-la-e that we may draw the first important conclusion from the experimental data: the surface reaction is first-order. The scatter increases with higher temperature data (due to the increasing error of the factor \( (1 - \dot{m}/\dot{m}_{DC}) \) in Eq. (IV-4) as we move toward diffusion-controlled temperatures) -- but at all temperatures the slope of the (visually) best-fit line is very close to unity.

C. Determination of the Activation Energy of the Surface Chemical Reaction

If \( n \) is set equal to unity in Eq.(IV-1), and Eq. (IV-4) used, we obtain:

\[
\dot{m} = k_R \ p_{10} \ (1 - \dot{m}/\dot{m}_{DC}) \ \exp \left( -E_a/RT_0 \right)
\]

(IV-5)

It is clear from Eq. (IV-5) that, except deep in the reaction-controlled regime (\( \dot{m} \ll \dot{m}_{DC} \)), we will not be able to obtain the true activation energy \( E_a \), simply by plotting \( \dot{m} \) versus \( 1/T_0 \) on semi-log paper. \( E_a \) is the slope...
Fig. IV-la. Log-log plot of experimental values of $\dot{m}$ versus calculated values of $p_{10}$ from Eq. IV-14, at $T_0 = 1150^\circ$K.
Fig. IV-1b. Log-log plot of experimental values of $\dot{m}$ versus calculated values of $p_{10}$ from Eq. IV-4, at $T_0 = 1225^\circ$K.
Fig. IV-1c. Log-log plot of experimental values of \( m \) versus calculated values of \( p_{10} \) from Eq. IV-4, at \( T_0 = 1300^\circ \text{K} \).
Fig. IV-1d. Log-log plot of experimental values of $\dot{m}$ versus calculated values of $p_{10}$ from Eq. IV-4, at $T_0 = 1375^\circ$K.
Fig. IV-1b. Log-log plot of experimental values of $m$ versus calculated values of $p_{10}$ from Eq. IV-4, at $T_0 = 1450\text{°K}$.
(on a semi-log plot) of \( \frac{n}{1 - n/n_{DC}} \) versus \( T_0 \), at a given value of \( p_{\infty} \).

In Figs. IV-2a-e all the kinetic data obtained in this study are presented; raw and corrected data are plotted as a function of \( T_0^{-1} \), parametrically in \( p_{\infty} \). Points considered to lie in the "primary" (i.e., low temperature) diffusion-limited temperature regime are indicated. (See discussion later in this chapter for distinction between "low" and "high" temperature diffusion controlled regimes.)

The activation energy is obtained by drawing and taking the slope of the (visually) best line through the corrected data points. The values of activation energy and \( k_R \) calculated from Figs. IV-2a-e are tabulated as a function of bulk oxygen concentration in Table IV-2.

The best kinetic data were obtained in the oxygen-helium runs of Fig. IV-2a, for which Eq. (IV-5) is nearly a perfect model. Correcting the raw data produces a good line with slight deviation, from the lowest, reaction-controlled temperatures up to temperatures just below the diffusion-controlled regime. The activation energy of the reaction is 40 kcal/gmole, which agrees well with the data obtained in argon-diluted systems (Figs. IV-2b, c, d, e); but the corrected data lines of the argon runs suffer considerably more deviation than those of the helium runs, and cover a smaller temperature range.

The data of Fig. IV-2a (0.5% oxygen in helium) are more accurate than those of the argon runs for at least two reasons. In the first place, the helium-oxygen runs were performed after the experimental techniques had been developed by long experience nearly to the point of perfection. All disks in this series had BBT holes for accurate temperature measurement. The helium series was next to the last to be run; the series which followed, 0.2% oxygen in argon (Fig. IV-2b), also was quite good. Secondly, the
Fig. IV-2a. Rates for 0.5% O₂ in helium.
Fig. IV-2b. Rates for 0.2% O₂ in argon.

Primary diffusion-controlled regime

\[ \dot{m}_{DC} = 2.25 \times 10^{-5} \text{ g/cm}^2 \text{sec} \]

\[ E_a = 40 \text{ kcal/mole} \]

0.2% O₂ (in argon)

- \( \dot{m} \) (Raw Data)
- \( \dot{m} \) (1 - \( \dot{m} / \dot{m}_{DC} \))^{-1}
Fig. IV-2c. Rates for 0.5% \( \text{O}_2 \) in argon.
Fig. IV-2d. Rates for 2\% O\(_2\) in argon.
Fig. IV-2e, Rates for 5% O₂ in argon.

(a) Primary diffusion-controlled regime.
Table IV-2  Experimentally determined values of $E_a$ and $k_R$

based on data of Figs. IV-2a, b, c, d, e.

<table>
<thead>
<tr>
<th>Nominal oxygen concentration</th>
<th>$E_a$ (kcal/gmole)</th>
<th>$k_R$ (g/atm-cm$^2$-sec)$\times10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2% (in argon)</td>
<td>40</td>
<td>3.5</td>
</tr>
<tr>
<td>0.5% (in argon)</td>
<td>40</td>
<td>2.2</td>
</tr>
<tr>
<td>2%  (in argon)</td>
<td>(49)</td>
<td>(82)</td>
</tr>
<tr>
<td>5%  (in argon)</td>
<td>39</td>
<td>2.3</td>
</tr>
<tr>
<td>0.5% (in helium)</td>
<td>40</td>
<td>2.6</td>
</tr>
</tbody>
</table>
diffusion coefficient of oxygen in helium is greater than that of oxygen in argon; therefore diffusion control will take effect at a higher temperature with helium than with argon diluent. The primary diffusion-controlled regime begins at about 1500°K for argon systems, but at about 1650°K for the helium system. This difference gives the researcher leeway to get more, and more accurate, points in the "mixed" regime.

On the negative side, the effect of variable molecular weight is in theory more pronounced for helium than for argon. This effect does not appear in the data of Fig. IV-2a, but it would be interesting to perform a series of runs with higher concentration (say 5% oxygen in helium) to see whether the effect of variable molecular weight actually is observable. If so, it would make helium a less attractive diluent, despite the fact that the best data obtained in this study came from the helium diluent runs.

D. Oxidation Behavior at Very High Temperatures (> 1850°K)

It may be seen from Figs. IV-2a-e that most of the data fall into these separate regions: (1) a linear, low-temperature, reaction-controlled regime; (2) curving of the data line as the temperature is increased into the mixed regime where diffusional resistance is becoming important; and finally (3) a plateau at the onset of diffusional dominance. In Figs. IV-2b, d, e it is quite clear that the data has "flattened" into diffusion-control at a temperature of about 1520°K, and this temperature has been taken as the lower limit of the "primary" diffusion-controlled regime. A quite analogous phenomenon occurs for the helium oxygen data of Fig. IV-2a at about 1670°-1700°K. The "primary" region for the data of Fig. IV-2c was selected to have a lower limit of 1670°K because of the well-defined, definitely diffusion-controlled, cluster of points in that region.
The upper limit of the "primary diffusion-controlled regime" was chosen, somewhat arbitrarily, to lie at about 1760°K for the argon-oxygen data and at about 1850°K for the helium-oxygen data. (It should be noted that 1850°K could have been chosen as the upper limit for all data taken, with equal consistency.) An upper limit to the "primary" regime had to be set because data taken at temperatures above the upper limit appear to be influenced by a different, less understood, diffusional mechanism, possibly involving also a change of reaction mechanism on the disk surface.

The existence of a fourth regime, of extremely high temperature diffusion-control, was suggested by the appearance of the scanty data taken at temperatures above 1850°K. If we examine the data points in Figs. IV-2a, b, c, d, above the "primary" diffusion-controlled regime, it will be noted that (excepting Fig. IV-2b), these high temperature data points lie significantly above or below the lines drawn to indicate the average $m_{DC}$. (There were no data taken above 1600°K in the series of Fig. IV-2e.)

