FINAL REPORT
PROJECT NO. B-146
MECHANISM AND ACTIVATION ENERGY FOR DIFFUSION THROUGH SINGLE CRYSTAL AND POLYCRYSTALLINE HIGH TEMPERATURE MATERIALS

By
WILLIS E. MOODY
Professor, School of Ceramic Engineering

CONTRACT NO. AT (40-1)-2420
UNITED STATES ATOMIC ENERGY COMMISSION

DECEMBER 1961
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ABSTRACT

The diffusion coefficients, D, and activation energies, $E_a$, for helium passing through single and polycrystalline Al$_2$O$_3$ were determined in the temperature range of 300° to 900° C. The coefficients of diffusion of helium in single crystal and polycrystalline Al$_2$O$_3$ can be experimentally determined from approximately 300° C and above by means of a mass spectrometer. The most probable basic mechanism for diffusion in a single crystal Al$_2$O$_3$ as indicated by the experimentally determined activation energy value, 0.32 ev, was an atom-vacancy interchange type occurring along edge dislocations. It was found that D for polycrystalline Al$_2$O$_3$ occurred in the range of $10^{-7}$ cm$^2$/sec to $10^{-11}$ cm$^2$/sec for densities greater than approximately 3.70 gm/cc. The experimentally determined activation energy, 0.13 to 0.83 ev, indicated the most probable basic mechanism for diffusion through polycrystalline Al$_2$O$_3$ to be an atom-vacancy interchange type occurring mainly along grain boundaries. Annihilation of imperfections was the probable cause of discontinuities in the curves for the values of D for single and polycrystalline Al$_2$O$_3$.

The feasibility of determining the concentration gradient for argon and krypton in Al$_2$O$_3$ has been demonstrated with a vacuum x-ray fluorescence unit.
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I. INTRODUCTION

The Final Report summarizes the information developed and accomplishments of a 3-year program. Work was initiated on 1 July 1959 under Atomic Energy Commission Contract No. AT (40-1)-2420. Three Progress Reports were submitted under the dates of 1 February, 1959, 1960, and 1961. The work was carried out under the direction of Dr. Willis E. Moody in the laboratories of the School of Ceramic Engineering and of the Engineering Experiment Station.

The objective of this program was to advance in a systematic manner the basic scientific knowledge of mass transport phenomena and imperfections in metallic oxide, ceramic, materials. Alumina was selected as a metallic oxide, having desirable high temperature characteristics, and capable of being formed as a single crystal and as a polycrystalline material. The inert gases, helium, neon, argon, krypton, and xenon, were considered for the diffusing gas for two reasons. First, as these gases are assumed to have zero valence, any complications from valency considerations would be eliminated. Second, the range of atomic size of these gases should permit obtaining data on diffusion as a function of atomic size. Due to measurement equipment limitations, the work reported herein was confined to the study of helium diffusion.

Towards the close of the contract period, x-ray fluorescent equipment became available. Sufficient work was done to demonstrate the feasibility of employing this technique to determine the concentration gradient of argon and krypton in alumina.
II. SURVEY OF LITERATURE

A. Inert Gases

Helium gas is the lightest of all the inert gas series and remains atomic, rather than assuming a molecular configuration, in the gaseous state. It has an atomic radius of 0.93 Å, which approximates the size of many metal atoms and other types of ions. It has been suggested\(^1\) that helium will not diffuse through the close-packed structure of some metals because of a lack of chemical affinity.

In the case of the more open lattice structures, typical of which are ceramic oxides, diffusion of gases has been found to be a function of the atomic size if no chemical affinity exists.\(^1\) However, imperfections such as edge dislocations and other surface conditions may provide adequate entrance sites for atoms or ions to enter the close-packed structure. It should be pointed out that the conditions necessary for an atom and/or ion to pass through the theoretical surface are not well understood or defined to any extent.

Table I lists the properties of the helium gas used in this work. The relative sizes of the inert gas atoms are given in Table II.

B. Alumina Structure

The compound alpha-Al\(_2\)O\(_3\) falls into a general group designated by the form R\(_2\)O\(_3\). In this group, there is a definite gradient of sizes of the metal ions composing the compounds. In general, the greater the charge on the ion,

\(^1\) P. S. Flint, The Diffusion of Hydrogen through Materials of Construction, KAPL - 659, Knolls Atomic Power Laboratory, 1951, p. 9.
TABLE I
PROPERTIES OF AMARILLO GRADE A HELIUM\(^{(2, 3)}\)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Atomic Number</td>
<td>2</td>
</tr>
<tr>
<td>Atomic Weight</td>
<td>4.003</td>
</tr>
<tr>
<td>Melting Point</td>
<td>-272.2 °C (26 atmospheres)</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>-268.9 °C (1 atmosphere)</td>
</tr>
<tr>
<td>Purity</td>
<td>99.99(^+)%</td>
</tr>
<tr>
<td>Chief Impurities</td>
<td>H(_2), Ne, N(_2), O(_2), A, C(_2) (18.2 ppm total)</td>
</tr>
<tr>
<td>Purity Measurement</td>
<td>Mass Spectrometer</td>
</tr>
<tr>
<td>Atomic Radius</td>
<td>0.93 (\text{Å})</td>
</tr>
<tr>
<td>Atomic Velocity at 300° K</td>
<td>(1.252 \times 10^5) cm/sec</td>
</tr>
<tr>
<td>Atomic Velocity at 600° K</td>
<td>(1.92 \times 10^5) cm/sec</td>
</tr>
<tr>
<td>Atomic Velocity at 900° K</td>
<td>(2.36 \times 10^5) cm/sec</td>
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TABLE II
INERT GAS ATOMIC SIZE\(^{(4)}\)

<table>
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<tr>
<th>Element</th>
<th>Radius ((\text{Å}))</th>
<th>Volume ((\text{Å}^3))</th>
</tr>
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<tr>
<td>He</td>
<td>0.93</td>
<td>3.36</td>
</tr>
<tr>
<td>Ne</td>
<td>1.59</td>
<td>16.8</td>
</tr>
<tr>
<td>A</td>
<td>1.91</td>
<td>29.1</td>
</tr>
<tr>
<td>Kr</td>
<td>2.01</td>
<td>33.9</td>
</tr>
<tr>
<td>Xe</td>
<td>2.20</td>
<td>44.6</td>
</tr>
</tbody>
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the smaller will be its atomic radius. With small metal ions that have \( \frac{r_R}{r_0} \) less than 0.60, oxygen ions can approach nearer to a close-packing, and such metallic and close-packed sesquioxides are often found in the arrangement typified by \( \text{Cr}_2\text{O}_3 \). Its symmetry is rhombohedral with a unit cell containing two molecules and having dimensions given in Table III. The space group is \( \text{D}_{3d}^6 (R\overline{3}c) \).

In this structure each aluminum ion has three oxygen ions at a distance of 1.89 Å and three more at 1.93 Å. The nearest \( 0-0 \) distance is 2.49 Å.

