r = local radius, cm.
r^{+} = reduced radius (r/R), dimensionless
R = Boltzman constant (cal./mole/°K.) or pipe radius (cm.)
$\dot{S}$ = strain rate, $-du/dx$ ($-du/dr$ for tube flow), sec.$^{-1}$
T = absolute temperature, °K.
T^{+} = reduced temperature, $(T - T_i)/(T_R - T_i)$, dimensionless
u = local velocity, cm. sec.$^{-1}$
w = mass flow rate, g. sec.$^{-1}$
z = axial coordinate, cm.
z^{+} = $N_{Gz}{}^{-1}$, $z\,k/w\,C$

Greek Letters

$\Delta H^{\ddagger}/R$ = constant in Equation (1), °K. [$\Delta H^{\ddagger}$ is interpreted (*11*) to be the activation energy for flow]
π = 3.1416
ρ = density, g. cm.$^{-3}$
τ = shear stress, dynes cm.$^{-2}$ (momentum flux)
$\Psi(H)$ = $(\Delta H^{\ddagger}/R)(1/T_i - 1/T_R)$, dimensionless

Subscripts

i = inlet
iso = isothermal
niso = nonisothermal
o = outlet
R = wall

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Mass Transport in Porous Materials under Combined Gradients of Composition and Pressure

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An expression is derived for the analysis of gas-phase mass transport in porous media in the presence of gradients in pressure and mole fraction. The behavior of porous media is contrasted with that of capillary tubes. A continuous-flow diffusion and permeation apparatus was employed for studies of mass transport in a fritted glass diaphragm. Measurements were obtained at varying levels of pressure and cover both isobaric binary diffusion and the permeation of pure gases and gas mixtures. These experimental results and previous data obtained by Hewitt and Sharratt and by Mason, *et al.* bear out the form of the equation and successfully provide independent checks of the three constants necessary to characterize a given porous medium.

Gas-phase mass-transport phenomena in porous media are only partly understood for the situation in which mutual diffusion, Knudsen diffusion, and hydrodynamic flow all occur simultaneously. Nevertheless, these phenomena are important factors in the design of isotope separation equipment and nuclear reactors (*12, 13, 22, 23*), in predicting reaction rates in many catalysts (*38, 39*), and in the drying of porous materials (*18, 30, 44, 45*).

The study of transition-region diffusion in porous media can be divided into three major areas:

1. Purely diffusional mechanisms (isobaric conditions).
2. Combined diffusion and hydrodynamic flow (nonisobaric conditions).
3. Special phenomena such as surface flow, electro-osmosis, etc.

Equations for isobaric diffusion have been derived by Scott and Dullien (*48*) and by Evans, Watson, and Mason (*14*). These relationships, which will be discussed later, have been verified experimentally as well (*21, 48*).

Nonisobaric mass transfer is considerably more complicated. A total pressure gradient superimposes Newtonian flow upon diffusion whenever the mean pore diameter of a porous body is comparable in size to or larger than the mean free path length of a gaseous mixture within that body. This situation, where Newtonian flow, Knudsen diffusion, and mutual diffusion all occur simultaneously, is the subject of this paper. The additional complications which are presented by surface diffusion or other special phenomena are not dealt with here.

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The structures of most porous bodies cannot be represented by simple mathematical functions; therefore, a model is normally adopted for the derivation of mass transfer relationships. For transition-region diffusion one of two models is generally used, the capillary model or the dusty gas model.

CAPILLARY MODEL

The first model, which treats porous media as a bundle of long capillaries, has yielded a number of useful results, and has played an important part in the development of the theory of mass transport in porous materials (*40, 48*). Nevertheless, the capillary model has always been recognized as not being completely realistic. A discussion of the limitations of this model has been given by Scheidegger (*46*). Other pertinent criticisms have been given by Fatt (*17*) and Wiggs (*54*).

It is important to recognize that the flow of a pure gas is most porous media differs qualitatively as well as quantitatively from flow in a bundle of capillaries. A plot of the ratio of the molar flux to the pressure gradient, $N/(dP/dL)$, vs. pressure always exhibits a curve with a minimum at some finite low pressure for long capillaries (*32*). A similar plot for most porous materials yields a straight line (*1, 5*). Mathematical formulations have been given which predict the existence of this minimum in the permeability vs. pressure relationship for long capillaries (*25, 40*). A simple physical description of the cause of this difference between capillary tubes and most porous media is suggested in the following paragraphs.

