Study of the diffusion of certain gases through pyrex glass using a mass spectrometer

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A STUDY OF THE DIFFUSION OF CERTAIN GASES THROUGH PYREX GLASS USING A MASS SPECTROMETER

by

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CHAPTER I

INTRODUCTION

The ever increasing use of glass in industry, and in the construction of laboratory apparatus, has created a need for more basic research on its properties. The diffusion of gases through glass is of interest to those involved in the design of high-vacuum apparatus, such as electron tubes, and may also offer some insight into the structural characteristics of the glass.

In this study, helium and neon were chosen as the diffusing gases. This choice was made since their physical properties suggested the probability of rapid diffusion. Their inert nature also suggested that interactions with the glass should be less important than with non-inert gases. In this case the diffusion should obey a linear diffusion equation for which a solution could be easily obtained. The term "pyrex" is used to indicate a Corning 7740 glass.

Until the work of Rogers et al. (1) only measurements of steady state flow rates had been made. These yielded values for the permeability constant but not for the true diffusion coefficients. Rogers et al. obtained values for the diffusion coefficient for helium in pyrex glass by suddenly putting helium into a py-
A glass cylinder and observing the diffusion rate with an ionization gauge. The term "pump-in" method will be used to designate a procedure of this sort, where initially there is no gas inside either the cylinder or the glass walls of the cylinder and where the diffusion rate is recorded from the time gas is admitted until near steady state equilibrium. In this method, a pressure gradient exists across the glass while observations are being made. The term "pump out" method will be used to designate a process where steady state equilibrium is first achieved under a pressure gradient, the gradient is then removed, and observations are made while the gas diffuses out of the glass.

Hayden and Wehrenberg (2) made a study of the diffusion of helium through glass using the pump-out method. This study is a continuation of that project. Additional diffusion coefficients for helium at different temperatures have been obtained by both the pump-in and pump-out methods. Values have also been obtained for neon by both methods.

The diffusion rates are observed by means of a continuously pumped mass spectrometer, and recorded on a Brown recording potentiometer. The observed peak height, of the recorded data, is proportional to the diffusion rate, or flux and from this the diffusion coefficient for the gas, at that temperature, can be calculated.
Subsequent chapters deal with experimental technique, the derivation of equations which describe the pump-in and pump-out methods, the experimental results, and the analysis of the experimental data.
Plate I gives a schematic diagram of the experimental arrangement. The tube through which the gas diffuses consists of a section of 12.00 mm o.d. pyrex tubing having a wall thickness of 1.00 mm. The gas is then passed into a mass spectrometer. Relative peak height is then recorded. In the case of helium at higher temperatures, measurements were made over about three orders of magnitude.

The temperature of the diffusion cell was set and sustained by means of a nichrome furnace connected to a Variac. It was monitored by means of an iron-constantan thermocouple and a Leeds and Northrup type K potentiometer. A rough graph was prepared indicating equilibrium temperature as a function of furnace voltage. This was used as a guide in setting the furnace at the desired temperature. Variable room temperature and variable line voltage made a process of successive approximations necessary however, the temperature was allowed to stabilize for about four hours and then the sample was admitted into the diffusion cell.

Pressures in the neighborhood of 76 cm were used for the helium and 30 cm for the neon. The pressure was observed on a mercury manometer.
The mass spectrometer was a 60 degree instrument having a 6 in radius of curvature. Samples on the order of \(10^{-8}\) cc at s.t.p. were observable, but no absolute calibration of the instrument was undertaken.
PLATE 1. SCHEMATIC DIAGRAM OF EXPERIMENTAL SETUP
Chapter III

A MATHEMATICAL THEORY OF THE DIFFUSION PROCESS

In this section, equations are derived which describe the diffusion process. The results derived here will be used to interpret the data obtained.

I. THE DIFFUSION EQUATION

For any system in which matter is conserved, the equation of continuity must hold.

\[ \nabla \cdot \vec{J} = -\frac{\partial \rho}{\partial t} \]  

\( \vec{J} \) is called the current density and is defined by the relationship:

\[ \vec{J} = \rho(x,y,z)\vec{v} \]

where \( \vec{v} \) represents the velocity at point \( (x,y,z) \) and \( \rho \) is the density.

In the case of diffusion, the following relationship is usually assumed.

\[ \vec{J} = -\rho \nabla \rho \]

This equation is often called Fick's law of diffusion. \( D \) is a constant of proportionality called the diffusion coefficient or constant.
Substitution of (3) into the continuity equation (1) yields:

\[ D \frac{\partial^2 \rho}{\partial t^2} = \frac{\partial \rho}{\partial t} \]

This relationship is called the diffusion equation.

Since the experimental set-up has cylindrical symmetry, it is convenient to work in a cylindrical coordinate system. Equation (4) takes the form:

\[ \frac{\partial^2 \rho}{\partial r^2} + \frac{1}{r} \frac{\partial \rho}{\partial r} = \frac{1}{D} \frac{\partial \rho}{\partial t} \]

where:
- \( a \) is the inner radius of the diffusion cell,
- \( b \) is the outer radius of the diffusion cell,
- \( L \) is the length of the cell,
- \( r \) is the radial distance from the axis of the cell.