This arrangement is probably best viewed as a slightly distorted hexagonal close-packing of molecules in which aluminum ions occur above and below the midpoints of the oxygen ion triangles of the close-packed oxygen layers. Six oxygen ions surround each aluminum ion, and each oxygen ion is surrounded by four aluminum ion sites. Two-thirds of the octahedral sites are occupied by aluminum ions while the remaining ones are vacant to fulfill the conditions of net electrical neutrality and stoichiometry of the compound. Aluminum ions and holes are arranged so as to give a maximum separation of like charges and a minimum separation of unlike charges, \(^{5,6}\) Figs. 1 and 2. The packing would be perfect if \( \alpha \) were 53° 47' instead of the measured value of about 55° 17', and all the oxygen ions were equidistant from the aluminum ions. \(^4\)

Fig. 1 represents a plan view of the \( \alpha-\text{Al}_2\text{O}_3 \) structure looking down on the aluminum ions and holes over the close-packed oxygen ion layer. Fig. 2 shows a schematic diagram of the aluminum ion and hole distribution in a

---


TABLE III
ALPHA-ALUMINA CRYSTAL DIMENSIONS\(^{(4)}\)
AND PHYSICAL DATA

<table>
<thead>
<tr>
<th>Form</th>
<th>(\alpha)-Al(_2)O(_3)</th>
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<tr>
<td>Symmetry</td>
<td>Rhombohedral</td>
</tr>
<tr>
<td>(a_0)</td>
<td>4.76280</td>
</tr>
<tr>
<td>(b_0)</td>
<td>-</td>
</tr>
<tr>
<td>(c_0)</td>
<td>13.00380</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>31 degrees</td>
</tr>
<tr>
<td>Coordination Number of Al to O</td>
<td>6:4</td>
</tr>
<tr>
<td>Remarks</td>
<td>(\text{Cr}_2)O(_3)) type</td>
</tr>
<tr>
<td>Melting Point</td>
<td>2050° C</td>
</tr>
<tr>
<td>Dislocation Annealing Temperatures</td>
<td>900° C - Basal Plane</td>
</tr>
<tr>
<td></td>
<td>2000° C - Prismatic Plane</td>
</tr>
<tr>
<td>Parting</td>
<td>Rhombohedral Planes</td>
</tr>
<tr>
<td>Slip</td>
<td>Prismatic and basal</td>
</tr>
<tr>
<td>Theoretical Density</td>
<td>3.98 gm/cc</td>
</tr>
</tbody>
</table>

simple hexagonal lattice. The simple rhombohedral cell is also shown. A close examination of these figures reveals no straight line path through the lattice. For any gas penetration to take place, some sort of activated, step-by-step diffusion process would be necessary to supply energy for motion.

Several other forms of alumina are found in nature or occur through artificial means. Beta and zeta forms contain small amounts of alkali and alkaline earth oxides. Gamma types, of which there are many subdivisions
Figure 1. Basal Plane $\text{Al}_2\text{O}_3$.
Figure 2. Aluminum Ion and Hole Distribution in the Simple Hexagonal Lattice.
(chi, gamma, eta, delta, kappa, theta), all are structures that originally contained water and revert to the alpha form upon heating.\(^7\) Studies thus far reveal that the alpha crystalline form is stable from room temperature to 2000° C and exhibits no inversions or phase changes upon heating.\(^8\)

A polycrystalline material behaves quite differently from its single crystal counterpart. There are several reasons for this lack of correspondence. The presence of internal surfaces or grain boundaries can and does affect the various properties of a solid. The term "sintered alumina"\(^9\) became established in the literature in 1932 when Kohl described a new material called "sinterkorund" made from a Bayer alumina material either by slip casting or dry pressing and firing to 1800° C. He considered the firing and cooling step to be a recrystallization process.

In all cases, grain boundaries represent regions of misfit between two or more crystalline surfaces. The atoms in the boundary region are shared by adjacent lattices, but the force field in which the atoms find themselves is by no means uniform, and the region is in stress and permanent strain. Generally, a grain boundary is at a higher potential energy state than its surroundings. In summation, the properties of a polycrystalline substance that depend upon or are a function of the ionic bonds are affected by the presence of a boundary in the sense that the region is a lattice imperfection. It represents a discontinuity in the potential field, but it is not a barrier


that completely blocks electronic interchange. Mechanical properties depend upon ionic movements, and grain boundaries represent areas sufficiently different to modify the behavior of the material.

Crandall et al.\(^{10}\) observed internal friction peaks for polycrystalline Al\(_2\)O\(_3\) at 1080°C for high purity material and at 700°C for a material with a one per cent silica addition.

According to Tucker and Gibbs,\(^{11}\) single crystals of Al\(_2\)O\(_3\) normally contain approximately 10\(^7\) dislocations/cm\(^2\).

C. Theory of Diffusion

To fully appreciate the mathematics of diffusion, one must have a working knowledge of kinetics, thermodynamics, solubility phenomena, and steady state and nonsteady state flow. Numerous references are given in the literature dealing with the mathematical solutions of various systems that might be employed, such as plane surfaces, cylinders, and spheres.

The basis for the mathematics of diffusion lies with the two differential forms of Fick's Laws\(^ {12}\) dealing with steady and nonsteady state flow. They may be written:

\[
J = -D \frac{\partial c}{\partial x} \tag{1}
\]


where: \( J \) = current density, or quantity of substance passed per unit area per unit time per unit thickness

\[ D = \text{diffusion coefficient} \]

\[ \frac{\partial C}{\partial x} = \text{concentration gradient}. \]

Fick's second law may be derived from the first with the use of the particle continuity equation which results in:

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{2} \]

where: \( \frac{\partial C}{\partial t} = \text{change of concentration with change in time} \)

\[ \frac{\partial^2 C}{\partial x^2} = \text{rate of change of concentration gradient}. \]

The general theory of diffusion is based upon analogy to the flow of heat through solid media, as is exemplified in the classical works of Fourier and Lord Kelvin. However, new phenomena are observed in the actual diffusion processes of molecules and ions in and through solids which are not found in systems concerned with the flow of heat alone. Consequently, these phenomena require limitations to be imposed much more frequently on mass transfer systems than on heat transfer systems.

A quantitative consideration of the theory of diffusion involves an understanding of the diffusion equation, permeability, and the relationship between permeability, solubility, and diffusion coefficient.

There are two general types of gas flow through a solid: (A) diffusion processes and (B) molecular flow processes.

1. Diffusion Processes

There are three classical mechanisms by which an atom or an ion
may diffuse through a crystal. They are shown in Fig. 3 and are as follows:

1. Atom A and atom B may interchange places. They would move past each other in the lattice to reach the new sites.
2. Atom B may diffuse through interstitial sites in the lattice.
3. The diffusing atom may move by occupying vacant sites in the lattice.

The first mechanism involves breaking the bonds which surround atoms A and B. This requires an energy equal to the bonding energy of the material and is the most unlikely to occur. Experimental evidence seems uniformly to support this assumption.

The second mechanism involves a smaller amount of energy, but the number of interstitial sites available usually limits the process. The ion moves out of its normal site into the interstitial position and is accompanied by some lattice distortion due to the size of the ions and ion-ion energy interaction.

The mechanism requiring the least amount of energy is shown in Part 3 of Fig. 3. Crystals usually possess vacant lattice sites or missing atoms or ions, and these would be available as vacancies. It is necessary to overcome bonding forces on three sides of the atom for it to be moved. The new site is available with little additional energy expenditure.

In polycrystalline materials where grain boundaries represent areas of unequal energy potential, but not actual holes, small amounts of energy

1. INTERCHANGE BY ROTATION ABOUT A MIDWAY POINT, FORCING NEIGHBORING ATOMS APART.

2. MIGRATION THROUGH INTERSTITIAL SITES.

3. ATOMS EXCHANGE POSITION WITH VACANT LATTICE SITES.

Figure 3. The Three Basic Mechanisms of Diffusion.
supplied to a diffusing atom could cause the area to become a diffusing path. Grain boundaries and dislocations may also consist of holes in which the diffusing path is well defined.