The unfortunate aspect of this extreme high temperature data, besides its paucity, is that there is no consistent trend of data points; in some cases, these points lie above, and in others below, the line of the average $m_{DC}$. Further research, which would require redesign of the equipment used for this study to accommodate more easily 1800°K plus temperatures, is called for to resolve this discrepancy.

Further evidence of a change in surface mechanism above 1850°K is provided by the physical appearance of disks oxidized in the fourth regime.
Figure IV-3a shows a disk of molybdenum oxidized at 2020°K alongside a disk which underwent reaction at 1823°K. The latter disk is dull in tone, indicating the presence of a surface oxide remaining after reaction; the disk which was oxidized at the extremely high temperature is polished to a mirror-like finish, and apparently free of surface oxides during reaction. Photomicrographs of the same disks appear in Figs. IV-3b c, d, e. Figure IV-3b. at 100X magnification, shows a typical, smooth, highly polished area of the 2020°K disk; Fig. IV-3c shows an area near the same disk's BTM marked by cracking due to the strain of removing the disk from its holder after reaction.

The molybdenum sheet used as disk material in this research appeared to be composed of laminated material. This did not cause difficulties in runs at temperatures below 1850°K, but at higher temperatures embrittlement was quite severe and usually the disk cracked and/or bent on removal from its holder. Cracking and flaking of the disk (shown quite clearly in Fig. IV-3d) may have introduced error in weighing in the extreme high-temperature runs and may explain discrepancies previously noted. Non-laminated disk material, or some new disk/holder design, would be called for if further studies were to be carried out above the "primary" temperature regime range.

Photomicrographs of the disk oxidized at 1823°K are shown in Figs. IV-3d, e. The surface is rougher than that of the 2020°K disk, and some cracking due to embrittlement is present, but the surface appears to be cohering. Flaking away of the upper, laminated surface layers does not seem to be a problem.
Figure IV-3a  Disks after oxidation; at 2020°K (left) and 1823°K (right).
Figure IV-3b  Photomicrograph (100X) of typical surface area of molybdenum disk No. 15 after oxidation at 2020°K.

Figure IV-3c  Photomicrograph (200X) of area of molybdenum disk No. 15 near center black-body hole after oxidation at 2020°K. Note cracking and peeling away of top laminated surface layer. Due to manner of removal of disk from holder, maximum stress and cracking occurs near disk center, especially after embrittlement at extreme high temperatures.
Figure IV-3d  Photomicrograph (100X) of typical area of molybdenum disk No. 35, after oxidation at 1823°K.

Figure IV-3e  Photomicrograph (400X) of typical area of molybdenum disk No. 35, after oxidation at 1823°K.
E. Comparison of Rotating Disk Theory With Experimental Results for Completely Diffusion Controlled Oxidation

The experimental values of \( \dot{m}_{DC} \) tabulated in Table IV-3 are the averages, for a series of runs at a given bulk oxygen concentration, of all data points in the primary diffusion-controlled regime. In this regime, presumably the oxidation reaction at the disk surface takes place according to the same mechanism as in the reaction-controlled and "mixed" regimes.

The theoretical values of \( \dot{m}_{DC} \) in Table IV-3 were calculated from Eq. (II-29) with the variable molecular weight factor set equal to unity. The mass-spectrometric gas analyses were used for \( P_{L\infty} \), and values of \( g_{vp} \) were taken from Tables II-3 and II-4. For oxygen-argon calculations, \( g_{vp} \) was evaluated at 1520°K; for oxygen-helium, at 1670°K. The ratio \( \dot{m}_{DC}/P_{L\infty} \) is the experimentally determined rate divided by the bulk oxygen concentration.

The expressions derived theoretically in Section II for the diffusion-limited reaction rate, Eqs. (II-29) and (II-30), also predict that the rate will be proportional to the square root of the rotational speed of the disk. Assumption 6a requires that forced convection mass transfer dominate over natural convection mass transfer, and is valid if the disk stirring speed is sufficiently great. Due to physical difficulties encountered in making a rotating disk apparatus capable of operating at high temperatures under extreme oxidizing conditions, it was found not to be possible to rotate disks used in the present study faster than 15,000 rpm, and in fact only one data point at this high rotational speed was obtained. Nearly all runs were carried out at 9600 rpm, but the one data point at 15,000 rpm indicated that 9600 rpm was at least a lower limit on rotational speed necessary to insure forced convection dominance.

The results of four runs carried out with nominally 0.5% oxygen in argon in the diffusion-controlled regime (1725°-1756°K) are shown in
### Table IV-3: Experimentally measured and theoretically predicted values of the rate of diffusion-controlled oxidation of molybdenum

<table>
<thead>
<tr>
<th>$P_{100}$ (atm)</th>
<th>Experimental</th>
<th>$m_{\text{DC}}$ (g/cm$^2$ sec)$\times 10^5$</th>
<th>Theoretical</th>
<th>% Error</th>
<th>$\frac{m_{\text{DC}}}{P_{100}}$ (g/atm-cm$^2$ sec)$\times 10^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0018</td>
<td>$2.3 \pm 0.2$</td>
<td>1.9</td>
<td>+20</td>
<td></td>
<td>1.25±0.10</td>
</tr>
<tr>
<td>0.0054</td>
<td>$6.5 \pm 0.2$</td>
<td>5.7</td>
<td>+14</td>
<td></td>
<td>1.20±0.04</td>
</tr>
<tr>
<td>0.0190</td>
<td>$21.3 \pm 1.5$</td>
<td>20.2</td>
<td>+ 6</td>
<td></td>
<td>1.12±0.08</td>
</tr>
<tr>
<td>0.0503</td>
<td>$55.4 \pm 0.8$</td>
<td>53.3</td>
<td>+ 4</td>
<td></td>
<td>1.10±0.02</td>
</tr>
<tr>
<td>(in argon)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0053</td>
<td>$13.9 \pm 0.8$</td>
<td>11.2</td>
<td>+24</td>
<td></td>
<td>2.62±0.15</td>
</tr>
<tr>
<td>(in helium)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**NOTE:** In the above table, ± does not indicate a statistical data spread, but merely the range of the data taken in each series of runs within the "primary" diffusion-controlled regime.
Fig. IV-4 in a plot of $\hat{\mathbf{n}}_{DC}$ versus square root of rotational speed, 1500-15,000 rpm. The diffusion-limited reaction rate, well-established for this concentration as $6.47 \times 10^{-5} \text{ g/cm}^2\text{-sec}$ at 9600 rpm, is almost exactly proportional to the square root of rotational speed observed by means of the one data point, $8.00 \times 10^{-5} \text{ g/cm}^2\text{-sec}$ at 15,000 rpm.

Note that $8.0/6.47 = 1.24$ and that $(15,000/9600)^{1/2} = 1.25$. We may conclude that, for the present system, a true diffusion limited regime dominated by forced convection for rotational speeds above 9600 rpm, and behavior according closely with the theoretical Eq. (II,30) has been observed. Natural convection effects compete with forced convection effects at stirring speeds below 9600 rpm, as evidenced by the fact that the curve of Fig. IV-4 has an (extrapolated) non-zero reaction rate at zero stirring speed.

Two series of runs were carried out to test Assumption 1 of Section II (the steady state assumption), which requires that the reaction rate be independent of the reaction time, or the length of the run. This is shown to be the case in the reaction-controlled regime ($1310^\circ\text{K}$) by the series of four runs plotted in Fig. IV-5. The weight loss of the disk is closely proportional to the length of the run, for runs of 4-15 minutes.

The second series of runs were carried out in the diffusion-controlled regime ($1741^\circ\text{K}$) and are shown in Fig. IV-4. Again, the absence of an induction period is proved by the excellent linearity of the weight loss versus length of the run plot of Fig. IV-6.