II. THE STEADY STATE SOLUTION

After long periods of time, \( \frac{\partial \rho}{\partial t} = 0 \) and:

\[ \frac{d}{dr} \left( r \frac{d \rho}{dr} \right) = 0 \quad a \leq r \leq b \]

whence

\[ \rho = A \ln(r) + B \]

A and B are constants of integration. If the following boundary conditions are assumed:

\( t = \infty \), \( \rho(a) = \rho_a \); \( \rho(b) = \rho_1 \)

then:

\[ \rho(r) = \rho_1 \frac{(\ln r/a)}{\ln b/a} + \rho_a \frac{(\ln b/r)}{\ln b/a} \]
Under pump-in conditions, this solution becomes:

\[ p(r) = \frac{p_0 \ln \frac{b}{r}}{\ln \frac{b}{a}} \]

since \( p_1 = 0 \).

III. THE STEADY STATE PUMP-IN FLUX

The amount of gas diffusing into the spectrometer under steady state conditions in unit time is given by:

\[ Q = \int_{\text{cylinder}} (D \nabla p) \cdot \hat{n} \, ds \]

since the diffusion is in the radial direction, this reduces to:

\[ Q = -2\pi b L D (\nabla p)_b \]

and hence:

\[ Q = \frac{2\pi L D p_0}{\ln \frac{b}{a}} \]

Thus steady state flow is proportional to the initial pressure and to the diffusion constant.

IV. THE SOLUTION BY SEPARATION OF VARIABLES

Assume:

\[ p(r,t) = R(r) T(t) \]

Then \( R \) is a solution of the differential equation:

\[ \frac{d^2 R}{dr^2} + \frac{1}{r} \frac{dR}{dr} = -\alpha^2 R \]
T is a solution of the differential equation:

\[ \frac{dT}{dt} = -\alpha^2 D T \]

\( \alpha^2 \) is the separation constant. Equation (14) has the solution:

\[ T = T_0 e^{-\alpha^2 D t} \]

The substitution \( z = \alpha r \) reduces equation (13) to Bessel's equation of order zero. Since the range of \( r \) does not include the origin, the solution will be a combination of Bessel functions of the first and second kind.

\[ R(r) = A J_0(\alpha r) + B Y_0(\alpha r) \]

V. BOUNDARY CONDITIONS ON THE SOLUTION

The solution to the differential equation must satisfy the boundary conditions for the experimental set-up in order to be of any value. Both pump-in and pump-out solutions can be obtained from a single calculation if the following conditions are imposed.

\[ \rho(\infty,z,t) = \rho_0; \quad \rho(0,t) = \rho_1; \quad \rho(r,\infty) = f(r) \]

If the temperature is assumed constant, then the surface conditions are independent of time.

Consider the equation:

\[ \nabla^2 \phi - \frac{1}{D} \frac{\partial \phi}{\partial t} = 0 \]

Suppose a solution is needed in a region \( U \) with:
the boundary condition:

\[ V = \phi(x,y,z,t) \] along the boundary

and the initial condition:

\[ V = f(x,y,z) \text{ at } t = 0 \]

Assume that \( V \) can be represented by the sum of two other functions; \( V = u + w \) with the following properties.

(a) \( u \) is a harmonic function which satisfies the boundary conditions on equation (17).

\[ \nabla^2 u = 0 \quad u = \phi(x,y,z,t) \text{ on the boundary} \]

(b) \( w(x,y,z,t) \) is a solution of equation (17) which vanishes on the boundary and is such that \( u + w \) satisfies the initial condition. In general, \( w \) is represented as an infinite sum of elementary solutions.

A function \( V \), which can be represented in the above manner will satisfy the diffusion equation, the boundary condition and the initial condition. The solution is then unique.

The steady state solution, equation (8), is harmonic and satisfies the boundary conditions on the cylinder at \( a \) and \( b \). In order to satisfy property (b) above, the constants of equation (16) must be chosen in such a way that \( R \) vanishes along the surface (at \( a \) and \( b \)). A superposition of these functions must then be taken in order to satisfy the initial condition.

Equation (16) becomes then, on the boundary:

\[ R(a) = \alpha J_0(a \alpha) + \beta Y_0(a \alpha) = 0 \quad (18) \]

\[ R(b) = \alpha J_0(b \beta) + \beta Y_0(b \beta) = 0 \quad (19) \]
For a non-trivial solution, the determinant of the coefficients must vanish and so:

\[(20) \quad \int_0^a (d \, \bar{a}) \, J_0 (d \, b) \, - \int_0 (d \, b) \, J_0 (q \, a) = 0 \]

If we take \( k = J_0 (q \, b) \) then: \( B = - \int_0 (d \, b) \)

Equation (16), i.e. \( R(r) \) vanishes identically when \( r \) is equal to \( b \). By equation (20) it also vanishes when \( r \) is equal to \( a \). The roots of equation (20), \( \gamma_n \), are known to be real and simple(4), and further more, to every positive root \( \gamma_n \), there corresponds a negative root \( -\gamma_n \).