The two methods of data analysis have been:

Method A. It is assumed that the concentration gradient is equivalent to the difference in concentration of He on each side of the barrier divided by barrier thickness. The diffusion coefficient is then calculated from a simplification of equation (1) to:

\[
D = \frac{M LV}{\Delta t A (C_1 - C_2)}
\]  

\(A\) = area diffusing gas passes through  
\(C_1\) = concentration on high pressure side  
\(C_2\) = concentration on low pressure side  
\(L\) = barrier thickness  
\(V\) = unit volume  
\(\Delta t\) = time for diffusion  
\(M\) = number of diffused atoms  
\(D\) = coefficient of diffusion.

Method B. Rogers, Buritz and Alpert\(^{(14)}\) developed a method for simultaneously measuring the diffusion coefficient, solubility, and permeability for a gas in a single sample of solid material. The method utilizes solutions of the diffusion equation which makes it possible to calculate the diffusion parameters from data in the early part of the transient period, early-time approxi-

ation, or in the steady-state gas flow, late-time approximation. This technique requires a continuous recording of the pressure build-up of the diffusing gas on the low pressure side of the barrier.

Solutions for equation (1) are obtained as follows:

1. Early-time approximation

Slope = \( \frac{d^2}{4D} \)

\( d \) = barrier thickness

\( D \) = coefficient of diffusion

Slope = slope of line of Fig. 4.\(^{(14)}\)

2. Late-time approximation

\( D = \frac{d^2}{6t_c} \)

\( D \) = coefficient of diffusion

\( d \) = barrier thickness

\( t_c \) = characteristic time as shown on Fig. 5.\(^{(14)}\)

3. Solubility (late-time approximation)

\( P = DS \)

\( P \) = permeability

\( D \) = coefficient of diffusion

\( S \) = solubility.

a. Activation Energy. It has been experimentally determined that values of \( D \) may be expressed by a relation of the following form:

\[
D = D_0 \exp \left( -\frac{E_a}{kT} \right)
\]

where:

\( D_0 \) = diffusion constant

\( E_a \) = activation energy
Figure 4. Data Presentation for Early Time Approximation.
Figure 5. Data Presentation for Late Time Approximation.
k = Boltzmann constant

T = absolute temperature.

The activation energy of a system may be defined as the energy that must be put into a system in order to start a reaction, rearrange a structure, or shift atoms. The rate at which diffusion takes place is a function of the activation energy for the particular diffusion process.

If the natural logarithm is taken of equation (4), an arithmetic plot of \( \ln D \) versus \( 1/T \) will yield a straight line. The magnitude of the slope of the line will be a function of the activation energy and the Boltzmann constant. Thus:

\[
\ln D = \ln D_0 + \frac{E_a}{k} \frac{1}{T}
\]  

(5)

Fig. 6 shows a schematic representation of a barrier which has to be overcome by the activation energy.

Moody et al.\(^{15}\) have calculated a classical activation energy by considering the atoms as tunneling through the structure with the tunnel being formed by a missing atom and imaginary springs based on Young's modulus of elasticity holding the atoms in place. A hole or tunnel was created in the plane by the removal of an atom, thereby creating a vacancy. The activation energy was considered as being that which was required to compress the atoms and thereby enlarge the hole or vacancy in the plane of atoms to such an extent as to allow the diffusing atom to pass through. The fundamental equation was as follows:

Figure 6. Potential Energy Curve Showing the Activated State.
where: Area = $\lambda^2$, where $\lambda$ is diameter of missing atom

Force = $k \Delta \lambda$, where $k$ is a constant for imaginary spring and $\Delta \lambda$ is movement in compression or in tension as diffusing atom passes through

$Y$ = Young's modulus of elasticity, lb./sq. in.

$\Delta L$ = change in length

$L$ = total length.

This leads to

$$\frac{k \Delta \lambda}{\lambda^2} = Y \frac{\Delta L}{L} \quad (7)$$

where

$$k = Y \lambda \quad (8)$$

The work required to move one atom to a position $\lambda/2$ away from its equilibrium site to allow the diffusing atom to pass through the atom plane was as follows:

$$\text{Work} = \text{force} \times \text{distance} \quad (9)$$

$$\text{Work} = \int_0^{\lambda/2} kx \, dx = \left[ \frac{1}{2} kx^2 \right]_0^{\lambda/2} = \frac{y \lambda^3}{8} \quad (10)$$

The activation energy was computed to a close approximation by a summation of the work required to move the nearest and next nearest neighbors a distance of $\lambda/2$ in compression in one direction and in tension in other directions.
b. The Diffusion Constant. There have been many values of the diffusion constant published in the literature. These values have been accepted at face value with little speculation as to the significance of the constant. Zener\(^{(16)}\) has approached the problem of evaluating \(D_o\) mathematically in the following manner. The normal diffusion equation for small concentrations is given by equation (4). \(D\) may also be described by the three dimensional random walk problem:

\[
D = \frac{1}{6} \sum_i \tau_i l_i^2 \tag{11}
\]

where \(\tau_i\) is the rate at which a jump is made of type \(i\) and \(l_i\) is the jump distance. The crux of the problem of evaluating \(D_o\) values lies in the definition of \(\tau_i\).

\(\tau_i\) may be expressed by:

\[
\tau = v \exp \left(-\frac{\Delta G}{KT}\right) \tag{12}
\]

where \(v\) is the frequency of vibration leading to the saddle point, and \(\Delta G\) is the isothermal work moving across the saddle. \(K\) is the Boltzmann constant, and \(T\) is the absolute temperature at which the potential barrier exists.

We separate \(\Delta G\) into its components by:

\[
\Delta G = \Delta H - T\Delta S \tag{13}
\]

From thermodynamics:

\[
\Delta H = d \left( \frac{\Delta G}{T} \right) d \left( \frac{1}{T} \right) \tag{14}
\]

We define:

\[
\frac{H}{K} = -\frac{d \ln D}{d \left( \frac{1}{T} \right)}
\]  

(15)

Thus, equation (15) may be written in component form:

\[
\tau = v \exp \left( \frac{\Delta S}{K} \right) \exp \left( -\frac{H}{kT} \right)
\]  

(16)

with

\[
\Delta S = \frac{d \Delta G}{dT}
\]  

(17)

Equation (17) may now be examined on the right side. Formerly \( \Delta S \) was considered to be either plus or minus; plus corresponding to a loosening of the lattice, and minus corresponding to a tightening of the lattice.

Equation (17) does not allow for this. \( \Delta G \) does not increase with temperature (at least it is unlikely) and this casts doubt upon experiments with negative values of \( \Delta S \). The above derivation assumes that all lattice sites are equivalent.

When the matrix is not homogeneous, the possibility exists that there are certain paths along which diffusion will have a lower energy of activation than through the bulk of the matrix. Since at any one time only a fraction of the atoms will be in this path, the associated \( D_o \) will be lower than the value that corresponds to homogeneous diffusion. If the major portion of the diffusion occurs along these paths, \( \Delta S \) may be smaller than theoretical and may even be negative.

In this manner, low or even negative values of \( D_o \) may be explained by inhomogeneities which furnish short circuit diffusion paths. Grain boundaries
are a major source of such paths along with dislocations. Zener postulates that if these inhomogeneous areas were removed, values of ΔS would become positive and values of D₀ would be approximately 10⁻² cm²/sec.