So far in this chapter there has been no detailed discussion of a most important systemic variable: the flow rate at which the inlet gas mixture is admitted to the oxidizing system. A certain minimum flow rate
Fig. IV-4. Diffusion-limited reaction rate as a function of disk rotational speed. 0.5% O₂ in argon.
Fig. IV-5. Weight loss versus length of oxidation run for nominally 2\% oxygen in argon in the reaction-controlled regime (T_0 = 1310^\circ K).
Fig. IV-6. Weight loss versus length of run for nominally 0.5% oxygen in argon in the diffusion-controlled regime ($T_o = 1741 \degree K$).
of gas to the disk is suggested by the nature of the solutions to the flow equations, presented in Section II. In particular, it was shown that the axial velocity at which gas, assuming an infinite disk and medium, is pulled by rotation toward the disk is proportional to the square root of the stirring speed; see Assumption 6 and Eq. (II-18). It is possible to calculate this minimum velocity from the fluid properties and use this result to compute the flow velocity required to supply gas to the reacting disk without back-mixing. But it was found that this procedure, in view of the many approximations involved in deriving the flow equations, tended to underestimate the flow velocity required. A better procedure was to carry out runs in the diffusion controlled regime with varying inlet gas flow rates. This way it was not necessary to have precise temperature control with each run (since reaction rate is nearly temperature-independent in the diffusion controlled regime); and the flow rate necessary to achieve maximum reaction rate in the diffusion controlled regime should also be rapid enough to prevent back mixing in the reaction controlled regime, where reaction rate is nearly independent of convective flow characteristics.

Figure IV-7 shows diffusion limited reaction rate as a function of inlet gas flow rate for five runs using nominally 0.5% oxygen in argon. All runs were made at the standard 9600 rpm rotational speed and an inlet gas temperature of 580°C. The graph shows that a flow rate greater than 800 cm³/min is sufficient to prevent back-mixing; for a 1/2 inch diameter flow guide, the flow rate required to achieve the theoretical approach velocity to the disk ($\omega_0 = 0.886 \sqrt{v_0}$) under these conditions is 660 cc(STP)/min. Most runs carried out used a flow rate of 935 cm³/min.

The series of photomicrographs on Figs. IV-8 to IV-16 shows post-oxidative disk surface conditions as a function of temperature. Highest reaction temperatures are shown first.
Fig. IV-7. Diffusion-limited reaction rate versus inlet gas flow rate, using 0.5% oxygen in argon.
Figure IV-8a  Photomicrograph (100X) of typical area of molybdenum disk No. 14 after oxidation at 1727°K. This disk was used only for this run.

Figure IV-8b  Photomicrograph (400X) of disk No. 14 after its single oxidation run at 1727°K.
Figure IV-9a  Photomicrograph (100X) of typical area of disk No. 30 after oxidation at 1704°K. This disk was previously oxidized in runs at 1953°, 1632°, and 1490°K and this previous series of runs appears to have pre-formed the surface to some extent. Compare roughness of this disk with relative smoothness of disk of Figure IV-8.

Figure IV-9b  Photomicrograph (400X) of disk No. 30 after oxidation at 1704°K. Note fine pits and regularity of crack patterns.
Figure IV-10a Photomicrograph (100X) of disk No. 31 after oxidation at 1582°K. This disk experienced previous runs at 1287° and 1733°K.

Figure IV-10b Photomicrograph (400X) of typical area of disk No. 31 after oxidation at 1582°K.
Figure IV-lla Photomicrograph (100X) of typical area of disk No. 29 after oxidation at 1442°K. This disk was run twice previously, at 1352°K and at 1197°K.

Figure IV-11b Photomicrograph (400X) of typical area of disk No. 29 after oxidation at 1442°K.
Figure IV-12a Photomicrograph (100X) of typical area of disk No. 36 after oxidation at 1394°C. This disk was run previously at 1822°C.

Figure IV-12b Photomicrograph (400X) of typical area of disk No. 36 after oxidation at 1394°C.
Figure IV-13a Photomicrograph (100X) of typical area of disk No. 34 after oxidation at 1320°K. This disk was oxidized only once.

Figure IV-13b Photomicrograph (400X) of typical area of disk No. 34 after oxidation at 1320°K.
Figure IV-14a Photomicrograph (100X) of typical area of disk No. 33 after oxidation at 1273°K. This disk was previously run at temperatures of 1192°K and 1213°K.

Figure IV-14b Photomicrograph (400X) of typical area of disk No. 33 after oxidation at 1273°K. Disks oxidized at lower temperatures have much the same appearance and for that reason are not shown.
Figure IV-15  Photomicrographs of typical areas of disk No. 9 after oxidation at 1543°K (no prior runs) and quenching with pure argon rather than the usual helium-hydrogen mixture. Clockwise from upper left: 100X, 200X, and 400X.
Figure IV-16 Photomicrograph (200X) of area of disk No. 40. This disk was oxidized three times in the following order: 1678°, 1973° and 1186°K. The appearance of this disk illustrates the principle that runs should be carried out in order of increasing temperature, particularly when cracking at extreme high temperatures preconditions the disk surface against accurate results at lower temperatures.
V. DISCUSSION OF EXPERIMENTAL RESULTS

A. Comparison with Previous Studies

Rosner and Allendorf\textsuperscript{9} have summarized and compared previous kinetic data on the oxidation of molybdenum on the basis of an oxidation probability, $\epsilon$, which is defined as the ratio of the flux of molybdenum atoms (regardless of their chemical state of aggregation) away from the reacting surface, to the collision flux of oxygen molecules incident on the surface. That is,

\[ \epsilon \cdot \left[ \text{molar flux of } O_2 \text{ incident on hot molybdenum surface} \right] \equiv \left[ \text{molar flux of molybdenum in any state of chemical aggregation away from hot surface} \right] \]

or

\[ \epsilon \cdot Z_{O_2} \equiv Z_{Mo} \quad (V-1) \]

In the case of the present study with the rotating molybdenum disk in gas at atmospheric pressure, the molar flux of oxygen impinging on the disk surface in the fluid volume adjacent to the surface is given by:

\[ Z_{O_2} = \frac{1}{4} (n/N_{Av}) \bar{v} = \frac{1}{4} \left( \frac{P_{10}}{RT_0} \right) \left( \frac{\delta RT_0}{\pi M_1} \right)^{1/2} \quad (V-2) \]

In Eq. (V-2) use has been made of the ideal gas law to evaluate $n$, the number density of oxygen molecules per unit volume in the neighborhood of the disk surface; and $\bar{v}$ is the mean molecular speed near the disk surface. $N_{Av}$ is Avogadro's number and $M_1$ is the molecular weight of oxygen.

Since the molybdenum oxidation reaction has been shown to be first order in surface oxygen partial pressure, Eq. (IV-2) may be rewritten as:

\[ Z_{Mo} = \left( \frac{1}{M_{Mo}} \right) \hat{\mu}(T_0) = \left( \frac{1}{M_{Mo}} \right) k_R p_{10} \exp\left( -\frac{E_a}{RT_0} \right) \quad (V-3) \]

Combining Eqs. (V-1) to (V-3):

\[ \epsilon(T_0) = \left( \frac{1}{M_{Mo}} \right) \left( 2\pi M_{Mo}RT_0 \right)^{1/2} k_R e^{-E_a/RT_0} \quad (V-4) \]
Figure V-1 compares the results of the helium-oxygen runs in the present research with the kinetic results of four previous studies. The most striking feature of the present data (curve F) is that the activation energy of the oxidation reaction is nearly twice that obtained by any previous research: approximately 40 kcal/gmole as compared to earlier results, which averaged about 24 kcal/gmole. These results of the present study would be questionable but for the undeniable linearity of most of the corrected Arrhenius plots of Figs. IV-2a-e (in particular that of Fig. IV-2a) and the good agreement between values of \(E_a\) and \(k_R\) obtained for different oxygen concentrations and different diluent gases.

