range of applicability of these approximations can be estimated from the results illustrated in Figures 8 and 9.

NOTATION

a = radius of sphere
B = $k\delta/k'a$
C = heat capacity
$f_i\{z\}$ = function of z defined by Equations (13a) and (13b)
$f_s\{z\}$ = function of z defined by Equations (3a) and (3b)
g = acceleration due to gravity
h = heat transfer coefficient
k = thermal conductivity
K = thermal diffusivity = $k/\rho C$
L = latent heat of solidification
n = any integer
R = $C_f(T_f - T_s)/L$
q = heat flux density
t = time
T = temperature
u = velocity
V = $k\sqrt{K_f}(T_o - T_f)/k_f\sqrt{\pi K}(T_f - T_s)$
x = distance
ΔT = $T_s - T_o$

Greek Letters

α = $(\sigma - 1)/(\sigma + 1)$
β = volumetric coefficient of expansion
ν = kinematic viscosity
δ = thickness of insulation
λ = coefficient defined by Equation (22)
σ = $\sqrt{k\rho C/k'\rho' C'}$
$\Phi(x)$ = e^{z^2} erfc z
ρ = density

Subscripts

i = interface
f = of frozen materials, or freezing front
o = initial
s = surface
u = of unfrozen material

Superscripts

$(')$ = insulation

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Significance of Pressure Gradients in Porous Materials:

Part I. Diffusion and Flow in Fine Capillaries

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Equations are derived for the effect of a total pressure gradient on flow and diffusion of a binary gas system in a fine capillary. The results apply over the pressure and pore radius regimes from Knudsen flow to Poiseuille flow.

Application of the equations to a pure component leads to an expression for the permeability which predicts the observed minimum flow in the slip-flow region. This expression agrees well with Knudsen's data for carbon dioxide and for new measurements for nitrogen in a glass capillary (radius = 0.01244 cm.).

Gaseous diffusion in porous media at constant pressure has been explained effectively in recent years (*2, 7, 8*). The development applies when both Knudsen and bulk diffusion are significant, a situation of common occurrence in porous catalysts. In some applications diffusion with a pressure gradient is also of interest. For example, in a gas-solid catalytic reaction for which there is a change in number of moles, a pressure difference will exist along the catalyst pores. Evans, Watson, and Mason (*3*) have used a dusty-gas model successfully to treat the diffusion problem with variable pressure. These authors also proposed two methods of relating the flow to the pressure gradient: an extension of the dusty-gas model, and application of the equation of motion.

The purpose of Part I of this paper is to show that an equation with no disposable constants can be derived for

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a single capillary. When this result is applied to a pure component, an expression is obtained for the permeability which may be employed over the complete range of flow from Knudsen to Poiseuille. This result predicts the minimum in the flow observed originally by Knudsen. Then in Part II the single-capillary equation is adapted to porous media and applied for either pure component or binary systems by introducing a model of the pore structure.

EQUATIONS FOR FLOW AND DIFFUSION IN A CAPILLARY

The binary gas mixture in the cylindrical pore is assumed to be at constant temperature and to behave as an ideal gas system. At constant pressure, the diffusion flux N_A° of component A is (2, 7, 8)

$$N_A^{\circ} = \frac{-D_{AB}\dfrac{dC_A}{dx} + (N_A^{\circ} + N_B^{\circ})y_A}{1 + \dfrac{D_{AB}}{D_{KA}}} \tag{1}$$

Similarly, the constant pressure, diffusion flux for component B is given by

$$N_B^{\circ} = \frac{-D_{AB}\dfrac{dC_B}{dx} + (N_A^{\circ} + N_B^{\circ})y_B}{1 + \dfrac{D_{AB}}{D_{KB}}} \tag{2}$$

where the Knudsen diffusivity is defined in terms of the pore radius a and the mean molecular speed $\bar{v}$ as follows:

$$D_{KA} = \frac{2}{3}\bar{v}_A a \tag{3}$$

$$\bar{v}_A = \left(\frac{8RT}{\pi M_A}\right)^{1/2} \tag{4}$$

At a fixed pressure, the total concentration $C_A + C_B$ is constant. Hence, Equations (1) and (2) can be added to give the following well-known relationship between the diffusion rates:

$$-\frac{N_B^{\circ}}{N_A^{\circ}} = m = \left(\frac{M_A}{M_B}\right)^{1/2} = \frac{D_{KB}}{D_{KA}} \tag{5}$$