2. Molecular Flow Processes

Molecular flow processes have been reviewed by Barrer(12) and are of four major types:

(1) Molecular Effusion: If one has an orifice of area A with a diameter small compared to the mean free path of the gas, the number of molecules or atoms effusing in a unit time is given by the kinetic theory equation:

\[
\frac{dN}{dt} = AN_o \frac{(P_1 - P_2)}{\sqrt{2\pi MRT}}
\]

(18)

Where \(N_o\) is Avogadro's Number, \(M\) is the mass of a mole of the material, \(R\) is the gas constant, \(T\) is the absolute temperature, and \((P_1 - P_2)\) is the pressure differential. Equation (18) gives the flow rate through a hole in a thin plate of area A in atoms/sec. At a constant temperature for a given gas, flow rate is linearly proportional to the square of the radius of the hole, the effusion pressure, and Avogadro's number. For varying temperatures, flow rate is dependent upon the square root of the temperature, the square of the radius, and the effusion pressure.

(2) Molecular Streaming or Knudsen Flow:(17) When the path is of considerable length, molecules or atoms will collide with its walls on the way through. If all the collisions were perfectly elastic, the flow through the tube would be identical with the effusion velocity through a thin plate and would be independent of the tube length. Knudsen, therefore, assumed that for each of \(N\) molecules striking the wall, a fraction, \(f\), was emitted with a random

velocity distribution, and (1-f) was specularly reflected. Some are returned in the direction from which they came and more return the greater length of the tube. Knudsen showed that the net rate of flow in molecules or atoms per second is given by:

$$\frac{dN}{dt} = \frac{1}{2} B \frac{1}{\sqrt{2\pi MR}} \left( \frac{P_1}{\sqrt{T_1}} - \frac{P_2}{\sqrt{T_2}} \right) \frac{1}{L} (\frac{2-f}{2}) \tag{19}$$

where L is the length of the tube. B is a constant dependent upon the shape of the tube. For a capillary tube of circular cross section the constant B takes on the value $16/3 r^3 \pi$, where r denotes the radius of the capillary.

Equation (19) is the general Knudsen equation. For a given gas, the flow rate is linearly proportional to the cube of the radius, the pressure differential from one end of the capillary to the other, the length of the capillary and the friction factor for atoms rebounding from the walls of the capillary as well as the square root of the temperature.

(3) Poiseuille or Streamline Flow: For a compressible fluid obeying the perfect gas law, Poiseuille's law may be written:

$$\frac{dN}{dt} = \frac{16 r^4 \pi}{128 L \eta} \int \frac{1}{\eta RT} p dp \tag{20}$$

where $\eta$ is the viscosity of the fluid, which for an isothermal process with $\eta = \text{a constant}$ becomes:

$$\frac{dN}{dt} = \frac{16 r^4 \pi}{128 L \eta} \frac{1}{RT} \frac{P_1^2 - P_2^2}{2} \tag{21}$$

This may also take the form:
where \( \rho = \frac{1}{2} (P_1 + P_2) \) is the mean pressure in the tube. Also:

\[
\frac{dN}{dt} = \frac{16r^4\pi}{128L} \frac{1}{\rho} (P_1 - P_2) \tag{22}
\]

Two corrections may be applied to Poiseuille's formulas. Part of the pressure difference is used to overcome friction and the remainder produces kinetic energy of motion. There may be specular reflection from the surface of the capillary in the boundary layer of gas of thickness \( A \) where \( A \) is equal to the mean free path. The coefficient of slippage is then \( \left( \frac{2-f}{2} \right) A \). Barrer applies both of these corrections to equation (20) and the new equation becomes:

\[
\frac{dN}{dt} = \frac{1}{L} \frac{3\pi^2r^3}{4} \frac{1}{\sqrt{2\pi MRT}} (P_1 - P_2) \left( \frac{2-f}{2} \right) \tag{24}
\]

which is the equation given for Knudsen Molecular Streaming except for the numerical constants, which are somewhat different. Flow rate is linearly proportional to the pressure and to the other system constants.

(4) Turbulent Flow: The types of flow known as streamline change when a certain mass velocity \( W \) is reached. A quantity, \( R \), called the Reynolds Number, is defined by:

\[
R = \frac{r_hWp}{\eta} \tag{25}
\]

where \( r_h \) denotes the ratio, \( \frac{\text{cross section}}{\text{periphery}} \), and is the so-called hydraulic
radius, which for circular tubes is one-quarter of the diameter, \( d \). The symbols \( \rho \) and \( \eta \) have the significance of fluid density and viscosity, respectively. It has been determined that for circular tubes, streamline equations do not hold when \( R \) is greater than 580. The differential equation of flow is:

\[
- \frac{\partial p}{\partial x} = \frac{B \rho W^2}{2r_h}
\]

(26)

where \( B \) is a constant and varies for different shapes of tubes. Mass velocity, or flow rate, is a complex function of the square root of the Reynolds number, fluid density, and hydraulic radius at a constant temperature.

D. Diffusion through Alumina

Studies on the penetration of gases in polycrystalline alumina have been conducted recently by several sources. Hayes et al.\(^{18}\) and Kingery et al.\(^{19}\) have investigated this phenomenon from 25° to 1800° C. Table IV lists values of helium permeabilities of some ionic type crystals.

Hayes et al., working in temperature regions up to 1700° C with oxygen and nitrogen as the diffusing gas, have found that a combination of Knudsen flow and diffusion along the grain boundaries is the probable mechanism. He also found that the most elevated temperatures greatly shorten the life of the alumina, and a massive breakdown of structure occurs. The samples employed by Hayes were of a density of approximately 3.5 gm/cm\(^3\), and the method of analysis

---


TABLE IV
HELIUM PERMEABILITIES OF IONIC CRYSTALS

<table>
<thead>
<tr>
<th>Substance</th>
<th>Permeability at °C in Cc/Hr/Cm²/Mm thickness/Atm. Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quarts (cut perpendicular to optic axis)</td>
<td>&lt; 0.05 x 10⁻⁸</td>
</tr>
<tr>
<td>Mica (cleavage plate)</td>
<td>&lt; 0.06 x 10⁻⁹</td>
</tr>
<tr>
<td>Calcite (cleavage plate)</td>
<td>&lt; 0.05 x 10⁻⁸</td>
</tr>
<tr>
<td>Fluorite</td>
<td>&lt; 0.20 x 10⁻⁸</td>
</tr>
<tr>
<td>Rocksalt</td>
<td>&lt; 0.20 x 10⁻⁶</td>
</tr>
<tr>
<td>Selenite (cleavage plate)</td>
<td>&lt; 0.70 x 10⁻⁹</td>
</tr>
<tr>
<td>Beryl (cut perpendicular to optic axis)</td>
<td>&lt; 0.10 x 10⁻⁸</td>
</tr>
<tr>
<td>Beryl (cut parallel to optic axis)</td>
<td>&lt; 0.15 x 10⁻⁷</td>
</tr>
</tbody>
</table>

was based on pressure build-up techniques rather than a diffusion products analysis.