In order to attempt to understand the unexpectedly large activation energy, it is necessary to examine briefly the experimental conditions of the other kinetic results displayed in Fig. V-1. Curve A is the data of Rosner and Allendorf\(^\text{18}\) which was obtained in a "diffusion-free" electrically heated filament system, using 3\% oxygen in the helium at 1 Torr pressure. Curves B and C are from the study of Berkowitz-Mattuck et al\(^\text{4}\) also using a "diffusion-free" mass spectrometric, hot molybdenum sheet system. Curve B employed pure molecular oxygen at \(0.6 \times 10^{-3}\) Torr and curve C data were contained with pure oxygen at \(1.8 \times 10^{-3}\) Torr. Figure V-1 shows only the data in the lowest temperature region of the Berkowitz-Mattuck study; their system enabled kinetic measurements at temperatures as high as 2100°K.

It is interesting to note that the slope of curve C is close to that of the present data, curve F, in the approximate temperature range of 1500°-1650°K, the lowest temperatures of the Berkowitz-Mattuck study. At higher temperatures, which are above the temperature range of the present study, the Berkowitz-Mattuck data decreases in slope. Curve D is an almost perfect asymptote to curve C if extrapolated to very high
Fig. V-1. Summary of molybdenum oxidation probabilities.
temperatures [see Fig. 1 of reference 9]. Thus the Berkowitz-Mattuck data agree with the present data in terms of activation energy at low temperatures, but revert to behavior more commonly found in the molybdenum oxidation literature at higher temperatures.

The differences in slope and general behavior between curves B and C indicate that the reaction mechanism becomes complex at low oxygen pressures and temperatures above about 1650°K; curve B continues to decrease in slope at higher temperatures (outside the range of Fig. V-1), actually reaching a maximum oxidation probability at about 1900°K.

The marked dissimilarity between the two curves also serves to point out an experimental fact noted by several researchers: that the oxidation kinetics depend on total system pressure; the increase of a factor of three in oxygen pressure between B and C caused the significant change in shape observed. In particular, the maximum oxidation probability of curve B does not appear in curve C, at least not below 2100°K.

Unlike A, B and C both curves D and E represent data taken under conditions of pressure and flow geometry in which diffusional effects might be expected to play an important role in determining the reaction rate. Curve D is the work of Schryer and Modisette;12 in their apparatus, molybdenum sheets were suspended from a balance into a hot furnace. The gas mixture was air at atmospheric pressure. Schryer and Modisette attempted to correct their data to account for diffusional effects, but in view of the extremely complex conditions of their system (flat plate geometry, high oxygen concentration and reaction rate), it would seem possible to obtain at best an approximate correction.

The data of curve E were obtained by Gulbransen et al.13 using a furnace and balance apparatus and rod shaped molybdenum specimens; the
ambient gas was pure oxygen at 76 Torr. Both weight loss and oxygen consumption measurements were made, and it was established by this means that (at least at 1000°C) the stoichiometry of the reaction was that one molybdenum atom reacted for each 1-1/2 oxygen molecules consumed. Gulbransen did not attempt detailed calculation to eliminate the effect of diffusional resistance (except experimentally, by varying the size of his specimens), and of course for the conditions of his experiment that would have been difficult indeed. Curve E extends only to 1400°C, which appeared to be the upper limit of the reaction-controlled regime for a specimen of 0.3 cm² surface area.

The data of curves D (definitely diffusion-influenced, with attempted corrections) and E (assumed to be in the reaction-controlled regime) are in good agreement, but disagree radically with the data of the present study in curve F. The reasons for this discrepancy of nearly a factor of two in activation energy values is not immediately apparent, but some insight may be gained by examining reaction orders reported in Gulbransen’s paper.

Gulbransen et al assumed that, for a molybdenum specimen of given surface area, the reaction-controlled regime extended to a temperature at which an Arrhenius plot (their Fig. 6) of the rate data departed from linearity. It was found that smaller surface area samples encountered diffusional limitations at higher temperatures than molybdenum specimens of larger surface area.

Table III and the accompanying discussion in the Gulbransen paper shows molybdenum oxidation rate as a function of oxygen pressure in the range, 5-76 Torr. This data was for a molybdenum oxidation rate as a function of oxygen pressure in the range, 5-76 Torr. This data were for a molybdenum specimen of 1.215 cm² surface area, and examination of Fig. 6 in that paper reveals that for a specimen of that size, the "reaction-controlled" regime
extends up to about 1220°K (as compared to perhaps 1670°K for a molybdenum rod of one-tenth that surface area). The apparent order of the oxidation reaction with respect to oxygen pressure varies from 1.5 at 1075°K; to about 0.5 at 1473°K; to about 0.14 at 1873°K. In the absence of data for this sample at 1220°K, it is necessary to assume that the reaction order is about 1.0 at this temperature; and therefore that the reaction order is varying with temperature, even in the regime assumed by Gulbransen et al to be reaction-controlled. This is untenable, particularly in light of the present research, which indicates (with diffusional effects corrected) that the order of the reaction is constant at unity over the range, 1150°-1450°K.

It is reasonable to question whether the kinetic data of Gulbransen et al were free of diffusional effects over the temperature range they considered to be "reaction-controlled." It is clear that departure from linearity on an Arrhenius plot in the case of molybdenum oxidation near atmospheric pressure is an indication that diffusional limitations are interfering with measurement of true surface kinetics. But the converse is not necessarily true: Arrhenius plot linearity of oxidation rate data does not necessarily imply reaction-control; it is not always true that linearity indicates that true surface kinetics are dominant.

To illustrate in an indirect manner the unreliability of Arrhenius plot linearity as indicator of true surface kinetics (or rather, as a criterion for determining whether oxidation is taking place in the reaction-controlled regime), consider the uncorrected molybdenum oxidation data in Fig. IV-2d of the present paper. In raw form these data appeared to be linear, with an activation energy of about 33 kcal/gmole over the range, 1100°-1420°K. In contrast, the raw data of the helium-oxygen runs of Fig. IV-2a appeared non-linear on an Arrhenius plot, with no well-defined activation energy.
When diffusional effects were taken into account, however, the situation was reversed; the helium-oxygen data were found to be linear, and the data of Fig. IV-2d so non-linear and inconsistent with other results that it was necessary to conclude that experimental procedures were deficient.

The Schryer and Modisette data of curve D (which agrees well with the Gulbransen, curve E) must be questioned despite the researchers' attempts to correct for diffusional effects. The very large reaction rates encountered by using air at atmospheric pressure, create many theoretical difficulties (large interfacial velocity, effect of variable molecular weight, heat release at reacting surface, transport limitations on products) that were not accounted for in the simple, flat-plate diffusion calculation performed by Schryer and Modisette. No attempt was made by them to measure the order of the reaction (which was tacitly assumed to be unity in their calculation). In short, Schryer and Modisette may be credited with having proved that diffusional effects do indeed affect observations of molybdenum oxidation kinetics, but the limitations of their method allowed no possibility of estimating these effects accurately.

Since the present study represents the only attempt in the literature to date to measure molybdenum oxidation kinetics in the vicinity of atmospheric pressure in which also an effort was made accurately to calculate the effect of diffusional limitations, it is reasonable to conclude that the present results are substantially correct, and that previous research was hampered by diffusional effects that could not accurately be estimated or (as in the case of the Gulbransen et al paper) which may have existed despite the researchers' attempts to eliminate them.

As for large discrepancies between the data of curves A, B and C and the present study's curve F, it can only be postulated that there is apparently a different oxidation mechanism at work in low-pressure, "diffusion-
free" studies than that in effect at or near atmospheric pressure.

B. A Possible Reaction Mechanism

Any mechanism postulated for the oxidation of molybdenum metal based on the results obtained in the present research would have to explain the following observations:

1. The oxidation rate varies as the first power of the surface oxygen partial pressure in the temperature range, 1150°-1450°K.