In the Knudsen flow regime only a very small fraction of the molecules entering a long capillary emerge from the opposite end; most exit from the end they entered. The fraction passing through is given by $4d/3L$. Molecules entering with flight paths nearly parallel to the axis of the tube have a higher probability of passing through than those with other flight paths; all molecules entering in the exact direction of the axis pass through without striking the wall. Consequently molecules with relatively long flight paths contribute a large fraction to the actual flux, even though they represent only a small fraction of the total molecules present.

As the pressure is increased to the point where the number of intermolecular collisions rivals the number of wall collisions, the number of long-flight-path molecules passing through decreases exponentially with pressure as these molecules are deflected toward the walls by collisions with other molecules. This effect causes the molar flux per unit pressure gradient to decrease with increasing pressure, before increasing again at higher pressures because of the advent of Poiseuille or viscous flow.

Because of the tortuous flow paths in common porous materials there is no possibility for a flight path between wall collisions to be more than a few pore diameters long. Therefore the Knudsen permeability is not controlled by very long flight paths, and there is no mechanism present to cause a minimum permeability at pressures where wall collisions and intermolecular collisions are both important.

This conclusion is not dependent upon the distribution of pore sizes present in porous media. Permeabilities made up of transport through capillaries of various diameters will show a minimum value at some pressure if the fluxes through the individual capillaries each show a minimum. Calculations have been made for various distributions of capillary diameters using Knudsen's semiempirical equation for flow in a capillary at low pressures (*32*). Results for capillaries of uniform diameter, for an equal probability of capillary diameters from zero to the maximum, and for a polynomial approximation to a normal distribution all show that the minimum value of $N/(dP/dL)$ is 95% of the value at very low pressures.

As a consequence of this inherent qualitative difference in the flux of pure gases in the two types of media, the model of a bundle of long capillaries cannot successfully reproduce the transition region flow behavior of most porous materials.

DUSTY GAS MODEL

The dusty gas model of porous media does not possess the disadvantage raised in the foregoing discussion. This model treats the porous medium as a collection of large dust particles. If these dust particles are considered to be giant molecules, the desired transport equations for a binary gas mixture diffusing through a porous body can be deduced by considering the entire system to be a ternary mixture composed of the binary components and the dust molecules. The following conditions are imposed on the system in order that the porous medium (the dust) be isotropic and stationary in space:

$$N_D = 0; \qquad \frac{dC_D}{dx} = 0$$

This type of model was first proposed by Deriaguin (*8* to *10*), who solved the Maxwell-Boltzmann equation in order to obtain numerical expressions for the effective diffusivities in terms of the properties of the dust molecules. This procedure is very complex and is valid only for dilute dusty gases, that is, very porous solids such as steel wool. Although this or equivalent procedures have been used by others (*3, 33, 34*), the method of Evans, Watson, and Mason (*14, 15*) is much simpler to use. This latter approach, however, only yields flux equations in terms of effective diffusivities. The numerical values of these parameters must be determined experimentally. This situation, however, circumvents the virtually impossible task of characterizing the porous structure exactly by means of mathematical functions.

Since the Maxwell-Boltzmann equation is valid only for dilute gases, it might be supposed that the dusty gas model, which is based on this equation, should fail for most types of porous media, which are usually very dense. This is not necessarily true, however, because the only dense component is the dust, which is constrained by boundary conditions to a zero net diffusion rate. The diffusing components behave as dilute gases both in their interactions with each other and in their interactions with the dust particles.

PAST ANALYSES

Scott and Dullien (*48*) and Evans, Watson, and Mason (*14*) have derived identical equations for isobaric transition region diffusion. For the binary case these may be written*

$$\vec{N}_A = -\frac{c_2 D_{AB} K_A}{(K_A + c_2 D_{AB})RT}\nabla P_A + \frac{y_A K_A}{K_A + c_2 D_{AB}}(\vec{N}_A + \vec{N}_B) \quad (1)$$

$$\vec{N}_B = -\frac{c_2 D_{AB} K_B}{(K_B + c_2 D_{AB})RT}\nabla P_B + \frac{y_B K_B}{K_B + c_2 D_{AB}}(\vec{N}_A + \vec{N}_B) \quad (2)$$

---

* Limiting forms of Equations (1) and (2) have been derived previously by Bosanquet (*2*), Present and Bethune (*41*), and Pollard and Present (*40*).