Kingery et al. studied the self diffusion of $^{18}O$ in the lattice of single and polycrystalline alumina and found the probable mechanism of diffusion to be movement along holes produced by defects. He found the diffusion rate in polycrystalline alumina to be somewhat higher with a slightly lower activation energy than that found in single crystals. He made no assumptions from his data regarding ion-ion interaction. At temperatures less than 1450°C, variable results were obtained, possibly because of structure sensitive diffusion. At higher temperatures grain boundary diffusion played an important role.
III. PROCEDURE

A. Barrier and Tube Fabrication

Figure 7 shows examples of the alumina single crystal and polycrystalline barriers and tubes which were fabricated. The single crystal alumina barrier can be observed more clearly in Figure 8. The barrier and other materials and sources are given in Table V, VI, and VII. The properties of the single crystal $\text{Al}_2\text{O}_3$ were essentially the same as those in Table I. $\text{UO}_2$ was investigated to some extent as a possible barrier material. It was difficult at that time to obtain large specimens of dense polycrystalline $\text{UO}_2$, and so it was abandoned as a barrier material. A limited investigation was made on the cleavage and fracture of $\text{UO}_2$ and $\text{ThO}_2$, and a copy of the published report is presented in Appendix A of this report. The alumina tubes used were 98 per cent alumina and were made by Coors Porcelain Company, Golden, Colorado, and American Lava Corporation, Chattanooga, Tennessee. A faceting goniometer and a 100-mesh diamond grinding wheel mounted on the polishing wheel proved satisfactory for shaping the exterior profile of the barriers. The polishing wheel setup was placed in a glove box, Fig. 9. The sonic grinder (Fig. 10), Raytheon Mfg. Co., Model 2-334, was very satisfactory for drilling the 1/4-inch-diameter holes. Boron carbide, $\text{B}_4\text{C}$, was used as the abrasive for the sonic grinder. Shaping the barrier was a somewhat slow operation which required from 2 to 3 days for the more difficult single crystal alumina. The dimensions of the barriers are given in Table VIII. All density determinations were made with a mercury volumeter and a standard analytical balance.

A large number of different materials were investigated as bonding materials. Only the materials forming a bond at temperatures above $1500^\circ\text{C}$ were
Figure 7. Alumina Tubes and Barriers.
Figure 8. Single Crystal Alumina Barrier.
### TABLE V

**BARRIER MATERIALS**

<table>
<thead>
<tr>
<th>Barrier</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycrystalline $\text{Al}_2\text{O}_3$</td>
<td>1. Tucalox, General Electric Co.</td>
</tr>
<tr>
<td></td>
<td>2. $100% \text{Al}_2\text{O}_3$, hot pressed, refired to $1820^\circ\text{C}$ in oxidizing atmosphere, Carborundum Co., Niagara Falls, N. Y.</td>
</tr>
<tr>
<td>Polycrystalline $\text{UO}_2$</td>
<td>100% $\text{UO}_2$, $\text{H}_2$ firing, Mallinckrodt Nuclear Corp., St. Louis, Mo.</td>
</tr>
<tr>
<td>Single Crystal $\text{Al}_2\text{O}_3$</td>
<td>Oxyhydrogen flame process, Linde Co., New York, N. Y.</td>
</tr>
<tr>
<td>Single Crystal $\text{UO}_2$ and $\text{ThO}_2$</td>
<td>Electric arc melt growth, Norton Co., Worcester, Mass.</td>
</tr>
</tbody>
</table>

### TABLE VI

**PROPERTIES OF LUCALOX ALUMINA**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal Form</td>
<td>$\alpha - \text{Al}_2\text{O}_3$</td>
</tr>
<tr>
<td>Purity</td>
<td>$99.9^+ % \text{Al}_2\text{O}_3$</td>
</tr>
<tr>
<td>Structure</td>
<td>Polycrystalline</td>
</tr>
<tr>
<td>Density</td>
<td>$3.98 \text{ gm/cc}^{-1}$ avg.</td>
</tr>
<tr>
<td>Porosity</td>
<td>Gas Tight, essentially zero</td>
</tr>
<tr>
<td>Melting Point</td>
<td>$2040^\circ\text{C}$</td>
</tr>
<tr>
<td>Chief Impurity</td>
<td>MgO</td>
</tr>
<tr>
<td>Average Grain Size Before Sintering</td>
<td>$\sim 3 \mu$</td>
</tr>
<tr>
<td>Average Grain Size After Sintering</td>
<td>$\sim 7 \mu$</td>
</tr>
</tbody>
</table>
considered suitable. The most satisfactory seal compositions for the alumina-to-alumina bond are given in Table IX; composition A for bonding polycrystalline specimens and composition B for bonding single crystal to polycrystalline material. A limited study was made on $\text{UO}_2$ to $\text{Al}_2\text{O}_3$ bonding materials. The first attempt to make such a bond was not successful in that the bond did not react to any appreciable extent with the $\text{UO}_2$ (Fig. 11). The bond consisted of components which will form solid solutions or eutectics with both $\text{UO}_2$ and $\text{Al}_2\text{O}_3$. The specimens, Fig. 11, were fired to 1700° C in a hydrogen atmosphere. The composition of the bond was as follows:
Figure 9. Grinding Wheel and Faceting Goniometer.

Figure 10. Sonic Grinder.
<table>
<thead>
<tr>
<th>Series</th>
<th>Crystal Form</th>
<th>Barrier Thickness (Cm)</th>
<th>Barrier Diameter (Cm)</th>
<th>Test Thermal Treatment (Cycles)</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Polycrystalline</td>
<td>0.168</td>
<td>0.635</td>
<td>2</td>
<td>- -</td>
</tr>
<tr>
<td>B</td>
<td>Polycrystalline</td>
<td>0.168</td>
<td>0.635</td>
<td>2</td>
<td>- -</td>
</tr>
<tr>
<td>C</td>
<td>Polycrystalline</td>
<td>0.155</td>
<td>0.635</td>
<td>1</td>
<td>- -</td>
</tr>
<tr>
<td>F</td>
<td>Polycrystalline</td>
<td>0.076</td>
<td>0.635</td>
<td>1</td>
<td>3.901</td>
</tr>
<tr>
<td>G</td>
<td>Polycrystalline</td>
<td>0.109</td>
<td>0.635</td>
<td>1</td>
<td>- -</td>
</tr>
<tr>
<td>H</td>
<td>Polycrystalline</td>
<td>0.107</td>
<td>0.635</td>
<td>1</td>
<td>3.875</td>
</tr>
<tr>
<td>J</td>
<td>Polycrystalline</td>
<td>0.180</td>
<td>0.635</td>
<td>1</td>
<td>3.703</td>
</tr>
<tr>
<td>X</td>
<td>Single Crystal Barrier ⊥ to C axis</td>
<td>0.173</td>
<td>0.635</td>
<td>1</td>
<td>Approx. Theoretical</td>
</tr>
<tr>
<td>Z</td>
<td>Single Crystal Barrier ⊥ to C axis</td>
<td>0.229</td>
<td>0.635</td>
<td>1</td>
<td>Approx. Theoretical</td>
</tr>
</tbody>
</table>

*Letters missing from A through P, and Y denote specimens that developed cracks in barrier before diffusion runs could be completed sufficiently for data analysis.*
Figure 11. \( \text{Al}_2\text{O}_3 \) Bonding to \( \text{UO}_2 \).
TABLE IX
SEAL COMPOSITIONS IN MOLES

<table>
<thead>
<tr>
<th>Material</th>
<th>% wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO₂</td>
<td>40</td>
</tr>
<tr>
<td>TiO₂</td>
<td>5</td>
</tr>
<tr>
<td>ThO₂</td>
<td>10</td>
</tr>
<tr>
<td>Al₂O₃*</td>
<td>45</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>100%</td>
</tr>
</tbody>
</table>

*Composition same as Coors Composition of tube:

94% Al₂O₃
2% MgO and CaO
4% SiO₂

From Figure 11, it can be observed that the UO₂ cracked away from the original flat surface as obtained by cutting slabs with a diamond saw. This may have been caused by a too rapid cooling rate or by occluded gases as the slabs were a polycrystalline material. Subsequent firings at very slow rates tended to give a much better bond between the Al₂O₃ and UO₂. Figure 12 shows some of the better bonds developed with long firing schedules at the designated
Figure 12. Al₂O₃ Bonding to UO₂.
temperatures. Additions of UO$_2$ were made to a base seal composition as follows:

<table>
<thead>
<tr>
<th>Material</th>
<th>% wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium Feldspar</td>
<td>57.2%</td>
</tr>
<tr>
<td>Silica</td>
<td>34.5%</td>
</tr>
<tr>
<td>Kaolin Clay</td>
<td>8.3%</td>
</tr>
<tr>
<td></td>
<td>100%</td>
</tr>
</tbody>
</table>

UO$_2$ additions of 25, 50, and 75% as shown in Figure 12.