2. The activation energy of the reaction is constant at about 40 kcal/gmole in the temperature range, 1150°-1600°K.

3. The stoichiometry of the reaction is 1-1/2 oxygen molecules consumed for each molybdenum atom reacted. This was shown to be the case at 1275°K by Gulbransen et al.¹³; and is further supported by the fairly close agreement (within 15%) between experimental and calculated values of the diffusion-controlled reaction rate (see Table IV-3), the latter of which were based on an assumption of the 1-1/2:1 stoichiometry.

4. According to previous studies, summarized by Rosner and Allendorf,² the oxidation rate depends on total gas pressure as well as oxygen partial pressure. (The total pressure was not varied in the present study.) Since the inert carrier gas cannot itself affect the reaction rate, this effect must be due to the reduced efficiency of product removal as the total pressure is increased, which caused back reaction by re-absorption of products and re-formation of surface oxides and oxygen.

5. There is a thick oxide coat of undetermined composition on the surface during oxidation, at temperatures up to and including the primary diffusion-controlled temperature regime. This has been observed visually and in photomicrographs in the present research, and is confirmed in Fig. 2 of the paper by Gulbransen et al.¹³ This oxide coat does not grow in
thickness with time and does not act to retard the reaction, as do the usual oxide scales, since the reaction rate has been shown (Figs. IV-5 and IV-6) to be independent of length of run. Oxygen must diffuse through the surface oxide coat to react with the molybdenum base metal.

The various rate processes taking place according to the above five points are shown in Fig. V-2. Again, subscript 1 represents oxygen; 2 inert gas; and 3 product oxide (assumed to be MoO$_x$ or (MoO$_3$)$_3$). Superscript A denotes absorption onto, and E emission from, the oxide-gas interface.

If the various processes associated with molybdenum oxidation and illustrated schematically in Fig. V-2 were to be considered in detail, the rate expression would take a complex form indeed. For example, the surface oxide coat has been indicated as MoO$_x$. If the coat is sufficiently thick, the number $x$ might vary through the thickness $d$, decreasing in value as the oxide-metal interface 2 is approached. For the purpose of this brief consideration, $x$ will be considered constant and later, for simplicity, taken to be unity. The oxide coat in this model therefore is considered to be MoO.

A material balance may be made at once, based on the assumptions of steady state and assuming a 1-1/2:1, O$_2$:Mo stoichiometry:

$$\dot{m} = R^E_3 - R^A_3 = (2/3)(R^A_1 - R^E_1) = (1/x) R_d$$  \hspace{1cm} (V-5)

Consider the following mechanism:

$$O_2(g) \xrightarrow{k_1^A} 2O(1) \hspace{1cm} (V-6)$$

$$(3-x)O(1) + MoO_x(s) \xrightarrow{k_3^A} MoO_3(g) \hspace{1cm} (V-7)$$
Fig. V-2. Schematic diagram of molybdenum oxidation processes, in accordance with discussion points 1-5 of the text. All processes occur at steady-state; the thickness \( d \) of the oxide coat remains constant in time. \( R_d \) is the rate of diffusion of oxygen through the oxide to the base metal; \( \dot{m} \) is the overall oxidation rate, or rate of consumption of base molybdenum metal.
\[ 0(1) \rightarrow 0(2) \quad \text{(solid-state diffusion)} \quad (V-8) \]

\[ x \ 0(2) + \text{Mo}(s) \rightarrow \text{MoO}_x(s) \quad \text{(at interface 2)} \quad (V-9) \]

Let \( n \) be the surface concentration of atomic oxygen at interface 1; equation (V-5) becomes, using the above rate constants:

\[ \dot{m} = k \frac{E}{k_2} n^{3-x} - k \frac{A}{k_3} P_{30} = (2/3) \left( \frac{k_1^A P_{10}}{k_1} - k \frac{E}{k_2} n^2 \right) = \frac{(Dn/xd)}{(V-10)} \]

where \( D \) is the diffusion coefficient of oxygen in solid \( \text{MoO}_x \).

Setting \( x=1 \), solving for \( n \) in equation (V-10), this expression for the rate of oxidation is obtained:

\[ \dot{m} = \frac{(2/3)}{k_1^A} P_{10} \left[ 1 - \left( \frac{k_1^E}{k_1^A} \right) \left( \frac{2/3 \ k_1^A + k_3^E}{2/3 \ k_1^A + k_3^E} \right) \right] \quad (V-11) \]

The ratio, \( \frac{P_{30}}{P_{10}} \) is determined by the respective rates of diffusion of product and reactant through the diffusion boundary layer to and from interface 1. Neglecting the effect of variable molecular weight, equation (II-29) may be generalized to apply to product as well as reactant diffusion:

\[ \dot{m} = \pm \frac{(a/b)}{g_{i2}} \left( P_{i1} - P_{i2} \right); \ i = 1, 3 \quad (V-12) \]

where \( a/b \) is an appropriate stoichiometric coefficient, + sign is chosen for reactant, - chosen for product diffusion, and \( g_{i2} \) is the mass-transfer coefficient of either reactant or product through the boundary layer, defined analogously to equation (II-30) as:

\[ g_{i2} = \frac{M}{R} \left( \frac{\Omega}{2\pi} \right)^{1/2} \frac{D_{i2,0}}{\sqrt{\nu_{i2,1}}} \frac{T_f}{T_0}; \ i = 1, 3 \quad (V-13) \]
Assuming that the product is monomeric molybdenum trioxide diffusing toward a zero bulk concentration, equation (V-12) becomes:

\[ \dot{m} = \frac{2}{3} g_{12} (p_{10} - p_{10}) = g_{32} p_{30} \quad (V-14) \]

\[ \dot{m}_{DC} = \frac{2}{3} g_{12} P_{10} \quad (V-15) \]

Combining equations (V-14) and (V-15):

\[ \frac{p_{30}}{P_{10}} = \frac{(2/3) (g_{12}/g_{32})}{1 - \frac{\dot{m}_{DC}}{\dot{m}} \frac{m_{DC}}{m}} \quad (V-15) \]

Use of equation (V-15) in the rate expression, equation (V-11), would lead to a non-linearity in the plot of \( \dot{m} \) versus \( p_{10} \), which was not observed within the limits of experimental accuracy of the present study. This would indicate that reabsorption of oxide product from the boundary layer is not a large effect; that is \( k_A \) is small. Equation (V-11) assumes in this case the simpler form:

\[ \dot{m} = \frac{2}{3} k_A^E k_{10} p_{10} \left( \frac{2}{3} k_1^E + k_3^E \right) \quad (V-16) \]

This expression for the reaction rate is first order in surface oxygen partial pressure, and satisfies the second condition, of constant activation energy, if either \( k_1^E \ll k_3^E \) or \( k_1^E \gg k_3^E \).

The above, extremely simplified, mechanism leads to the simple rate expression, equation (V-16), but does not account for the effect of total system pressure observed by others in the literature. In this mechanism, total system pressure would influence the reaction rate only if absorption of oxide product (reversal of the reaction) onto the disk surface were important. In that case, the rate expression would be equation (V-11) with (V-15) inserted; the total system pressure could then affect the reaction through the pressure dependence of \( \dot{m}_{DC} \), since diffusivity is inversely
proportional to total pressure (see equation (V-13)), but the reaction would not have a simple, temperature-independent order with respect to oxygen partial pressure. Further studies with a variable total pressure rotating disk system are required to further explore these implications of the mechanism proposed.
VI. CONCLUSIONS

This work represents the first study of a refractory metal oxidation process in which the gas phase diffusional resistance has been accurately assessed from first principles. The major advantages of the rotating disk for experiments of this type are:

1) The forced-convection diffusional resistance is accurately known.

2) By operating at a sufficiently high rotational speed, natural convection transfer can be rendered insignificant compared to forced convection mass transfer.

3) The entire oxidizing surface of the disk is uniformly accessible, which permits meaningful kinetic data to be obtained from simple weight loss measurements.