The coefficients c_1 (in K_A and K_B) and c_2 are effectiveness factors for the porous medium. They are geometric factors which are functions of the structure of the porous body but are independent of the diffusing fluids. c_2 is dimensionless and c_1 has dimensions of length. Very precise experiments (*55, 56*) indicate that c_1 differs slightly from one diffusing gas to another. This variation in c_1 may be neglected in most cases.

Equations (1) and (2) remain valid when a pressure difference is imposed across the system. These relationships, however, account only for diffusive fluxes and do not provide any information concerning Newtonian flow which occurs in the presence of a pressure gradient whenever the Knudsen number is of the order of 10 or less. The Knudsen number is usually defined as the ratio of the mean free path of the gas to an average pore diameter. Thus a new problem arises: How do the diffusive and hydrodynamic components of the flux interrelate? Various expressions which combine these phenomena in any one of several ways have been proposed in the literature (*11, 12, 24, 37, 53*). These studies, however, were usually directed toward specific situations in which various of the pertinent effects were small or negligible; therefore they lack generality. In addition, some of these equations do not reduce to the limiting form which has been found experimentally for pure gases in porous media.

MASS TRANSPORT EQUATION

Derivation

Equations (1) and (2) contain two unknowns, N_A and N_B. Furthermore, the effect of a total pressure gradient is not readily deduced from these relationships. By making use of the following identities:

$$P_A = y_A P \tag{3}$$

$$P_B = y_B P \tag{4}$$

$$y_A + y_B = 1 \tag{5}$$

and by solving Equations (1) through (5) simultaneously, the following result is obtained:

$$\vec{N}_A = -\frac{c_2 D^o{}_{AB}\, K_A P}{(c_2 D^o{}_{AB} + K_m P)RT}\nabla y_A - \frac{K_A(c_2 D^o{}_{AB} + K_B P)y_A}{(c_2 D^o{}_{AB} + K_m P)RT}\nabla P \tag{6}$$

The quantity $D^o{}_{AB}$ is independent of pressure and has been introduced for that reason.

Equation (6) does not contain a hydrodynamic flow term because Equations (1) and (2) account only for diffusive phenomena. Recently Mason, et al. (*36*) have shown theoretically that in the first approximation for the dusty gas model the total flux of a gas is simply the sum of the component viscous and diffusive fluxes. For a component in a gas mixture, the flux of component A due to hydrodynamic flow is given by the well known D'Arcy equation (*7, 46*):

$$\vec{N}_A\ (\text{D'Arcy}) = -\frac{c_o P y_A}{\mu_m RT}\nabla P \tag{7}$$

The constant c_o is related to the permeability of the porous material, and has units of length squared. Like the constants c_1 and c_2, c_o is independent of properties of the fluid flowing and depends only on the geometric structure of the porous body. Although Equation (7) was first formulated empirically from experimental data, it has been derived theoretically more recently from the Navier-Stokes equations (*20, 27, 28, 51*). These derivations are quite general because they do not depend on any model for the porous material.

Adding Equations (6) and (7) yields the final result:

$$\vec{N}_A = -\frac{c_2 D^o{}_{AB}\, K_A P}{(c_2 D^o{}_{AB} + K_m P)RT}\nabla y_A - \left[\frac{K_A(c_2 D^o{}_{AB} + K_B P)}{c_2 D^o{}_{AB} + K_m P} + \frac{c_o P}{\mu_m}\right]\frac{y_A}{RT}\nabla P \tag{8}$$

The corresponding flux relationship for component B is obtained by interchanging the subscripts A and B. In deriving Equation (8) it is not necessary to add in separately the contributions of Knudsen or slip flow because these are both diffusive phenomena.

The derivation of Equation (8) presented here is the same as that appearing elsewhere (*18*). Related work by Mason, et al. (*36*) appeared concurrently and independently. It can be shown that equation (63) given by Mason, et al. is indeed identical to Equation (8) although it appears in a quite different form. The derivation of Equation (8) has been included here because the formulation and derivation given in the present work, while different from that given by Mason, et al. (*36*), have some definite advantages from the viewpoint of engineering utility.