This technique was discontinued as suitable specimens of UO$_2$ were not readily available for barrier materials.

B. Diffusion Cell

The diffusion cell system is shown in Fig. 13, and Fig. 14 is a schematic diagram of the system. It was designed to operate in pressure ranges on the order of $10^{-5}$ mm Hg to a lower limit of $2 \times 10^{-6}$ mm Hg. This last figure represents the lower limit of the pressures obtainable with the mass spectrometer pumping station. The other side of the barrier was maintained at one atmosphere pressure of helium, Amarillo grade A. The furnace volume surrounding the assembly could be pumped down to the micron range, and it could be continually purged with a gas of zero helium content such as nitrogen.

The vacuum on the high vacuum side of the barrier was obtained from the pumping station included in the mass spectrometer unit. The station consisted of a mechanical pump, oil diffusion pump, and a cold trap charged with liquid nitrogen. Pressures inside the system were measured with a cold cathode discharge gauge located at the mass spectrometer tube, and an ion gauge and thermocouple gauge located at the end of the furnace assembly. The mass spectrometer
Figure 13. Diffusion Cell.
Figure 14. Diffusion Cell Schematic.
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was a standard Veeco Model MS-9A helium leak detector with an OA2 tube in the amplifier. All permanent connections in the system were silver soldered, and critical "0" ring connections were lubricated with Apiezon L high vacuum grease. Furnace "0" rings, not in the high vacuum assembly, were lubricated with Celvacene heavy vacuum grease.

The barrier and tube assembly was surrounded by a Kanthal resistance heating element powered, optionally, by a saturable reactor and temperature controller, or by a powerstat. Thermocouples were placed inside and on the exterior of the assembly at the barrier.

The entire system was checked for leaks after assembly with a helium leak detector and helium probe. Usually a minimum of 3 days was required to pump down and degas the system to operating pressures of about $10^{-5}$ mm Hg.

The electrical stability of the entire system, including the heating element, recorders, and the mass spectrometer with its pumping station, was maintained with Sola constant-voltage transformers. These transformers insured constant specimen temperature at all temperature levels and constant pumping speeds in the mass spectrometer unit. The apparent sensitivity of the instrument would have varied with the pumping rate of the station if the pumping rate had been held constant. Sensitivity checks that did not vary beyond the limits of error set by the manufacturer as well as the constant temperature held on the specimen confirmed the stability of the electrical system.

A base line was established in the system before helium gas was admitted. The base line represented the lower limits of the sensitivity of the mass spectrometer, about $3 \times 10^9$ atoms/sec. Both sides of the barrier were at pressures of approximately $10^{-5}$ mm when the base line was established. Helium at one atmosphere was admitted to the high pressure side of the barrier and the
high vacuum side of the system was continuously sampled with the mass spectrometer to determine the presence of any diffusion products. Records were made of the pressure on the high vacuum side of the barrier, as well as the barrier temperature.

The mass spectrometer had been calibrated to detect flow rates of helium down to $1.5 \times 10^{-10}$ std. cc/sec.$^{-1}$, or $2.5 \times 10^{9}$ atoms/sec, with the aid of a Veeco Model SC-4 Sensitivity Calibrator. The instrument was recalibrated twice a day during the duration of each run.

When a steady state had been reached between leak rate, temperature, and pressure, after approximately 72 hours, the system was considered at equilibrium, and a higher temperature level was obtained. The temperature levels investigated were room temperature and 100°C temperature levels from 300°C to the operating limits of the furnace, approximately 1000°C. After the helium reached a steady flow at each temperature level, it was removed to observe the time necessary for the flow rate to decrease. Extremely fast times are indicative of Knudsen or turbulent flow rather than diffusion.

Fig. 15, Series J, is a typical example of the flow rates and temperatures-vs.-time types of curves obtained for the various barrier materials. Details of how this system was operated are given in Fig. 15.

One polycrystalline $\text{Al}_2\text{O}_3$ barrier was analyzed by the early-time and late-time approximation technique. There was very good agreement between the values obtained and those found from the more reliable steady-state method for the coefficient of diffusion. However, the values of solubility for helium were not realistic and could have been erratic due to small errors in the value of $D$. 
Figure 15. Data Presentation on Series J.
C. Krypton and Argon Concentration Gradient Determination

The feasibility of determining the concentration gradient of argon and krypton in Al$_2$O$_3$ was demonstrated. A Philips Electronic Instruments Division vacuum x-ray spectrograph, Model 52360 with pulse height analyzer, was used with a NaCl crystal to detect argon K$_\alpha$, and with a LiF crystal to detect krypton K$_\alpha$. In order to set up the pulse-height analyzer for argon, it was necessary to use silver L$_\alpha$, (4.154 Å) as a close substitute for argon K$_\alpha$. Under these conditions the argon and krypton contents of single crystal Al$_2$O$_3$ could be detected for specimens heated to 1000° C, for 24 hours, in those atmospheres. Fig. 16 shows the heights of the peaks obtained with all x-ray conditions duplicated except as specified for specimen C. The remaining traces of argon in the vacuum are the cause of the small peak for the no-argon specimen, Fig. 16A. These same specimens were run on a helium x-ray spectograph without a pulse-height analyzer and no significant differences could be deduced between the specimens with or without the inert gas content. It was necessary to visit the Philips Laboratory at Mount Vernon, New York, to obtain use of the vacuum x-ray fluorescence equipment.
Figure 16. Argon and Krypton X-Ray Fluorescence Recorder Curves.
IV. DISCUSSION OF RESULTS

A. Coefficient of Diffusion and Activation Energy

The crystalline structure of Al₂O₃ is close packed rhombohedral with the plane of highest atomic density normal to the c-axis. According to Tucker and Gibbs(11) single crystals of Al₂O₃ normally contain 10⁷ dislocations/cm². Since there are no apparent phase transformations in Al₂O₃ between 25° and 1000° C, any grain boundary growth in the polycrystalline Al₂O₃ and any appreciable change in the number of dislocations in the single crystal should produce a change in the diffusion coefficient, D, values. The physical dimensions of the specimens and the diffusion data for a typical run are given in Table VIII and Fig. 15, respectively.

The ln values of the coefficients of diffusion, D, approximate a straight line when plotted versus the reciprocal of temperature for all the diffusion runs except Series G. The slope of the line is a function of the activation energy. Although a discontinuity in the diffusion coefficient occurs at an elevated temperature, the values approximate separate straight lines with varied slopes above and below the temperature as shown in Figs. 17, 18, and 19. The coefficient of diffusion equations are given in Table X. The calculated activation energy, Moody, et al. method,(15) Fig. 20, for interstitial diffusion of helium through the basal plane of the Al₂O₃ lattice was 5.7 ev while a value of 0.2 ev was calculated for an edge dislocation activation energy. Fig. 20 shows the relative sizes of the inert gas series of atoms relative to the edge dislocation.