If there is a pressure gradient along the pore length x, there will be a flow contribution F to the mass fluxes N_A and N_B. Hence

$$N_A + N_B = N_A^{\circ} + N_B^{\circ} + F \tag{6}$$

Evans and colleagues have shown (2) that the flux N_A with a pressure gradient can still be represented by Equation (1), provided the effect of pressure on D_{AB} is taken into account. Then

$$N_A = \frac{-D_{AB}\dfrac{dC_A}{dx} + (N_A + N_B)y_A}{1 + \dfrac{D_{AB}}{D_{KA}}} \tag{7}$$

Combining Equations (1), (5), and (6) to obtain an expression for $N_A + N_B$, and substituting the result into Equation (7), one gets

$$N_A = \frac{-D_{AB}\dfrac{dC_A}{dx}}{1 - (1-m)y_A + \dfrac{D_{AB}}{D_{KA}}} + \frac{Fy_A}{1 + \dfrac{D_{AB}}{D_{KA}}} \tag{8}$$

The analogous equation for N_B is

$$N_B = \frac{-D_{AB}\dfrac{dC_B}{dx}}{1 - \left(1 - \dfrac{1}{m}\right)y_B + \dfrac{D_{AB}}{D_{KB}}} + \frac{Fy_B}{1 + \dfrac{D_{AB}}{D_{KB}}} \tag{9}$$

or

$$N_B = \frac{-D_{AB}m\dfrac{dC_B}{dx}}{1 - (1-m)y_A + \dfrac{D_{AB}}{D_{KA}}} + \frac{Fy_B}{1 + \dfrac{D_{AB}}{D_{KB}}} \tag{10}$$

Addition of mN_A and N_B from Equations (8) and (10), and noting that $C_A + C_B = P/RT$, gives

$$mN_A + N_B = \frac{-\dfrac{D_{AB}}{RT}m\dfrac{dP}{dx}}{1 - (1-m)y_A + \dfrac{D_{AB}}{D_{KA}}} + F\left[\frac{my_A}{1 + \dfrac{D_{AB}}{D_{KA}}} + \frac{y_B}{1 + \dfrac{D_{AB}}{D_{KB}}}\right] \tag{11}$$

The expression for flow in the low pressure, or small pore, regions must include a contribution due to slip at the wall. Scott and Dullien (9) by using modern kinetic theory concepts derive the slip flow term as

$$F_{sl} = -\frac{4a}{3M\bar{v}}\frac{dP}{dx} \tag{12}$$

The evaluation of the slip term in a binary gas is somewhat ambiguous. However it appears that little error will be introduced by supposing that

$$M\bar{v} = M_A\bar{v}_A y_A + M_B\bar{v}_B y_B \tag{13}$$

If Equations (12) and (13) are combined, and the Poiseuille contribution is included, the total flow F is

$$F = -\left[\underset{\text{Poiseuille}}{\frac{a^2P}{8\mu}} + \underset{\text{Slip}}{\frac{4a\,RT}{3(M_A\bar{v}_A y_A + M_B\bar{v}_B y_B)}}\right]\frac{1}{RT}\frac{dP}{dx} \tag{14}$$

Equation (14) can be expressed in terms of the Knudsen diffusivities by employing Equations (3) and (4). If this is done, and F from Equation (14) is substituted into Equation (11), then

$$m\,N_A + N_B = -\frac{C}{RT}\frac{dP}{dx} \tag{15}$$

$$C = \frac{mD_{KA}}{1 + [1-(1-m)y_A]\dfrac{D_{KA}}{D_{AB}}} + \left[\frac{a^2P}{8\mu} + \frac{D_{KA}\pi}{4[y_A + (1-y_A)/m]}\right]\left[\frac{my_A}{1 + \dfrac{D_{AB}}{D_{KA}}} + \frac{1-y_A}{1 + \dfrac{D_{AB}}{D_{KB}}}\right] \tag{16}$$