4) The boundary layer is generated by motion of the solid surface rather than by motion of the gas; this feature avoids the necessity of pumping large quantities of a hot gas past the reacting surface to generate a boundary layer (as is the case in flat plate, stagnation flow, or cross flow cylinder geometries).

5) The rotating disk can be made quite small (~1/2 in. diameter, 0.04 in. thick) and operated at temperatures as high as 2000°K and rotational speeds up to 15,000 rpm.

The experiments on the molybdenum-oxygen system have shown that:

1) A completely diffusion limited rate of oxidation is achieved at temperatures in excess of ~1650°K. The onset of complete diffusion control depends in a known manner on the disk speed, gas transport properties, and the kinetics of the surface reaction. The observed diffusion-limited rate was ~15% larger than the prediction of rotating
disk theory. This agreement is considered quite satisfactory. The discrepancy may be due to: edge effects from not using an infinite disk; residual variable property effects not accounted for by the approximate analytical method used to evaluate this phenomenon; estimation of gas phase transport properties from kinetic theory; or enhancement of transfer by thermal diffusion (the Soret effect). In any case, these effects do not significantly alter the good agreement between theory and experiment in the diffusion limited region. The difference in the oxidation rates with argon and helium diluents is satisfactorily predicted by the theoretical effect of the diffusion coefficient on the mass transfer coefficient.

2) In the presence of a gas phase diffusional resistance, extraction of surface chemical kinetic parameters from the measurements requires that the diffusional step be well defined, as it is for the rotating disk. If diffusional effects are not correctly eliminated, the apparent reaction order and activation energy of the surface reaction are severely affected.

3) The reaction: Mo(s) + O₂(g) → MoO₃(g) is of order 1.00 ± 0.03 with respect to oxygen and exhibits a rate constant of

\[ R_R = (2.7 \pm 0.05) \times 10^4 \exp \left\{ - \frac{40,000 \pm 300}{RT} \right\} \frac{gm}{afm \cdot cm^2 \cdot sec} \]

over the temperature range 1100°-1500°K. These results are based upon experiments with a 25-fold variation in oxygen partial pressure in argon diluent and on a set of experiments at a single oxygen concentration in helium diluent.

All results are for a total gas pressure of 1 atm. The effect of variation of total gas pressure on the surface kinetics, which has been observed by other investigators, was not explored.
VII. ACKNOWLEDGMENTS

This work was supported by the United States Atomic Energy Com-
mmission through the Lawrence Radiation Laboratory.

I would like to express my appreciation to Professors D. R. Olander,
V. E. Schrock, and I. Cornet of the University of California College of
Engineering, who served on the Committee for this thesis.
APPENDIX A

Estimation of Fluid Properties of Dilute Mixtures of Oxygen in Argon and Helium

The principal reference cited in this appendix will be Reference 20, The Properties of Gases and Liquids, by Robert C. Reid and Thomas K. Sherwood. The first fluid property to be estimated is the diffusivity of oxygen in argon and helium. Reid and Sherwood20,524 give, for a binary gas mixture of components 1 and 2:

\[
D_{12} = \frac{(1.858 \times 10^{-3}) T^{3/2} \left(\frac{1}{M_1} + \frac{1}{M_2}\right)^{1/2}}{P \sigma_{12}^2 \Omega_D}
\]  

(A-1)

where \(D_{12}\) is the diffusivity of the gas mixture in cm\(^2\)/sec, \(T\) is the absolute temperature in degrees Kelvin, \(M_1\) and \(M_2\) the molecular weights of components 1 and 2 respectively, and \(P\) the total pressure of the system in atmospheres. \(\Omega_D\) is the collision integral for diffusion, tabulated in Reid and Sherwood20,524 as a function of \(kT/\varepsilon_{0,12}\), where \(k\) is Boltzmann's constant and \(\varepsilon_{0,12}\) is a parameter of the Lennard-Jones interaction potential between molecules of type 1 and 2. Since values of \(\varepsilon_{0,12}\) are not usually available for gas pairs, this parameter is estimated by the geometrical mean:

\[
\varepsilon_{0,12} = \left(\varepsilon_{0,1} \varepsilon_{0,2}\right)^{1/2}
\]  

(A-2)

where \(\varepsilon_{0,1}\) is the Lennard-Jones parameter for pure component 1, tabulated for many gases in Reference (20,632).

The second Lennard-Jones potential parameter in Eq. (A-1) is the collision diameter for interaction between 1 and 2, \(\sigma_{12}\), which is estimated as the simple average of \(\sigma_1\) and \(\sigma_2\), in Angstroms. \(\sigma_1\) is also
tabulated \(20.63^2\) for many gases, and is obtained from analysis of data on gas viscosities.

Using the data in Reid and Sherwood in Eq. (A-1), we are able to tabulate \(D_{12}\) for argon-oxygen and helium-oxygen in Tables A-1 and A-2. The diffusivity of oxygen in argon is plotted in Fig. A-1.

Walker and Westenberg have measured the binary diffusivity of nitrogen in helium, which is very close to \(D_{02-He}\). They report:

\[
D_{He-N_2} = (2.48 \times 10^{-5}) T^{1.783} \text{ (cm}^2/\text{sec)} \text{(helium trace)}
\]  

(A-3)

They found that \(D_{He-N_2}\) with trace nitrogen was lower than Eq. (A-3) by about 6%. That is,

\[
\frac{D_{He,N_2} (N_2 \text{ Trace})}{D_{He-N_2} (He \text{ Trace})} = 0.943 \text{ at 298}^\circ\text{K}
\]  

(A-4)

which verifies experimentally that \(D_{12}\) for this system is nearly independent of concentration.

The figures in the last column of Table A2 were obtained from Eq. (A-3) multiplied by a factor of \(D_{02-He}/D_{N_2-He}\) calculated from Eq. (A-1). This latter factor was 1.07, nearly independent of \(T\).

The values of \(D_{02-He}\) calculated by Eq. (A-1) agree within 2% to 10% with the modified, experimentally obtained diffusivities of Walker and Westenberg, which gives added faith in the reliability of Reid and Sherwood's estimated correlations. It seems most reasonable to use, however, the diffusivities based on experimental data in future calculations, and for that reason, the Walker and Westenberg values of \(D_{02-He}\) are plotted in Fig. A-2.

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>kT/(\epsilon_{0,12})</th>
<th>(\Omega_D(kT/\epsilon_{0,12}))</th>
<th>(D_{O_2-\text{Ar}}) (cm(^2)/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>580</td>
<td>5.81</td>
<td>0.8180</td>
<td>0.613</td>
</tr>
<tr>
<td>1073</td>
<td>10.75</td>
<td>0.7365</td>
<td>1.71</td>
</tr>
<tr>
<td>1300</td>
<td>13.03</td>
<td>0.7187</td>
<td>2.34</td>
</tr>
<tr>
<td>1600</td>
<td>16.04</td>
<td>0.6951</td>
<td>3.30</td>
</tr>
<tr>
<td>1900</td>
<td>19.04</td>
<td>0.6715</td>
<td>4.43</td>
</tr>
</tbody>
</table>

The log-log plot (Fig. A-1) of \(D_{O_2-\text{Ar}}\) versus T shows that the diffusivity of oxygen in argon over this temperature range is proportional to \(T^{1.67}\).

Table A2. Binary diffusivity of oxygen in helium at atmospheric pressure as a function of temperature. Comparison of estimation using Eq. (A-1) with modified data of Walker and Westenberg.²

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>kT/(\epsilon_{0,12})</th>
<th>(\Omega_D(kT/\epsilon_{0,12}))</th>
<th>(D_{O_2-\text{He}}) (cm(^2)/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1073</td>
<td>32.5</td>
<td>0.616</td>
<td>6.20</td>
</tr>
<tr>
<td>1300</td>
<td>39.4</td>
<td>0.598</td>
<td>8.53</td>
</tr>
<tr>
<td>1600</td>
<td>48.5</td>
<td>0.579</td>
<td>12.0</td>
</tr>
<tr>
<td>1900</td>
<td>57.6</td>
<td>0.564</td>
<td>16.0</td>
</tr>
</tbody>
</table>
Fig. A-1. $D_{O_2-Ar}$ as a function of $T$. 