The only condition remaining is the initial condition on the solution: \( \phi(r, 0) = f(r) \)

This condition can be satisfied provided that \( F(r) \) can be expanded in terms of the Bessel functions. \( F(r) \) is equal to \( f(r) = \) (steady state solution).

\[(21) \quad F(r) = \sum_{m=1}^{\infty} a_m (J_0 (d \, m \, b) \, J_0 (d \, m \, r) - J_0 (d \, m \, b) \, J_0 (d \, m \, r)) = \sum_{m=1}^{\infty} a_m (U_0 (d \, m \, r)) \]

If this is assumed, then the constants in the expansion given by equation (21) can be obtained by multiplication by \( r U_0 (d \, m \, r) \) and an integration:

\[(22) \quad \int_a^b r U_0 (d \, m \, r) \, f(r) \, dr = \sum_{m=1}^{\infty} \int_a^b a_m (U_0 (d \, m \, r)) \, U_0 (d \, m \, r) \, dr \]
If \( c \) and \( \beta \) are root, then the integrals have the values (5):

\[
\int_{a}^{b} r \, \nu_{0} (\alpha r) \, dr = 0
\]

\[
\int_{a}^{b} r \, \nu_{0}^{2} (\alpha r) \, dr = 2 \left[ \frac{J_{0}^{2} (\alpha a) - J_{0}^{2} (\alpha b)}{\pi^{2} \alpha^{2} \nu_{0}^{2} (\alpha a)} \right]
\]

Substitution into equation (22) yields:

\[
(23) \quad \int_{a}^{b} F (r) \, r \, \nu_{0} (\alpha r) \, dr = \int_{a}^{b} R_{n} \, \nu_{0}^{2} (\alpha r) \, dr
\]

\[
R_{n} = \frac{\pi^{2} \alpha^{2} \nu_{0}^{2} (\alpha a)}{2 \left( J_{0}^{2} (\alpha a) - J_{0}^{2} (\alpha b) \right)} \int_{a}^{b} r \, \nu_{0} (\alpha r) \, F (r) \, dr
\]

**VI. THE PUMP-IN SOLUTION**

Under pump-in conditions, \( \rho (r, \theta) = 0 \) and equation (9) is the required solution \((u)\) to Laplace's equation. Then for \( F (r) \) we have:

\[
(24) \quad F (r) = - u = - \frac{\rho_{0} \, 2\pi \, b / r}{\nu_{0} \, b / a}
\]

Equation (23) becomes:

\[
(25) \quad R_{n} = - \frac{\pi^{2} \alpha^{2} \nu_{0}^{2} (\alpha a) \rho_{0}}{2 \, 2\pi \, b / a \left( J_{0}^{2} (\alpha a) - J_{0}^{2} (\alpha b) \right)} \left\{ \int_{a}^{b} \rho_{0} \, dr - \int_{a}^{b} \rho_{0} \, r \, \nu_{0} \, dr \right\}
\]

The required integrals are (5).

\[
(26) \quad \int_{a}^{b} r \, \nu_{0} (\alpha r) \, dr = 2 \left\{ \frac{J_{0} (\alpha a) - J_{0} (\alpha b)}{\pi^{2} \alpha^{2} \nu_{0}^{2} (\alpha a)} \right\}
\]

\[
(27) \quad \int_{a}^{b} r \, \nu_{0} (\alpha r) \, 2 \nu_{0} \, dr = 2 \left\{ \frac{J_{0} (\alpha a) \, 2 \nu_{0} (\alpha b) - J_{0} (\alpha b) \, 2 \nu_{0} (\alpha a)}{\pi^{2} \alpha^{2} \nu_{0}^{2} (\alpha a)} \right\}
\]

Upon substitution, equation (25) simplifies into:

\[
(28) \quad R_{n} = \frac{\pi \, \rho_{0} \, (\alpha a) \, J_{0} (\alpha b) \, \rho_{0}}{\nu_{0} \, J_{0}^{2} (\alpha a) - J_{0}^{2} (\alpha b)}
\]
The expansion of equation (24) is given by:

\[ F(r) = \sum_{n=1}^{\infty} \frac{\pi j_0(d_m a) j_0(d_m b) L_0}{j_0^2(d_m a) - j_0^2(d_m b)} U_0(d_n r) \]

The final solution to the pump-in equation is given by:

\[ \rho(r,t) = \frac{P_0 b}{m b/a} + \sum_{n=1}^{\infty} \frac{P_0 j_0(d_m a) j_0(d_m b) U_0(d_n r)}{j_0^2(d_m a) - j_0^2(d_m b)} e^{-\gamma d_n^2 v t} \]

VII. The pump-in flux

The flux into the spectrometer during pump-in is given by:

\[ Q = -2\pi b L D \left( \frac{\partial \rho}{\partial r} \right)_0 \]

Now \( \frac{\partial \rho}{\partial r} \) has the value (5).