Equations (15) and (16) constitute the desired solution for flow and diffusion in terms of the pressure drop, the pore radius, the composition, and the diffusivities. The limiting forms are of interest. For a very small capillary, D_{AB}/D_{KA} and D_{AB}/D_{KB} both approach infinity. Equation (16) becomes

$$C = m\,D_{KA} \tag{17}$$

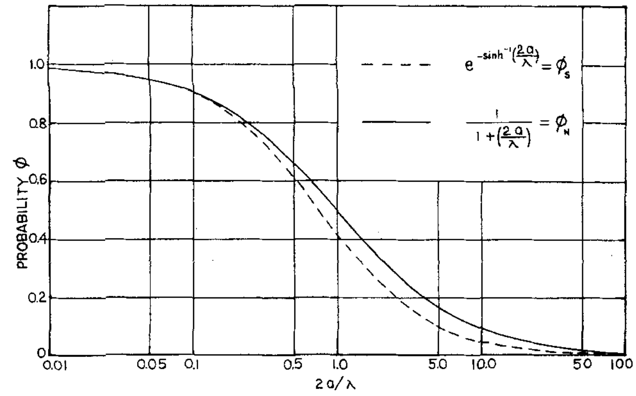

Fig. 1. Comparison of probability functions.

and Knudsen flow results. When the pore radius is of the order of 100 Å and the pressure is not extreme, common conditions in catalyst pores, no term in Equation (16) can be neglected. For very large pores, D_{AB}/D_{KA} and D_{AB}/D_{KB} approach zero, and the slip flow contribution is negligible with respect to Poiseuille flow. Then Equation (16) takes the form

$$C = \frac{a^2 P}{8\mu}\,(m y_A + y_B) \tag{18}$$

To test Equations (15) and (16) completely would require experimental data for combined flow and diffusion in a single capillary. A search for this type of information was not successful. However, Knudsen's data (*5*) for flow of a pure component can be compared with the appropriate special form of Equations (15) and (16). To obtain further data, new measurements are reported for nitrogen flow in a fine, glass capillary. These results are presented in the following sections.

PERMEABILITY IN PORES

For a pure component, $y_B = 0$, $y_A = 1$, $N_B = 0$, and $m = 1$. Then Equations (15) and (16) reduce to

$$N_A = -\frac{C}{RT}\frac{dP}{dx} \tag{19}$$

$$C = \underbrace{\left(\frac{1}{1+\frac{D_{KA}}{D_{AA}}}\right) D_{KA}}_{\text{(Knudsen flow)}} + \left(\frac{1}{1+\frac{D_{AA}}{D_{KA}}}\right) \times \left[\underbrace{\frac{\pi D_{KA}}{4}}_{\left(\begin{smallmatrix}\text{slip}\\ \text{flow}\end{smallmatrix}\right)} + \underbrace{\frac{a^2 P}{8\mu}}_{\left(\begin{smallmatrix}\text{Poiseuille}\\ \text{flow}\end{smallmatrix}\right)}\right] \tag{20}$$

In these expressions C becomes identical with the permeability, and Equation (20) indicates that C is the total of separate contributions due to Knudsen flow, slip flow, and Poiseuille flow.

Before comparison with experimental data, it is informative to consider the physical significance of the terms in parentheses in Equation (20). The path of a molecule in a tube is interrupted either by collision with the tube wall or with another molecule. Let the probability of collisions with the wall be Φ_N, that is

$$\Phi_N = \frac{\text{wall collision frequency}}{\text{total collision frequency}} \tag{21}$$

With this concept the total flux through the tube is

$$N_A = \Phi_N\ (\text{Knudsen flow}) + (1-\Phi_N)\,(\text{flow}) \tag{22}$$

Comparison of Equations (19) and (20) with Equation (22) shows that

$$\Phi_N = \frac{1}{1+\frac{D_{KA}}{D_{AA}}} \tag{23}$$

and

$$1-\Phi_N = \frac{1}{1+\frac{D_{AA}}{D_{KA}}} \tag{24}$$

Hence the coefficients of Equation (20) refer to the probability of wall or intermolecular collisions. Bosanquet (*1*) arrived at the same probability expressions from an approximate analysis of diffusion in the region where both bulk and Knudsen processes are significant. Pollard and Present (*6*), again in an approximate treatment for diffusion, obtained a probability function very nearly the same as that defined by Equation (23).