An equation similar to Equation (8) was given by Evans, Watson, and Mason (*15*). While correct in form this equation contained an arbitrary parameter for which the pressure dependence had to be determined experimentally. Subsequently the theoretical form for this pressure dependence has been determined by Gunn (*18*) and by Mason, et al. (*36*).

The transition region diffusion equations for multicomponent mixtures can also be obtained in a straightforward manner from the dusty gas model. For an n component mixture

$$\vec{N}_i - \vec{N}_i{}^o = -y_i\frac{c_o P}{\mu_m}\nabla P \tag{9}$$

The diffusive fluxes are obtained by solving n simultaneous equations, each of the following form:

$$\sum_{\substack{i=1\\ i\neq j}}^{n}\frac{y_j\,\vec{N}_i{}^o - y_i\,\vec{N}_j{}^o}{c_2\,D_{ij}} - \frac{\vec{N}_j{}^o}{K_j} = \frac{1}{RT}\nabla P_j \tag{10}$$

Equations (9) and (10) clearly indicate that, as in all multicomponent diffusion problems, computations for a real situation will be extremely complex.

It can be shown that Equation (8) reverts to the proper limiting forms in all cases. Some of these have been discussed by Mason, et al. (*36*). One rather interesting additional result will be given here; this is the case of isobaric diffusion. At sufficiently high pressures $K_m P >> c_2 D^o{}_{AB}$ and the term $c_2 D^o{}_{AB}$ in the denominators of Equation (8) may be neglected. Under these conditions Equation (8) simplifies to

$$N_A = -\frac{c_2\,D^o{}_{AB}}{\left[y_A\left(\sqrt{\frac{M_A}{M_B}} - 1\right) + 1\right]RT}\frac{dy_A}{dx} \tag{11}$$

With some algebraic manipulation it can be shown that Equation (11) uniquely satisfies both Fick's law (with a drift term included) and the experimentally proven flux ratio, $-\sqrt{M_B/M_A}$.

It is well known that in the Knudsen regime the ratio of diffusive fluxes N_A/N_B for isobaric counterdiffusion in a binary gas mixture is equal to $-\sqrt{M_B/M_A}$. This experimental result was expected on theoretical grounds as well.

In the continuum regime in free space the corresponding flux ratio is given by $-M_B/M_A$. In most porous materials, however, the flux ratio, $-\sqrt{M_B/M_A}$, is the same in all regimes. This fact has been proven experimentally (*12, 18, 21, 37, 47, 48, 50, 53*) and is also predicted (*14, 47*) by the diffusion equations (1), (2), and (8).

Certain limitations to Equation (8) warrant discussion. Deriaguin and Bakanov (9) have shown theoretically that a minimum occurs in the curve of permeability vs. average pressure for extremely porous bodies. This result, which is contrary to that found for most porous media, has been verified experimentally for materials such as steel wool (*49*). This result is not especially surprising because in this case the solid structure occupies a very small fraction of the total volume and the mesh spacing is relatively large. Thus there is a large contribution of relatively long flight paths to fluxes in the Knudsen regime, as occurs for capillaries. These structural properties of steel wool are absent in most porous materials, and therefore Equation (8) should be a valid relationship for most porous media of practical interest.

While flow in a particular type of material such as a bundle of capillaries is not readily generalized to apply to other porous media, a more general model, on the other hand, can be specialized for a single kind of material. Recently Mason and co-workers (*35, 36*) have been able to extend the dusty gas model to predict transition flow of pure gases in capillaries. This is accomplished by accounting for a composition effect in the Knudsen diffusivity. This is an interesting result because a bundle of capillaries is, in fact, a very special kind of porous material.

THE TRANSPORT PARAMETERS

Two separate problems exist in calculating transition region–mass transfer rates: the determination of the correct form of the transport relationships, and the quantitative characterization of the structure of the porous medium. Equation (8) gives the flux of a component in terms of the total pressure gradient, the composition gradient and the structural parameters c_o, c_1, and c_2. Equation (8) is thus a solution to the first of these two problems, and not the second.

In order to verify the form of Equation (8) using mass transfer data, the most accurate possible values of c_o, c_1, and c_2 are required; therefore, these should be measured directly. Constants c_o and c_1 can be obtained from flow data for a pure gas. c_2 can be obtained from a single diffusion experiment at constant pressure. Normally a direct measurement of these parameters is experimentally simpler, and certainly more reliable, than the measurement of pore size distribution, porosity and tortuosity, from which the desired quantities can be approximated.