\[ \frac{\partial \rho}{\partial r} = -q \left( \frac{2}{\pi d_b} \right) \]

The equation for pump-in flux reduces to:

\[ Q = 2\pi b L D P_0 + \sum_{n=1}^{\infty} \frac{\frac{4\pi L D P_0 j_0(d_m a) j_0(d_m b) e^{-\gamma d_n^2 v t}}{j_0^2(d_m a) - j_0^2(d_m b)}}{\frac{1}{b/a}} \]

The first five roots of equation (20) are given in references (5) and (6). These are, for values of \( b/a \) equal to 6/5:

- \( d_1 = 31.4028 \)
- \( d_2 = 62.8252 \)
- \( d_3 = 94.2434 \)
- \( d_4 = 125.6604 \)
- \( d_5 = 157.0770 \)
To the degree of accuracy with which the experimental measurements were taken, \( q_m \) can be replaced by \( 10 \pi n \). This implies that the diffusion rate is not particularly sensitive to physical geometry and that this problem is equivalent to diffusion through a slab having the same area as the mean cylinder and the same thickness as the actual tube.

A value of .5 cm was used in the roots, so the rest of the quantities should be in cgs units.

**VIII. APPROXIMATIONS FOR THE BESSEL FUNCTIONS**

The Bessel functions appearing in the solution can be approximated by means of the Poisson asymptotic form for large values of the independent variable \( \nu \).

\[
J_\nu(\nu) \sim \left( \frac{2}{\pi \nu} \right)^{1/2} \left\{ \cos \left( \nu - \frac{\pi}{4} \right) \left[ 1 - \frac{1^2 \cdot 3^2}{2! (8 \pi)^2} + \frac{1^2 \cdot 3^2 \cdot 5^2 \cdot 7^2}{4! (8 \pi)^4} - \ldots \right] \\
+ \sin \left( \nu - \frac{\pi}{4} \right) \left[ \frac{1^2}{1! \nu^2} - \frac{1^2 \cdot 3^2 \cdot 5^2}{3! (8 \pi)^3} + \ldots \right] \right\}
\]

It has been shown that the error introduced by truncating the series is not larger than the last term that is carried \( (7) \). If only first order terms are used, then the error is about .1 %, which is less than the experimental error. To first order terms:

\[
J_\nu(\nu) \sim \frac{(-1)^n}{n! \nu^{n/2}}
\]
(36) \( J_0 (d m b) \sim \frac{1}{\pi b n} \)  

(37) \( q_0 = 10 m^2 \)  

\( a = 5 \text{ cm.} \)  

\( b = 6 \text{ cm.} \)

For small values of time, the time dependent part must be nearly equal to the negative of the steady state solution, since the flux is zero at \( t \) equal to zero. The above approximations have the effect of replacing the term:

(39) \( \frac{1}{2} b / a \) by \( \sqrt{30} \)

It is reassuring to note that these are indeed very nearly equal.

Using the approximation implied by (39), the equation for pump-in flux reduces to:

(40) \( \phi = \frac{2 \pi H D C_0}{2 \pi b / a} \left\{ 1 + 2 \sum_{n=1}^{\infty} (-1)^n \frac{a}{2 \pi n \frac{b}{a}} \right\} \)

**IX. THE PUMP-OUT SOLUTION**

The boundary conditions for pump-out are:

\( \rho (a, t) = \rho (b, t) = 0 \);  \( \rho (r, 0) = C_o \),  

Since the functions \( U_0 (\theta, r) \) satisfy the boundary conditions at \( a \) and \( b \), and the differential equation, it is only necessary to take a combination of these functions which satisfy the initial condition:

\( F(r) = \rho (r, 0) = C_o \frac{\ln b / r}{\ln b / a} \)

The coefficients in the expansion will be exactly the same as in the pump-in case, except for a minus sign.
The solution to the pump-out equation is therefore:

\[ \rho (r, t) = - \rho_0 \sum_{n=1}^{\infty} \frac{d_n (d_n a)}{J_n^2 (d_n a) - J_n^2 (d_n b)} \frac{U_0 (d_n r)}{r} e^{-D_n^2 \frac{r^2}{a^2}} \]

\[ \times \quad \left( \frac{\rho_0}{a} \right)^2 \]

X. THE PUMP-OUT FLUX

The flux during pump-out is given by:

\[ \Phi = - \frac{4 \pi L P_0}{2} \sum_{n=1}^{\infty} (-1)^n e^{-D_n^2 \frac{r^2}{a^2}} \]

Let:

\[ z = (10 \pi)^2 \frac{r}{a} \quad \Phi (z) = \sum_{n=1}^{\infty} (-1)^n e^{-D_n^2 \frac{r^2}{a^2}} \]

\[ \Phi = \Phi (z) \left( - 2 \Phi (z) \right) \]

Values for \( \Phi (z) \) were computed on the Montana State University I.B.M. 1620 computer by Mr. Ken Bakke. These are listed in table I. Plate (2) shows a plot of this function. Plate (3) shows the pump-in function \( (1 + 2\Phi (z)) \)