Saphus Weber (*10*) developed from pure component considerations an expression for the total flow through capillaries. Expressed in terms of the permeability his result differed from Equation (20) in that the coefficient of the Poiseuille flow term was taken as unity rather than $(1 + D_{AA}/D_{KA})^{-1}$.

Scott and Dullien (*9*) derived an approximate expression similar to Equation (20) by applying the kinetic theory. Their equations were derived by supposing the molecules to be hard spheres. With this assumption, the results could be expressed in terms of a mean free path λ. Also for hard spheres $D_{AA} = (1/3)\,\overline{v}_A\,\lambda$. Then when one uses Equation (3) for D_{KA}, the ratio of the diffusivities is

$$\frac{D_{KA}}{D_{AA}} = \frac{2a}{\lambda} \tag{25}$$

If Equation (25) is substituted in Equation (20), the result is the same as that of Scott and Dullien except for a different probability function. Their function Φ_s is

$$\Phi_s = \exp\left[-\sinh^{-1}\frac{2a}{\lambda}\right] \tag{26}$$

These authors considered Φ_s to be the probability for a molecule to suffer two wall collisions without an intermediate molecular collision. Thus Φ_s would be expected to be less than Φ_N defined by Equation (21). Actually the difference is not very large as shown in Figure 1, where the two functions are plotted vs. $2a/\lambda$. The function proposed by Pollard and Present (*6*), while not shown in the figure, essentially coincides with the curve for Φ_N.

One can now compare the Scott and Dullien development with Equation (20) on a consistent basis by evaluating Φ_N from Equations (23) and (25) and Φ_s from Equation (26).

For this purpose use the experiments of Knudsen (*5*) for flow of carbon dioxide in capillary number 4. This consisted of twenty-four parallel tubes ($a = 0.00333$ cm.) about 2 cm. in length. These data were taken at about 25°C., where the viscosity is 1.52×10^{-4} poises. The integrated form of Equation (19) over a pore length L, when the pressure drop ΔP is small with respect to P, is

$$N_A = \frac{\Delta P}{RTL}\left[\Phi\, D_{KA} + (1-\Phi)\left(\frac{\pi D_{KA}}{4} + \frac{a^2 P}{8\mu}\right)\right] \tag{27}$$

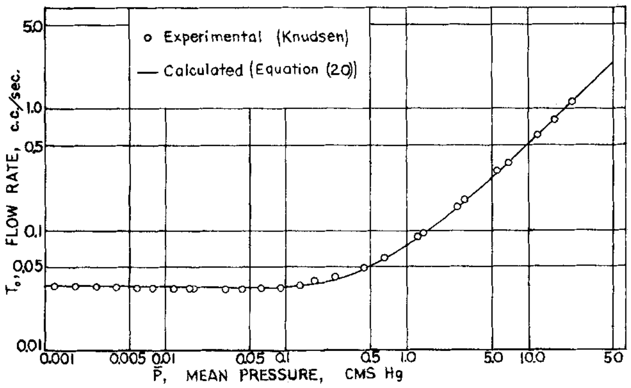

Fig. 2. Comparison of calculated and experimental flow rates for carbon dioxide in a glass capillary, experimental data from Knudsen.

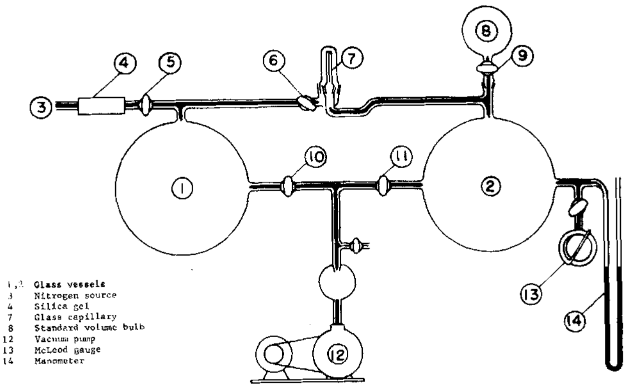

Fig. 4. Apparatus for capillary flow measurements.