Slope = 1.67
Fig. A.2. $D_{O_2-He}$ as a function of $T$.  

Slope = 1.79
Reid and Sherwood give this equation for the estimation of the viscosity of a pure gas:

\[ \mu = (2.669 \times 10^{-3}) \frac{(MT)^{1/2}}{\sigma \Omega_{\mu}} \text{(centipoises)} \]  

(A-5)

where \( \Omega_{\mu} = \Omega_{\mu}(\frac{K}{\ell^0}) \)

(A-6)

is the collision integral for viscosity, tabulated in Reference (20,399). Again, \( M \) is the molecular weight of the gas, and \( \sigma \) its Lennard-Jones parameter, tabulated in Reference (20,632). Equation (A-5) has been used to estimate the viscosities of argon, oxygen, and helium as a function of temperature, and the results of those calculations are tabulated on the following pages.

The following tables of viscosity show that, at a given temperature, the viscosities of argon, helium, and oxygen are of the same order of magnitude (actually, within a range of 50%). It would be expected that the viscosity of a mixture of a small concentration of oxygen in either helium or argon would be quite close to the viscosity of the pure inert gas. This hypothesis may be tested by using the Wilke estimation method to determine the viscosity of these mixtures from the pure gas viscosities already calculated. As outlined in Reference (20,421), the viscosity of a mixture of pure gases 1 and 2 is:

\[ \mu_{\text{mix}} = \frac{\mu_1}{1 + (\frac{x_2}{x_1}) \phi_{12}} + \frac{\mu_2}{1 + (\frac{x_1}{x_2}) \phi_{21}} \]

(A-7)

where
Table A3. Viscosity of oxygen as a function of temperature, from Eq. (A-5). See References (20, 399).

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>$kT/\epsilon_{0, O_2}$</th>
<th>$n_\mu (kT/\epsilon_0)$</th>
<th>$\mu_2$ (g·cm$^{-1}$·sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>580</td>
<td>5.436</td>
<td>0.9136</td>
<td>3.31 $\times 10^{-4}$</td>
</tr>
<tr>
<td>1073</td>
<td>10.06</td>
<td>0.8238</td>
<td>5.00</td>
</tr>
<tr>
<td>1300</td>
<td>12.18</td>
<td>0.8066</td>
<td>5.62</td>
</tr>
<tr>
<td>1600</td>
<td>15.00</td>
<td>0.7838</td>
<td>6.41</td>
</tr>
<tr>
<td>1900</td>
<td>17.81</td>
<td>0.7610</td>
<td>7.20</td>
</tr>
</tbody>
</table>

Table A4. Viscosity of argon as a function of temperature, from Eq. (A-5). See References (20, 399).

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>$kT/\epsilon_{0, Ar}$</th>
<th>$n_\mu (kT/\epsilon_0)$</th>
<th>$\mu_{Ar}$ (g·cm$^{-1}$·sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>580</td>
<td>6.217</td>
<td>0.8912</td>
<td>3.64 $\times 10^{-4}$</td>
</tr>
<tr>
<td>1073</td>
<td>11.50</td>
<td>0.8120</td>
<td>5.43</td>
</tr>
<tr>
<td>1300</td>
<td>13.93</td>
<td>0.7924</td>
<td>6.12</td>
</tr>
<tr>
<td>1600</td>
<td>17.15</td>
<td>0.7663</td>
<td>7.02</td>
</tr>
<tr>
<td>1900</td>
<td>20.36</td>
<td>0.7430</td>
<td>7.89</td>
</tr>
</tbody>
</table>
Table A5. Viscosity of helium as a function of temperature, from Eq. (A-5). See Reference (20,399).

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>$kT/\varepsilon_0$, He (20,632)</th>
<th>$n_{\mu}$ (kT/$\varepsilon_0$) (20,399)</th>
<th>$\mu_{\text{He}}$ (g-cm$^{-1}$-sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>580</td>
<td>56.75</td>
<td>0.6390</td>
<td>$3.09 \times 10^{-4}$</td>
</tr>
<tr>
<td>1073</td>
<td>104.99</td>
<td>0.5354</td>
<td>4.59</td>
</tr>
<tr>
<td>1300</td>
<td>127.2</td>
<td>0.5729</td>
<td>5.17</td>
</tr>
<tr>
<td>1600</td>
<td>156.56</td>
<td>0.5564</td>
<td>5.90</td>
</tr>
<tr>
<td>1900</td>
<td>185.91</td>
<td>0.5454</td>
<td>6.56</td>
</tr>
</tbody>
</table>

Table A6. Viscosity of dilute mixtures of oxygen in argon and helium, as estimated from the pure-component viscosities by the Wilke method. See Reference (20,421).

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>$\mu_{\text{Ar-O}<em>2}$ (g-cm$^{-1}$-sec$^{-1}$) ($x</em>{\text{O}_2} = 0.02$)</th>
<th>$\mu_{\text{He-O}<em>2}$ (g-cm$^{-1}$-sec$^{-1}$) ($x</em>{\text{O}_2} = 0.0053$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>580</td>
<td>$3.63 \times 10^{-4}$</td>
<td>$3.06 \times 10^{-4}$</td>
</tr>
<tr>
<td>1073</td>
<td>5.42</td>
<td>4.54</td>
</tr>
<tr>
<td>1300</td>
<td>6.11</td>
<td>5.11</td>
</tr>
<tr>
<td>1600</td>
<td>7.01</td>
<td>5.84</td>
</tr>
<tr>
<td>1900</td>
<td>7.88</td>
<td>6.50</td>
</tr>
</tbody>
</table>

(cf Table C4)  
(cf Table C5)

The viscosity of the gas mixtures is within 1% of the corresponding pure-component viscosity at all temperatures.
In these equations, \( \mu_i \) is the viscosity of pure component \( i \) (at a given temperature), \( M_i \) its molecular weight and \( x_i \) the mole fraction of \( i \) in the mixture.

Equation (A-7) has been applied to the data in Tables A3, A4, and A5 to determine the viscosity of a mixture of 2% oxygen in argon, and a mixture of 0.53 mole percent oxygen in helium. The results are shown in Table A6.

The Schmidt number for the oxygen-argon and helium-argon mixtures will be calculated next. The density of the gas mixture will be assumed for this purpose to be dependent on temperature only. The effect of variable molecular weight will not be considered at this point. Density will be calculated from the ideal gas law for a gas mixture:

\[
\rho_{12} = \bar{M}_\infty \frac{P}{RT} = (x_{1\infty} M_1 + x_{2\infty} M_2) \frac{P}{RT}
\]  

(A-10)

Table A7 below is an evaluation of \( Sc = \mu_{12} / \rho_{12} D_{12} \), for the 2% oxygen in argon and the 0.5% oxygen in helium systems, using values of diffusivity and viscosity from Tables A1, A2 and A6.

Thermal conductivity, heat capacity, and Prandtl number for the gas mixtures will be calculated next. The semi-empirical Bromley correlation discussed in Reid and Sherwood states a simple relationship between thermal conductivity and viscosity; in the case of oxygen, a linear, non-polar molecule, this relationship is of the form:
Table A-J. Schmidt number as a function of temperature for dilute mixtures of oxygen in argon and helium, neglecting the effect of variable molecular weight in the boundary layer.