For large values of \( t \) the pump-out solution has the asymptotic form:

\[ \Phi \sim \frac{4 \pi L P_0}{2} e^{-D_n^2 \frac{r^2}{a^2}} \]

or:

\[ \ln \Phi = \ln \left( \frac{4 \pi L P_0}{2} \right) - (10 \pi)^2 \frac{r^2}{a^2} \]

A plot of \( \ln \Phi \) versus \( t \) will have a slope of \(-\gamma^2 \).
TABLE I
VALUES OF $F(z) = \sum_{n=0}^{\infty} (-1)^n \exp -zn^2$

<table>
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PLATE 3. PUMP IN SOLUTION $G(z) = 1 + 2F(z)$
CHAPTER III

EXPERIMENTAL DATA

In this chapter, the experimental data are presented and analyzed in accordance with the theory developed in chapter II. The diffusion coefficients are obtained and tabulated.

I. HELIUM PUMP-OUT DATA

The logarithms of the observed peak heights are plotted against time after pump-out. The best straight line is then drawn through the points and the slope is determined in the region where the peak height has fallen to about one tenth its initial value. The diffusion constant is then given by:

\[ D = \frac{2.30}{(985)(60)T_0} \]

where \( T_0 \) is the time in minutes required for the peak height to change by a factor of 10.

Plates 4-9 show the pump-out data as plotted on semi-log paper. Table II lists the diffusion coefficients for helium as calculated by this method.
PLATE 6 HELIUM PUMP-OUT 392°
PLATE 7 HELIUM PUMP-OUT 349°
PLATE 8 HELIUM PUMP-OUT 371°
PLATE 9 HELIUM PUMP-OUT 416°
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Diffusion Constant (cm²/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>310</td>
<td>$1.54 \times 10^{-6}$</td>
</tr>
<tr>
<td>318</td>
<td>$1.62 \times 10^{-6}$</td>
</tr>
<tr>
<td>332</td>
<td>$1.92 \times 10^{-6}$</td>
</tr>
<tr>
<td>349</td>
<td>$2.05 \times 10^{-6}$</td>
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<tr>
<td>352</td>
<td>$2.16 \times 10^{-6}$</td>
</tr>
<tr>
<td>371</td>
<td>$2.67 \times 10^{-6}$</td>
</tr>
<tr>
<td>416</td>
<td>$4.11 \times 10^{-6}$</td>
</tr>
<tr>
<td>451</td>
<td>$5.03 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
II. HELIUM PUMP-IN DATA

Equation (40) for the pump-in flux can be written as:

\[ \phi = \phi_{ss} \left( 1 + 2 F(z) \right) = \phi_{ss} + 2 \phi_{ss} F(z) = \phi_{ss} G(z) \]

For large values of \( z \) only the first term in the series is significant and:

\[ \phi_{ss} - \phi = 2 \phi_{ss} e^{-\left(\frac{z}{\alpha}\right)^2} \]

\[ \int_0^\infty \left( \phi_{ss} - \phi \right) = \int_0^\infty 2 \phi_{ss} e^{-\left(\frac{z}{\alpha}\right)^2} \]

The diffusion constant can be determined from the slope of a plot of equation (49). Plates 10 and 11 show plots of this type for temperatures of 315°C and 416°C. The steady state value however is difficult to determine with any degree of accuracy. The maximum peak height observed in a reasonable period of time is less than the steady state value. A small change in temperature also causes a significant change in its value. For this reason, calculations involving the steady state value can only yield approximate values for the diffusion constants. Adding a small constant to the observed maximum decreases the calculated value of the diffusion constant. This implies that the diffusion constant calculated on the basis of the observed peak maximum is larger than the true constant.

If a family of curves of the logarithm of peak height versus \( t \) is plotted for different peak heights near the observed maximum, then the curves bend to the right of to
the left of some center straight line as is shown in plate 12. If this center straight line is assumed to correspond to the proper steady state value, and a value for the diffusion constant is calculated from its slope, then this value turns out to be quite close to that calculated by the pump-out method.

At:

318°  \( D = 1.64 \times 10^{-6} \, \text{cm}^2/\text{sec} \)

416°  \( D = 4.15 \times 10^{-6} \, \text{cm}^2/\text{sec} \)

Pump-out values were:

318°  \( D = 1.62 \times 10^{-6} \, \text{cm}^2/\text{sec} \)

416°  \( D = 4.11 \times 10^{-6} \, \text{cm}^2/\text{sec} \)

Values for \( D \) were also calculated from the pump-in measurements by fitting the experimental data to the theoretical curve at certain points.

Now \( G(1) = 0.3066 \). If \( t_0 \) is the time when the peak height has achieved 0.3066 of its maximum value, then

\[
D = \frac{i}{985 t_0}
\]

Similarly, \( G(1.5) = 0.5587 \) and \( G(2) = 0.7997 \)

\( D \) values calculated for these three points on the 318° run are:

\( D(0.3066) = 1.67 \times 10^{-6} \, \text{cm}^2/\text{sec} \);

\( D(0.5587) = 1.66 \times 10^{-6} \, \text{cm}^2/\text{sec} \);

\( D(0.7997) = 1.72 \times 10^{-6} \, \text{cm}^2/\text{sec} \)
A ratio method has also been used, which does not depend on the steady state value.