Here $\bar{P}$ is the arithmetic mean value. Knudsen reports data for the total flow rate in twenty-four tubes in the form

$$T_o = \frac{N_A(24\pi a^2)}{\Delta P} RT, \text{ cc./sec.} \qquad (28)$$

Combining Equations (27) and (28) one gets

$$T_o = \frac{24\pi a^2}{L}\left[D_{KA}\Phi + (1-\Phi)\left(\frac{\pi D_{KA}}{4} + \frac{a^2\bar{P}}{8\mu}\right)\right] \qquad (29)$$

This equation represents the Scott and Dullien derivation if $\Phi = \Phi_s$, and the theory of this paper if $\Phi = \Phi_N$, where

$$\Phi_N = \frac{1}{1+\dfrac{2a}{\lambda}} \qquad (30)$$

The mean free path of carbon dioxide at 1 atm. pressure and 25°C. is taken as 447 Å, based upon $\lambda = 419$ Å at 15°C. (*4*). At other pressures λ is supposed to be inversely proportional to pressure.

Figure 2 shows the data of Knudsen and the curve calculated from Equation (29) with either Φ_N or Φ_s used. Differences between the two probability functions are not apparent in this large-range figure. In the lower part of Figure 3 the data and calculated curves are for the low-pressure region. Here the small differences between calculated values of T_o with Φ_N and Φ_s used are evident. Both methods and the data show a minimum in the flow vs. pressure curve. Knudsen's data (Figure 3) indicate that the minimum occurs at $\bar{P} = 0.035$ to 0.040 cm. Hg. Differentiation of Equation (29) with either Φ_N or Φ_s used predicts a minimum at $a/\lambda = 0.49$, which corresponds to $\bar{P} = 0.050$ cm. Hg for this particular case of carbon dioxide at 25°C. and $a = 0.00333$ cm.

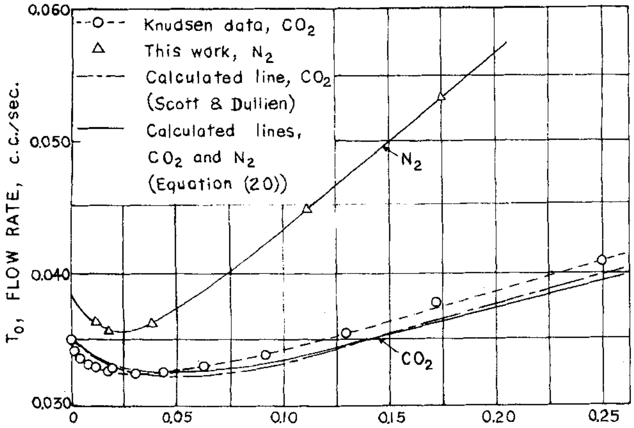

Fig. 3. Comparison of calculated and experimental flow rates for carbon dioxide and nitrogen in glass capillaries, low-pressure range.

As a further test of the prediction method, the flow of nitrogen through a glass capillary was measured at 23.5°C. In Figure 4 the capillary (7) (radius = 0.01244 cm.) was connected to two large vessels (V_1 = 15,900 cc., V_2 = 14,500 cc.). The method, similar to that employed by Knudsen, consisted of measuring the flow rates through the capillary by a mass balance of nitrogen in the two large vessels. Pressures P_1 and P_2 in both vessels were measured at the beginning with a gauge (*13*) or manometer (*14*). Then the change in pressure of vessel number 2 with time (a slow process) is followed with the gauge. From these data both the flow rate and pressure in vessel number 1 are calculated by a mass balance. The data are shown in Table 1.

Equation (20) was used to calculate the flow of nitrogen in this capillary, and the results are compared with the experimental data in the upper part of Figure 3.

These comparisons in Figure 3 suggest that a satisfactory permeability expression can be derived from diffusion considerations. Furthermore, it is seen that the diffusion equation is identical with the Scott and Dullien result based upon kinetic theory, except for small differences in the probability functions. The deviation of Equation (29) (with either Φ_N or Φ_s used) from Knudsen's data is not more than 3%. At very low pressures this divergence may be due in part to the use of an arithmetic mean pressure

TABLE 1. NITROGEN FLOW DATA

Capillary radius = 0.01244 cm., length = 4.96 cm.
Temperature = 23.5°C.
Viscosity = 1.78×10^{-4} g./(cm.)(sec.)
Mean free path = 654Å. at 1 atm.