The path traversed by the diffusing helium atom was considered as being between the barrier surfaces for the calculation of the coefficient of
Figure 17. Helium Diffusion through Single Crystal Al₂O₃ Perpendicular to C-Axis.
Figure 18. Helium Diffusion through Polycrystalline Al₂O₃.
Figure 19. Helium Diffusion through Polycrystalline Al₂O₃.
### TABLE X

**DIFFUSION COEFFICIENT EQUATIONS**

<table>
<thead>
<tr>
<th>Series</th>
<th>Equation</th>
<th>$D = D_0 \ e^{-\frac{Q}{kT}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{(1st \ Run)}$</td>
<td>$D = 9.5 \times 10^{-6} \ \text{cm}^2/\text{sec} \ e^{-\frac{0.103 \text{ ev}}{kT}}$</td>
<td></td>
</tr>
<tr>
<td>$A_{(2nd \ Run)}$</td>
<td>$D = 7.2 \times 10^{-6} \ \text{cm}^2/\text{sec} \ e^{-\frac{0.115 \text{ ev}}{kT}}$</td>
<td></td>
</tr>
<tr>
<td>$B_{(1st \ Run)}$</td>
<td>$D = 3.7 \times 10^{-8} \ \text{cm}^2/\text{sec} \ e^{-\frac{0.157 \text{ ev}}{kT}}$</td>
<td></td>
</tr>
<tr>
<td>$B_{(2nd \ Run, \ Before \ Inflection)}$</td>
<td>$D = 2.2 \times 10^{-8} \ \text{cm}^2/\text{sec} \ e^{-\frac{0.184 \text{ ev}}{kT}}$</td>
<td></td>
</tr>
<tr>
<td>$B_{(2nd \ Run, \ After \ Inflection)}$</td>
<td>$D = 2.3 \times 10^{-8} \ \text{cm}^2/\text{sec} \ e^{-\frac{0.142 \text{ ev}}{kT}}$</td>
<td></td>
</tr>
<tr>
<td>$C$</td>
<td>$D = 3.5 \times 10^{-5} \ \text{cm}^2/\text{sec} \ e^{-\frac{0.038 \text{ ev}}{kT}}$</td>
<td></td>
</tr>
<tr>
<td>$F$</td>
<td>$D = 1.52 \times 10^{-5} \ e^{-0.222 \ \text{ev}/kT}$</td>
<td></td>
</tr>
<tr>
<td>$G$</td>
<td>Exhibited laminar and turbulent flow</td>
<td></td>
</tr>
<tr>
<td>$H$</td>
<td>$D = 1.34 \times 10^{-8} \ e^{-0.413 \ \text{ev}/kT}$</td>
<td></td>
</tr>
<tr>
<td>$J$</td>
<td>$D = 1.26 \times 10^{-5} \ e^{-0.830 \ \text{ev}/kT}$</td>
<td></td>
</tr>
<tr>
<td>$X_{(Before \ Inflection)}$</td>
<td>$D = 5.2 \times 10^{-6} \ \text{cm}^2/\text{sec} \ e^{-\frac{0.310 \text{ ev}}{kT}}$</td>
<td></td>
</tr>
<tr>
<td>$X_{(After \ Inflection)}$</td>
<td>$D = 2.5 \times 10^{-9} \ \text{cm}^2/\text{sec} \ e^{-\frac{0.132 \text{ ev}}{kT}}$</td>
<td></td>
</tr>
<tr>
<td>$Z_{(Before \ Inflection)}$</td>
<td>$D = 7.3 \times 10^{-6} \ \text{cm}^2/\text{sec} \ e^{-\frac{0.326 \text{ ev}}{kT}}$</td>
<td></td>
</tr>
<tr>
<td>$Z_{(After \ Inflection)}$</td>
<td>$D = 9.8 \times 10^{-6} \ \text{cm}^2/\text{sec} \ e^{-\frac{0.774 \text{ ev}}{kT}}$</td>
<td></td>
</tr>
</tbody>
</table>

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Figure 20. Schematic Diagram for Calculated Activation Energies for Helium Diffusion through Basal Plane of Al₂O₃.
diffusion and diffusion constant. The values of $10^{-5}$ to $10^{-9}$ cm$^2$/sec, Table X, for the diffusion constant, $D_o$, are quite low in comparison to values$^{(16)}$ of $10^{-2}$ which are considered ideal for perfect crystals. Since $D_o$ is a function of many variables such as grain boundaries, dislocations, experimental accuracy, etc., it is beyond the scope of this investigation to elaborate extensively on the numerical value of the diffusion constant other than to state that the specimens could not be exact duplicates of each other in terms of imperfections.

B. Single Crystal Al$_2$O$_3$

For the case of the single crystal Al$_2$O$_3$, an inflection or discontinuity for diffusion, Fig. 17, was noted in the region of 725°C. A decrease in the diffusion coefficient on the order of one magnitude occurred in the temperature region noted, 725°C. This feature was consistent in Series X and Series Z, whose thickness differed by one-third. Following the sudden decrease, the diffusion coefficient value increased until the limiting temperature of the furnace was reached. The activation energy values determined for Series X and Series Z were in close agreement below the discontinuity temperature. Above the discontinuity temperature the activation energy values differed greatly.

The relative size of the helium atom would prohibit interstitial diffusion and would require a high activation energy value of approximately 5.7 ev. The calculated value of 0.2 ev for an edge dislocation mechanism agrees with the experimental results for the single crystal at temperatures up to the inflection temperature. Above the inflection temperature there is a wide variance of 0.6 ev in the determined activation energy values as shown in Fig. 17. At the inflection temperature, there appears to be an annealing of
imperfections in Series Z and a generation of additional types of imperfections in Series X. The annealing effect is in agreement with the theory of the annealing of edge dislocations on the basal plane at approximately 900°C.

Lattice parameter measurements made on single crystal Al₂O₃ barrier fragments indicate that an expanded lattice may occur in the diffusion barrier. Although the evidence was inconclusive, the presence of a typical diffusion concentration gradient is suggested by the comparative measurements made on fragments from different parts of the barrier.

There were two attempts to fabricate tubes with single crystal barriers cut parallel to the c-axis. On the first attempt, the barriers developed many parting and cleavage cracks during the fast seal firing. The second specimen was sealed satisfactorily but received a thermal shock from a power failure in the diffusion cell system and developed similar cracks.

C. Polycrystalline Al₂O₃

Figs. 18 and 19 show the results of helium diffusion through polycrystalline Al₂O₃. The coefficient of diffusion equations for each specimen are given in Table X. Series B and J exhibit inflection points at 525°C and 625°C with a decrease and increase in activation energy respectively. In each case, there was a marked increase in the helium flow rate. The single crystal specimen exhibited an opposite effect in that the flow rate decreased at a higher temperature. The effect from the inflection point for the polycrystalline specimen can be attributed to changes in the grain boundary. Below the discontinuity temperature, grain boundary defects and edge dislocations appear to constitute the diffusion mechanism. Above the inflection point, grain boundary defects may control the diffusion rate as the number of vacancies
increases due to higher temperatures. However, there is no satisfactory explanation for the occurrence of an inflection point. The activation energy value increase observed with second cycle heating Series B may be attributed to the annihilation of some grain boundary defects and edge dislocations. In general, the activation energy values were indicative of the atom-vacancy interchange mechanism along grain boundaries.

Series C appeared to have a laminar rather than a diffusion type of mass transport.

Certain points must be kept in mind when considering the experimental values of the activation energy. The steady-state leak rate readings at low temperatures, below 500° C, during the early portions of an experiment were subject to doubt. The thickness of the barrier plays an important role. If the barrier length is quite small, it is possible that only one grain occupies the entire length of the barrier. The grain boundary would be an extremely easy diffusion path and a low activation energy would be expected. If the path were longer, the diffusing gas atoms would have to follow several grain boundaries; and, where one boundary stopped, it would have to search for another path to reach the next grain boundary. A mechanism of this type would be much more "activated." The longer path length would also require a longer time to reach the equilibrium state. This would be especially true at lower temperatures. Experimental values of the steady-state readings would be uniformly low if insufficient time were spent at the temperature levels. Barriers were formed by ultrasonic impact grinding. If a barrier were formed of a thickness such that only one or two grains occupied the path length, it is possible that the entire barrier could be mechanically shocked by the method of formation, opening up new diffusion paths. The thickness of the barriers
used in this experimental work was such that there should be many grains in
the diffusion path. No correlation could be determined between the thick-
ness of the barriers and any experimental results in this investigation except
for the very thin barriers that exhibited laminar type mass transport.