Let: \( Q_2 = \varphi(t_2); \quad Q_1 = \varphi(t_1) \)

Set: \( Q_2 = 2 \cdot Q_1 \)

Values of \( t_2 \) and \( t_1 \) can be found such that the peak height at \( t_2 \) is twice that at \( t_1 \).

Then: \( \frac{Q_2}{Q_1} = \frac{1}{2} = \frac{G(s) \cdot t(t)}{G(s) \cdot t(t)} = \frac{G(t)}{G(t)} \)

Now: \( t_2 = \frac{t_1}{2}, \quad t_1 = D \cdot a \cdot t_1 \)

If \( 20(s) \) and \( G(s) \) are plotted and horizontal lines drawn between the two curves as shown in plate 13 then as the points \( P_1 \) and \( P_2 \) are moved, \( t_2/t_1 \) becomes a function of \( s_1 \). Plate 14 shows a graph of this function. The value of \( D \) can be determined from the two times \( t_2 \) and \( t_1 \) since \( s_1 = 985 \cdot D \cdot t_1 \). In practice, the functions were plotted on a two ft. square section of graph paper and intermediate points were linearly interpolated.

Table III lists the values at various times after pump-in up to about 90% of the observed steady state value. The constants calculated in this manner represent a mean value over the \( t_1 \) to \( t_2 \) time interval.

Initial diffusion seems to be somewhat faster than at near steady state. This is probably due to a slower initial pumping rate in the mass spectrometer and is discussed further in the conclusions.
\[ \log (q_{eq} - q) \]

- \( q_{max} = 1.15 \) (corrected data)
- \( q_{max} = 1.09 \) (observed)

**PLATE 10 HELIUM PUMP-IN 318^\circ**

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PLATE 12 DETERMINATION OF STEADY STATE FLOW AT 318°
### TABLE III

**Helium Diffusion Constants**

**Pump-in Method**

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>$t_1$ (min)</th>
<th>$t_2$ (min)</th>
<th>$D$ (cm²/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>310</td>
<td>3.22</td>
<td>3.68</td>
<td>$2.31 \times 10^{-6}$</td>
</tr>
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<td>310</td>
<td>3.68</td>
<td>4.32</td>
<td>$2.28 \times 10^{-6}$</td>
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<td>310</td>
<td>5.03</td>
<td>6.11</td>
<td>$1.91 \times 10^{-6}$</td>
</tr>
<tr>
<td>310</td>
<td>6.60</td>
<td>8.66</td>
<td>$1.78 \times 10^{-6}$</td>
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<td>11.44</td>
<td>22.0</td>
<td>$1.66 \times 10^{-6}$</td>
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<tr>
<td>332</td>
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<td>2.79</td>
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<td>$2.41 \times 10^{-6}$</td>
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<td>332</td>
<td>7.20</td>
<td>10.52</td>
<td>$2.12 \times 10^{-6}$</td>
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<td>350</td>
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<td>2.38</td>
<td>$4.95 \times 10^{-6}$</td>
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<td>3.50</td>
<td>4.28</td>
<td>$2.81 \times 10^{-6}$</td>
</tr>
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<td>5.50</td>
<td>7.65</td>
<td>$2.49 \times 10^{-6}$</td>
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<td>5.27</td>
<td>7.66</td>
<td>$2.83 \times 10^{-6}$</td>
</tr>
<tr>
<td>371</td>
<td>6.95</td>
<td>12.18</td>
<td>$2.67 \times 10^{-6}$</td>
</tr>
<tr>
<td>416</td>
<td>2.52</td>
<td>3.38</td>
<td>$5.04 \times 10^{-6}$</td>
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<tr>
<td>416</td>
<td>4.00</td>
<td>6.83</td>
<td>$4.51 \times 10^{-6}$</td>
</tr>
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<td>416</td>
<td>Curve fitting</td>
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<td>$4.11 \times 10^{-6}$</td>
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<tr>
<td>451</td>
<td>.835</td>
<td>.981</td>
<td>$1.02 \times 10^{-5}$</td>
</tr>
<tr>
<td>451</td>
<td>1.50</td>
<td>1.90</td>
<td>$7.32 \times 10^{-6}$</td>
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III. BECN DATA

Studies were made of the diffusion of neon in a manner similar to that for helium. The diffusion process is much slower. Times of the order of 24 hours are required for the peak height to decay two orders of magnitude. Temperature control is difficult over these long time periods and for this reason the measurements are not as accurate as those on the helium. Plates 15 to 18 show the pump-out data, and Table IV lists the diffusion constants.
PLATE 16 NEON PUMP OUT 425°
PLATE 17  NEON PUMP OUT 437°
### Table IV