Pressure, cm. Hg			
Vessel number 1, P_1	Vessel number 2, P_2	$\bar{P}$	T_o, cc./(sec.)
0.0192	0.00305	0.0111	0.0366
0.0312	0.00419	0.0177	0.0355
0.0690	0.00641	0.0377	0.0364
0.202	0.0218	0.112	0.0448
0.295	0.0568	0.176	0.0536

in Equation (29). This cannot be true as $\overline{P}$ approaches zero, for then ΔP is not negligible with respect to P.

SUMMARY

The method developed for calculating flow and diffusion for a binary system contains no arbitrary constants when applied to a single capillary. For the special case of a pure component system, agreement between experimental and predicted results is good. To apply the method to porous media requires a model of the pore structure. This problem is taken up in Part II.

ACKNOWLEDGMENT

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NOTATION

a = radius of cylindrical capillary or pore, cm.
C_A = concentration of component A, g. moles/cc.
C = flow parameter for a single capillary, defined by Equation (15), sq.cm./sec.
D_{AB} = bulk diffusivity in binary gas mixture A-B, sq. cm./sec.
D_{KA} = Knudsen diffusivity of gas A, sq.cm./sec.
F = flux due to a pressure difference, g. moles/(sec.)(sq.cm.); F_{sf} = slip flow contribution
M = molecular weight
m = $(M_A/M_B)^{1/2}$
N_A = flux of component A, g. moles/(sec.)(sq.cm.)
N_A° = diffusion flux of A, that is flux of A under constant pressure diffusion conditions, g. moles/(sec.)(sq.cm.)
P = total pressure, dynes/(sq. cm.)
R = gas constant, dyne (cm.)/(g. mole)(°K.)
T = temperature, °K.
T_o = flow rate per unit pressure drop, defined by Equation (28), cc./sec.
$\overline{v}$ = mean molecular speed, cm./sec.
x = distance in direction of diffusion, cm.
y = mole fraction of gas
Φ = probability of a molecule to be in Knudsen flow; Φ_s is defined by Equation (26), Φ_N by Equation (23)
μ = gas viscosity, poises
λ = mean free path, cm.

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Part II. Diffusion and Flow in Porous Catalysts

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Diffusion and flow rates through porous catalysts were measured under the conditions of finite pressure gradients for single- and two-component systems. For large pore (low density) alumina pellets the diffusion rate counter to the pressure gradient was severely depressed, while for small pore Vycor the pressure gradient had little effect.

The equations developed in Part I for flow and diffusion in a single capillary were extended to porous catalysts. The resulting prediction methods contain no parameters which require transport data for their evaluation, but pore size and void fraction information is needed. For the catalysts investigated, both the permeability and diffusion rates varied several thousand-fold. The calculated results predict the same extensive range and show the same effects of pressure gradient and pore properties. Also the quantitative agreement between calculated and experimental results is such that the theory provides a useful method of predicting transport rates through certain types of porous media.

The objective of this part of the paper is the measurement of diffusion rates, both counter to and in the direction of enforced pressure gradients, through typical porous catalysts. Also consideration is given to the prediction of diffusion and flow rates from easily measured, geometrical properties of the catalysts. In Part I equations were derived for a single capillary so that the objective here is to adapt the results to porous materials typical of solid catalysts. A random pore concept has been used (*4*) to treat the constant pressure case. The same model will be used in this part for diffusion and flow with a pressure gradient. The treatment is restricted to an isothermal binary system of gases A and B. The authors consider a pellet of thickness L across which diffusion and flow occur in one dimension. One face is exposed to gas A at a constant pressure P_1 and the other to B at a lower, constant pressure P_2. The problem is to determine the molal fluxes of A and B.

Flow of pure A through the same pellets was also measured and predicted by adapting the permeability equations of Part I.

EXPERIMENTAL METHOD AND APPARATUS

The permeability measurements were made with nitrogen supplied to both sides of the pellet chamber (8) as shown in Figure 1. For diffusion studies nitrogen and hydrogen were chosen to avoid surface effects and to utilize the large diffusivity of hydrogen. The apparatus was operated at pressures from