The helium flow rates through the two Lucalox alumina specimens, up to
700° C, were too low for any steady-state analysis. It may be possible to
obtain more reliable data by the early-time or late-time approximation tech-
nique. As the Lucalox alumina had been treated with small amounts of MgO to
aid in sintering and densification, 3.97 gm/gm/cc, which is almost theoreti-
cal density, it is quite possible that the Mg^{++} ions occupy the vacant sites
in grain boundaries and dislocations to give a structure with few if any readily
available diffusion paths.

For several reasons, Series G gave indications of mass transport phenome-
non other than diffusion. The specimen leak rates recorded were 500 to 1000
times greater than any obtained for the other specimens studied. The time
necessary to reach equilibrium was never in excess of 10 to 15 minutes.
During the heating cycle, the specimen leak rate was temperature dependent
and highly pressure dependent. The specimen leak rate after cycling from 400°
C to room temperature was higher than at 400° C. Specimen leak rate was still
pressure dependent. The higher leak rate after the heating cycle indicated
more structural damage to the material. The types of molecular flow processes
were considered in order to determine, if possible, the type of flow present
in this specimen.

A plot was made of \( \frac{dE}{dt} \), the equilibrium flow rate in atoms/sec, as a
function of the pressure on the high pressure side of the barrier at constant
temperature, Fig. 21. The equations for laminar flow all state that the flow
Figure 21. Equilibrium Helium Flow Rate versus Pressure for Series G.
rate at a constant temperature is linearly proportional to the pressure differential. The pressure on the high vacuum side of the barrier was < 10^{-5} \text{ mm Hg} and may be neglected. Any deviation from a linear function at a constant temperature would indicate a divergence from laminar flow.

Figure 21 shows that during the heating cycle at 195°C, the measured values approximate a straight line very closely. The flow is apparently laminar. At 383°C, the next temperature level, the same plot deviates from a straight line, and the flow rates increased, to indicate that it is turbulent flow. The system was then cooled to room temperature and helium again admitted to the system. The room temperature leak rates recorded were higher than at 382°C, indicating that still further damage had been done to the specimen. Again the plot deviated from a straight line, indicating a turbulent flow as the helium passed down the path.

The type of laminar flow experienced at 195°C can be predicted to some extent. The flow could not have been molecular effusion through a thin plate since the gas did have a finite distance to travel. This leaves molecular streaming or Poisueille types of flow. Since there is undoubtedly some friction as the gas collides with the walls of the flow path, the friction factor found in the Knudsen equation would have to be employed. When the Poisueille equation is corrected for friction on the walls, it assumes the form of the Knudsen equation. The type of flow experienced at 195°C was quite probably Knudsen flow on the basis of these facts.

One further point should be noted. The time necessary to reach equilibrium conditions of flow rate on Series G was approximately 10 minutes. Series F, H, and J all required a minimum of 8 hours to come to equilibrium. Series J, the thickest specimen studied, did not reach equilibrium conditions in less
than 3 days at the temperature levels studied (see Fig. 15). Since the barrier thickness of Series G and Series H are practically the same and the barrier thickness of Series F is even thinner, the length of time to reach a steady state flow rate is a strong argument for the diffusion mechanism of atom transport.
V. CONCLUSIONS

1. The coefficients of diffusion of helium mass transport in single crystal and polycrystalline Al$_2$O$_3$ can be experimentally determined by means of a mass spectrometer.

2. The equation for the coefficient of diffusion of helium through single crystal Al$_2$O$_3$ in the temperature range 200° to 700° C was determined to be:

$$D = 6.2 \times 10^{-6} e^{\frac{0.32 \text{ ev}}{kT}}$$

3. The activation energy calculated from the experimental data on helium diffusion through single crystal Al$_2$O$_3$ was 0.32 ev in the temperature range 200° to 700° C.

4. The most probable basic mechanism for diffusion of helium through single crystal Al$_2$O$_3$ is an atom-vacancy interchange type occurring along edge dislocations.

5. In the region around 725° C annealing of internal strains and annihilation of dislocations probably occurs in the single crystal Al$_2$O$_3$.

6. The mass transport rate of helium through polycrystalline Al$_2$O$_3$ may be affected by density and thickness and tends to decrease with repeated heatings to elevated temperatures.

7. Densities above 3.70 gm/cm$^3$ may be sufficiently high to give diffusion rather than laminar flow type mass transport.

8. Activation energies for diffusion of helium through polycrystalline Al$_2$O$_3$ varied from 0.10 to 0.80 ev and D$_o$ values varied from approximately $10^{-8}$ to $10^{-5}$ cm$^2$/sec.
9. The most probable basic mechanism for diffusion of helium through polycrystalline $\text{Al}_2\text{O}_3$ is an atom-vacancy interchange type occurring mainly along grain boundaries.
VI. PERSONNEL

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Respectfully submitted:

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VII. APPENDIX

Reprint of an Article from The Journal of the American Ceramic Society 42, No. 5 (May 1959) entitled "Thorium Oxide and Uranium Oxide Cleavage," by William B. Campbell, Vernon J. Hurst, and Willis E. Moody.
Thorium Oxide and Uranium Oxide Cleavage

by WILLIAM B. CAMPBELL, VERNON J. HURST, and WILLIS E. MOODY

The crystallographic properties of most natural crystals have been determined. However, some of the crystals in use today do not occur in nature. These synthetic crystals are in limited distribution and have not been studied extensively. Apparatus involving these synthesized crystals necessitates a knowledge of specific crystal properties such as cleavage planes and their associated imperfections. A search of the literature disclosed no information pertaining to the cleavage of ThO$_2$ or UO$_2$.

A thorium oxide crystal obtained from the electric furnace process by Norton Company, Worcester, Massachusetts, was examined by the writers with a two-circle optical goniometer, and the cleavage poles were plotted on a stereographic net. An oriented fragment of the same crystal was mounted on a Buerger precession camera and a plot of the axes was obtained. This plot was superimposed on the stereographic net. Although the uncertainty in translating the crystallographic orientation of the X-rayed fragment back to the parent crystal might easily be as much as 5°, the correspondence of the axes and cleavage poles clearly shows that the cleavage is cubic, i.e., parallel to the (100), (010), and (001) planes.

The cleavage of the specimen was good but not perfect. All three cleavage surfaces gave streaky and multiple reflections on the optical goniometer. On a stereographic plot the cleavage poles were grouped about the crystallographic axes as shown in Fig. 1. One cleavage reflection was offset 6° to 10° from $a$; another 12° from $b$; and the third cleavage gave a streaky reflection which ranged from $c$ to 24° away from $c$. This was attributed to internal strain in the synthesized crystal.

A synthesized urania (UO$_2$) crystal obtained from the same source was subjected to a similar investigation and was found to have no cleavage. Its fracture was conchoidal but in a few cases it was planar.

The single-crystal test specimens are shown in Fig. 2.

Fig. 1. Stereogram showing reflections from cleavages (black areas) as measured on the two-circle optical goniometer in relation to the crystallographic axes as determined by X-ray diffraction.

Fig. 2. Test specimens.