**NzOM Diffusion Constants**

**Pump-Cut Method**

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>Diffusion Constant (cm$^2$/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>420</td>
<td>$3.25 \times 10^{-8}$</td>
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<tr>
<td>425</td>
<td>$3.51 \times 10^{-8}$</td>
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<tr>
<td>437</td>
<td>$4.63 \times 10^{-8}$</td>
</tr>
<tr>
<td>451</td>
<td>$5.9 \times 10^{-8}$</td>
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</tbody>
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### TABLE V

**Nickel Diffusion Constants**

**Jump-In Method**

<table>
<thead>
<tr>
<th>Temperature $^\circ$C</th>
<th>$t_1$ (min)</th>
<th>$t_2$ (min)</th>
<th>$D$ cm$^2$/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>421</td>
<td>240.0</td>
<td>321.0</td>
<td>$4.95 \times 10^{-8}$</td>
</tr>
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<td>421</td>
<td>360.0</td>
<td>515.0</td>
<td>$4.05 \times 10^{-8}$</td>
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<tr>
<td>421</td>
<td>480.0</td>
<td>755.0</td>
<td>$3.62 \times 10^{-8}$</td>
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<tr>
<td>437</td>
<td>180.0</td>
<td>219.0</td>
<td>$5.18 \times 10^{-3}$</td>
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<tr>
<td>437</td>
<td>240.0</td>
<td>306.0</td>
<td>$4.60 \times 10^{-3}$</td>
</tr>
<tr>
<td>437</td>
<td>300.0</td>
<td>420.0</td>
<td>$4.63 \times 10^{-3}$</td>
</tr>
<tr>
<td>450</td>
<td>180.0</td>
<td>234.0</td>
<td>$6.60 \times 10^{-3}$</td>
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<tr>
<td>450</td>
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<tr>
<td>450</td>
<td>300.0</td>
<td>474.0</td>
<td>$5.60 \times 10^{-8}$</td>
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CHAPTER V

CONCLUSIONS

I. AGREEMENT OF THEORY AND EXPERIMENT

Plate 19 shows a plot of the helium pump-out data for $416^0$ superimposed on the theoretical curve. A vertical scale factor was chosen so that the observed maximum of 2.95 volts corresponds with 0.5 which is the theoretical maximum. Plate 20 shows the agreement between theory and experiment in the pump-in case. No attempt was made to match maximum values here. A vertical scale factor was chosen to match 2.80 volts with 1. The 2.8 value gave the best fit in the logarithmic plot (see plate 11), and was retained for this graph.

The close overall agreement between theory and experiment indicates that the flow process occurring is very nearly one of pure diffusion. The shape or position of the theoretical curve is not too sensitive to changes in the value of the diffusion constant.

The value of the diffusion constant to give the best fit is different in the two cases; being $4.31 \times 10^{-6}$ for the pump-out curve and $4.11 \times 10^{-6}$ for the pump-in curve.
This may be indicative of some structural change in the glass under pressure. In the pump-in case there is a pressure gradient across the glass which is not present after pump-out. At the beginning of a pump-out run, the peak height is observed to increase slightly over the pump-in steady state value. This effect is more noticeable with neon than with helium. (See plate 16.) The temperature also increases slightly. At first it was thought that this was due to the removal of convection currents in the cell at pump-out and that the increase in peak height was due to this temperature change. The peak height is observed to increase however, even when the temperature is maintained at a constant value by reducing the voltage on the nichrome furnace.

Deviations exist in the long time region of the pump-out curves. The semi-log plots are observed to curve to the right of the expected straight line after the peak height has decayed by a factor of 100. This is probably due to gas sticking in the mass spectrometer.

A similar situation also exists in the initial stages of the pump-in process. During a pump-in run
the pressure in the mass spectrometer increases from $10^{-7}$ mm to $10^{-5}$ mm as indicated on a Veeco ionization gauge. In the initial stages of a run, the pressure is at a steady state determined by the parameters of the system, and the net pumping rate is zero. As gas is admitted to the system, the pressure increases and so does the pumping rate. This competition between the pumping and diffusing processes may be responsible for the apparent increase in the diffusion constant with time as calculated by the ratio method.

II. COMPARISON OF THE TWO METHODS

The diffusion constants are more easily obtained from the pump-out data than from the pump-in data. The constants as calculated in the long time region of the pump-in curves agree fairly well with those obtained by the pump-out method. The errors involved in both methods are probably large, for the data-reduction methods already indicated. Fitting the experimental data to the theoretical curves probably yields the best values for the diffusion constants, but the labor involved is large. The sizable variations in $D$ encountered with the ratio method may be due to any or all of the following:

1. Errors in the interpolation graph (plate 14) due to too widely spaced points (table I).
(2) Gas sticking in the spectrometer. In this case the instrument tends initially to integrate the diffusion curve.

(3) A thin spot in the diffusion cell which initially allows too much gas through the system. This would not affect the pump-out data, and is not a probable cause since the observed effect is too large.