Integration of Equation (8)

Equation (8) must be integrated if it is to be applied to steady state transport across a medium of finite thickness. Two dependent variables are involved, P and y_A, both of which are functions of the spatial coordinates. An analytic form of the integrated equation has not been obtained; however, a partial integration in closed form is possible, and this simplifies the numerical process of integrating the entire equation. This partial integration gives mole fraction as a function of total pressure for the linear, steady state case:

$$\frac{F-(F+1)y_A}{F-(F+1)y_{A0}} = \frac{P^{-a_o}\, e^{-a_1P-a_2P^2}}{a_3[F-(F+1)y_{A0}]\int_{P_1}^{P} P^{1-a_o}\, e^{-a_1P-a_2P^2}\,dP + P_o{}^{-a_o}\, e^{-a_1P_o-a_2P_o{}^2}} \qquad (12)$$

where

$$a_o = \frac{F+1}{Fm+1}\,k_o$$

$$k_o = \frac{Fm-(Fm+1)y_A}{F-(F+1)y_A}$$

$$a_1 = \frac{F+1}{Fm+1}\left(\frac{K_B}{c_2D^o{}_{AB}} + \frac{c_o}{\mu_m K_A}\right)$$

$$a_2 = \frac{c_o}{2\mu_m\, c_2D^o{}_{AB}}$$

and

$$a_3 = \frac{c_o(1-m)}{(Fm+1)\,\mu_m\, c_2D^o{}_{AB}}$$

Equation (12) is based on the following assumptions: (a) The viscosity, μ_m, does not vary with composition. (b) k_o is a constant. The quantity k_o has a maximum range of values from 1 when y_A is 1 to m when y_A is 0. An arithmetic average value of k_o may be adopted in most cases, because k_o arises from a pressure diffusion term and its effect upon the calculated composition is usually small. In cases of doubt concerning the validity of assumption (b), the maximum effect on y_A can be evaluated from two calculations in which k_o is assigned values of 1 and m, respectively. Assumption (a) is more restrictive, because for many mixtures the viscosity varies considerably with composition. In this case Equation (12) is valid over a limited range of composition.

After the pressure dependence of the composition has been determined, the fluxes may be obtained by numerically integrating the following equation:

$$N_A = -\frac{Fm}{Fm+1}\left[K_A + \frac{c_o\,PK_m}{\mu_m\,K_B}\right]\frac{1}{RT}\,\frac{dP}{dx} \qquad (13)$$

$$N_B = \frac{N_A}{F} \qquad (14)$$

Equation (13) is obtained by rearrangement of Equation (8). A derivation of each equation in this section is given in appendix 4 of reference *18*. Another integration of Equation (8) has been given by Mason, et al. (*36*).

A special case of Equation (12) is the diffusion of a single component through a stagnant gas. In drying processes, for example, water vapor usually diffuses through whatever inert gases may be present. For this case F is zero, a_o is unity, and Equation (12) reduced to the following, somewhat simpler, form:

$$\frac{P_A}{P_{A0}} = \frac{e^{-a_1P-a_2P^2}}{\left\{e^{-a_1P_o-a_2P_o{}^2} - a_3P_{A0}\sqrt{\dfrac{\pi}{4a_2}}\, e^{a_1{}^2/4a_2}\left[\operatorname{erf}(a_2{}^{1/2}P_o + a_1/2a_2{}^{1/2}) - \operatorname{erf}(a_2{}^{1/2}P + a_1/2a_2{}^{1/2})\right]\right\}} \qquad (15)$$

where P_A = partial pressure of the stagnant component.

PREVIOUS EXPERIMENTAL WORK

Very few data are available for diffusion rates in the presence of a pressure gradient. Kaganer (*28*) measured the flow rates of each component of a nitrogen-helium mixture through a porous barrier. Unfortunately these experimental results cannot be related to the transport properties of the barrier because the effective diffusivity (c_2) was not measured independently. Evans, Truitt, and Watson (*13*) and Hewitt and Morgan (*24*) have measured diffusion rates with superimposed pressure gradients in porous graphite. In both cases these data appear to be quite accurate; however, the mean pore diameters were sufficiently large so that both diffusion and flow were outside the transition region. For this reason these experiments are not of major interest here.