<table>
<thead>
<tr>
<th>$T$ (°K)</th>
<th>$Sc_{Ar-O_2}$ ($x_{O_2} = 0.02$)</th>
<th>$Sc_{He-O_2}$ ($x_{O_2} = 0.0053$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>580</td>
<td>0.709</td>
<td>1.66</td>
</tr>
<tr>
<td>1073</td>
<td>0.700</td>
<td>1.52</td>
</tr>
<tr>
<td>1300</td>
<td>0.700</td>
<td>1.47</td>
</tr>
<tr>
<td>1600</td>
<td>0.700</td>
<td>1.43</td>
</tr>
<tr>
<td>1900</td>
<td>0.698</td>
<td>1.39</td>
</tr>
</tbody>
</table>
\[ \text{Mk/} = 1.30 \bar{C}_V + 3.40 - 0.70/T_r \quad \text{(A-11)} \]

where \( M \) is the molecular weight of the molecule, \( k \) the thermal conductivity (in cal cm\(^{-1}\) sec\(^{-1}\) °K\(^{-1}\)), \( \mu \) the viscosity of the gas (already computed in poises in Table A3), and \( \bar{C}_V \) the heat capacity at constant volume (in cal gmole\(^{-1}\) °K\(^{-1}\)). The reduced temperature is \( T_r = T/T_c \), and the critical temperature for oxygen is \( T_c = 154.6°K \) -- but the term involving \( T_r \) in Eq. (A-11) is negligible in the temperature range of interest.

The molar constant-volume heat capacity of oxygen, considering it to be an ideal gas, is \( \bar{C}_V = (7/2)R \), since the \( O_2 \) molecule has three translation modes, 2 axes of rotation, and one mode of vibration.\(^{20,170}\)

The molar constant-pressure heat capacity is calculated using the well-known relation for ideal gases, \( \bar{C}_P = \bar{C}_V + R \). Dividing \( \bar{C}_P \) by the molecular weight yields \( \bar{C}_P \).

Since both argon and helium are monatomic gases possessing only translational modes of energy storage, the molar constant-volume heat capacity of both gases is \( \bar{C}_V = (3/2)R \), assuming ideal-gas behavior.

The constant-pressure heat capacity per unit mass of a mixture of 2 mole percent oxygen in argon is:

\[ \bar{C}_{P,Ar-O_2} = (1/M_\infty)(x_{O_2}\bar{C}_{p,O_2} + x_{Ar}\bar{C}_{p,Ar}) = 0.1268 \text{ cal g}^{-1}\text{°K}^{-1} \quad \text{(A-12)} \]

The analogous expression for 0.53 mole percent oxygen in helium yields:

\[ \bar{C}_{P,He-O_2} = 1.202 \text{ cal g}^{-1}\text{°K}^{-1} \quad \text{(A-13)} \]
Clearly, even though the molar heat capacities of the individual components of the mixture are independent of temperature, $C_p,\text{mix}$ varies through the boundary layer because of the effect of variable molecular weight. The effect of variable molecular weight will be disregarded in the calculation of $\text{Pr} = (C_p \mu/k)_{\text{mix}}$.

The thermal conductivity of argon and helium are calculated by means of the Bromley correlation for monatomic gases:

$$Mk/\mu = 2.5 \bar{C}_v$$

From Table A8 it may be noted that, at a given temperature, the thermal conductivity of helium is about four times larger than the thermal conductivity of oxygen. Mixing oxygen with helium will lower the thermal conductivity of the mixture with respect to that of pure helium. However, for a mixture of 0.53 mole percent oxygen in helium, this effect is so small that it is as good for our purposes to use the thermal conductivity of pure helium in calculating the Prandtl number of the helium-oxygen mixture.

Similarly, mixing oxygen in small concentrations with argon will raise the overall thermal conductivity. The magnitude of this effect may be estimated for a mixture of 2 mole percent oxygen in argon by the empirical method of Brokaw. The thermal conductivity, $k_{\text{mix}}$, of a binary mixture is:

$$k_{\text{mix}} = q k_{m1} + (1 - q) k_{m2}$$

$$k_{m1} = x_1 k_1 + x_2 k_2$$

$$1/k_{m2} = x_1/k_1 + x_2/k_2$$

In the equations above, $k_i$ is the thermal conductivity of component i, $x_i$ the mole fraction of component i, and the factor q is determined by
the mole fraction of the lighter (in molecular weight) component of the mixture. Values of $q$ are tabulated in Reid and Sherwood.\textsuperscript{20,486}

Table A9 lists the results of applying Eqs.\textsuperscript{A-15-17} to the mixture of 2\% oxygen in argon, for which system the value of $q$ is approximately 0.324.

The Prandtl number, $Pr = (\bar{C}_p \mu/k)_{mix}$, for the two gas mixtures of interest may now be computed, using Eqs.\textsuperscript{A-12} and \textsuperscript{A-13} and the data in Tables A6, A8, and A9. The Prandtl numbers tabulated below are for pure binary mixtures of oxygen in argon and helium -- the presence of oxide products in the boundary layer is completely disregarded.
Table A-8. Thermal conductivity of oxygen, argon, and helium as a function of temperature, from Eqs. \((A-11)\) and \((A-12)\), using viscosity values computed in Tables A3, A4, and A5.

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>(k_{O_2}) (cal/cm² sec °K)</th>
<th>(k_{Ar}) (cal/cm sec °K)</th>
<th>(k_{He}) (cal/cm sec °K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>580</td>
<td>(1.27 \times 10^{-4})</td>
<td>(0.67 \times 10^{-4})</td>
<td>(5.76 \times 10^{-4})</td>
</tr>
<tr>
<td>1073</td>
<td>(1.93)</td>
<td>(1.01)</td>
<td>(8.54)</td>
</tr>
<tr>
<td>1300</td>
<td>(2.17)</td>
<td>(1.14)</td>
<td>(8.61)</td>
</tr>
<tr>
<td>1600</td>
<td>(2.48)</td>
<td>(1.31)</td>
<td>(11.0)</td>
</tr>
<tr>
<td>1900</td>
<td>(2.78)</td>
<td>(1.47)</td>
<td>(12.2)</td>
</tr>
</tbody>
</table>

Table A-9. Comparison of values of \(k_{Ar}\) from Table A-8 with values of \(k_{Ar}\) from Eq. \((A-13)\). \(k_{mix} = k_{Ar-O_2}\) is calculated for a mixture of 2 mole percent oxygen in argon.

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>(k_{Ar}) (cal/cm sec °K)</th>
<th>(k_{Ar-O_2}) (cal/cm sec °K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>580</td>
<td>(0.67 \times 10^{-4})</td>
<td>(0.686 \times 10^{-4})</td>
</tr>
<tr>
<td>1073</td>
<td>(1.01)</td>
<td>(1.02)</td>
</tr>
<tr>
<td>1300</td>
<td>(1.14)</td>
<td>(1.16)</td>
</tr>
<tr>
<td>1600</td>
<td>(1.31)</td>
<td>(1.33)</td>
</tr>
<tr>
<td>1900</td>
<td>(1.47)</td>
<td>(1.49)</td>
</tr>
</tbody>
</table>

The thermal conductivity of the mixture is only about 1% higher than the thermal conductivity of pure argon. The effect is even less for a mixture of 0.53% oxygen in helium.
Table A-10. Prandtl number as a function of temperature for pure binary mixtures of 2 mole percent oxygen in argon, and 0.53 mole percent oxygen in helium.

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>Pr(_{\text{Ar-O}_2})</th>
<th>Pr(_{\text{He-O}_2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>580</td>
<td>0.6711</td>
<td>0.639</td>
</tr>
<tr>
<td>1073</td>
<td>0.6709</td>
<td>0.639</td>
</tr>
<tr>
<td>1300</td>
<td>0.6709</td>
<td>0.639</td>
</tr>
<tr>
<td>1600</td>
<td>0.6709</td>
<td>0.640</td>
</tr>
<tr>
<td>1900</td>
<td>0.6705</td>
<td>0.639</td>
</tr>
</tbody>
</table>
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