Changes in the value of $D$ change the horizontal scale factor and hence the slope of the curve. As seen on plate 20, the curves tend to converge for values of $z$ less than 1. ($z$ is equal to $985 D t$.) Changes in $D$ in this region do not show up well on a graph of this size.

In that the curves used in the ratio method were prepared with some care, it is difficult to attribute more than about a 20% error to calculations at $z = 0.3$ and 5% at $z = 1$. 

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III. EXPERIMENTAL ERRORS

The largest systematic error is due to poor temperature control. Temperature changes have two effects on the data. A sudden shift in the temperature of short duration tends to immediately raise or lower the observed peak height. If the temperature is quickly corrected, the peak height returns to its proper place. A temperature change which persists for a longer period of time tends to change the internal diffusion rate, and this shows up at a later time as a shift in the peak height from the expected value. In the case of neon, fluctuations showed up several hours after they had occurred. The system apparently integrates out temperature changes.

Runs at 320° and 349° were repeated, after the system was heated to 450° overnight, in order to determine whether or not the diffusion rate depended on thermal history. The values of D obtained were in good agreement with one another. If a thermal hysteresis effect exists, then it is small, or disappears in the four hours needed to reach thermal equilibrium.
**IV. ACTIVATION ENERGIES**

A mathematical analysis of diffusion as a transport process predicts that the diffusion constants should be functions of temperature (3).

\[
D = D_0 e^{-E/RT}
\]

\(E\) is called the activation energy, \(T\) is the absolute temperature, \(R\) is the molar gas constant. Plates 21 and 22 show a plot of \(\log D\) versus \(1/T\). The values for \(E\) and \(D_0\) are as follows:

<table>
<thead>
<tr>
<th></th>
<th>(E)</th>
<th>(D_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He-pump-out</td>
<td>(7.13 \times 10^3) cal/mole</td>
<td>(7.5 \times 10^{-4}) cm(^2)/sec</td>
</tr>
<tr>
<td>He-pump-in</td>
<td>(6.94 \times 10^3) cal/mole</td>
<td>(6.76 \times 10^{-4}) cm(^2)/sec</td>
</tr>
<tr>
<td>He-pump-out</td>
<td>(2.0 \times 10^4) cal/mole</td>
<td>(6.7 \times 10^{-2}) cm(^2)/sec</td>
</tr>
<tr>
<td>He-pump-in</td>
<td>(1.54 \times 10^4) cal/mole</td>
<td>(1.8 \times 10^{-3}) cm(^2)/sec</td>
</tr>
</tbody>
</table>

The smallest values of \(D\) were used in the pump-in plots. The other values of \(D\) tend to line up with one another provided that they all correspond to the same value of \(s\), i.e. \(98.5^\circ\) or \(s\) is constant. The lines are roughly parallel, indicating that the activation energy does not change during a pump-in run, and that the ratio method is at least self-consistent. The neon pump-in constants given above are of questionable value, but they are included for comparison.
The helium constants compare favorably with those obtained by Hayden and Wehrenberg (2). They obtained values of $7.1 \times 10^3$ cal/mole for $E$ and $7.7 \times 10^{-4}$ cm$^2$/sec for $D_0$ using the pump-out method. Rogers et al. (1) obtained values of $6.5 \times 10^3$ cal/mole for $E$ and $4.8 \times 10^{-4}$ cm$^2$/sec for $D_0$. The work of Rogers et al. was done at a lower temperature.

V. ADDITIONAL RESEARCH

The mass spectrometer seems to be a useful instrument for diffusion studies. Data analysis has posed a more serious problem than instrumentation, and the full potentiality of the instrument was not realized in this study. The construction of more accurate tables and graphs for the pump-in and pump-out functions and the use of a standard leak in the spectrometer should show whether or not the diffusion coefficients are time dependent. Studies should also be made with different samples of glass to determine whether composition has a significant effect on the diffusion rates. The effects of pressure should also be studied.

During a pump-in run, the water vapor peak is observed to grow at a rapid rate and exceeds the
amplitude of the diffusing gas at steady state. It is a question, whether this water is due to out-gasing in the spectrometer or is torn from the glass by the diffusing gas. Studies on the diffusion of water vapor and deuterium oxide would answer this question.

The diffusion of hydrogen should be quite rapid and hence feasibly studied with the mass spectrometer.

Steady state flow rates should be obtained, from which the solubility of the gas in the glass can be calculated if the diffusion constant is known. The concentration of the gas in the glass can be obtained by integrating the pump-out curve. It would be interesting to see how these compare.

A mixture of neon and helium each having a partial pressure of 30 cm was run in order to determine whether the gases diffuse independently. No conclusive data was obtained during pump-in due to the large differences in diffusion rate. The helium pump-out rate was not changed by the presence of neon in the glass. The neon peak at pump-out was about half its steady state value. The experiment should be repeated with gases having more nearly the same diffusion rates.
PLATE 21 HELIUM ACTIVATION ENERGY
PLATE 22 NEON ACTIVATION ENERGY

$\log (D \times 10^8)$ vs. $\frac{1}{T}$

- $\circ$ = pump out
- $\bullet$ = pump in
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