Otani, Wakao, and Smith (*27*) measured combined diffusion and flow rates for nitrogen-hydrogen mixtures in Vycor glass and in compressed alumina pellets. Unfortunately, the data show random variations, and they fall in a region which is particularly sensitive to the measured values of the transport parameters of the media (that is, c_0, c_1, and c_2). Because of the uncertainty in these parameters, it is difficult to test Equation (8) by means of these data.

Evans, et al. (*16*) have reported particularly pertinent data for the diffusion of helium and argon in the presence of a pressure gradient. Mason, et al. (*36*) have shown that these results can be predicted with good accuracy by using Equation (8).

Finally, Hewitt and Sharratt (*23*) have measured the counterdiffusion of oxygen and nitrogen in porous graphite under conditions corresponding to the transition region. These investigators determined c_0 and c_1 from independent flow experiments using a pure gas. c_2 was found from the diffusion of nitrogen and oxygen at constant pressure. The standard deviations for permeability and Knudsen diffusivity values have been published (*24*). In the diffusion experiments a nitrogen stream and an oxygen stream were circulated past the respective ends of a graphite rod. The rates of diffusion of oxygen into the other stream were measured as the pressure on the nitrogen side was increased in a step-by-step manner. In this fashion the diffusion rates of oxygen were reduced by as much as 1,000 to 10,000 fold. These results provide a very severe test for any prediction method, because it is necessary to calculate the reduction in the diffusion rate over *four orders* of magnitude using only data obtained from pure gas flow and from diffusion at constant pressure. Experimental and theoretical values, calculated by means of Equations (12) and (13), are compared in Figure 1. The pressure difference across the graphite rod is plotted on the abscissa; and on the ordinate is plotted the ratio N_A/N_{A0}, where N_{A0} is the diffusion rate of oxygen at constant total pressure and N_A is the diffusion rate in the presence of a pressure gradient. The solid curves are the theoretical predictions based upon the measured transport parameters.

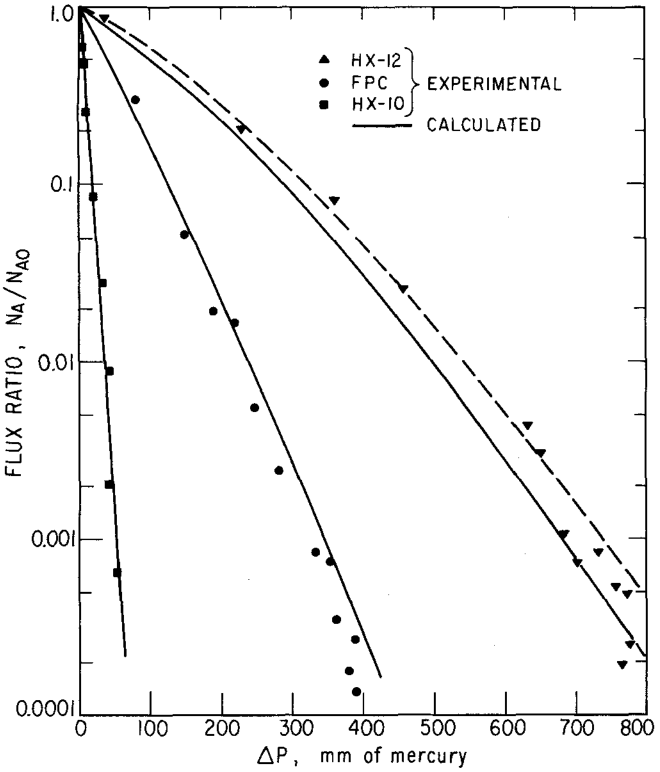

Fig. 1. Diffusion of oxygen in graphite against a pressure gradient.

The uncertainty in the values of c_1 and c_2 for the graphite is about 10%. Because of the exponential nature of Equation (12), a 10% error in these parameters can produce an error of 100% or more in the ratio N_A/N_{A0}. The dashed curve in Figure 1 gives the prediction for sample HX-12 with the effective isobaric diffusivity increased by 10% and with the other transport parameters left unchanged. The agreement between calculated and experimental values in Figure 1 falls well within the range of experimental error. A detailed sample calculation for these data has been given elsewhere (*18*).

The data presented in Figure 1 represent an important and successful test of the entire Equation (8) *in integrated form*. The integration process in this case was simplified by the fact that the viscosity and molecular weights of oxygen and nitrogen are quite similar. As a result the final relationship used in calculating the flux ratios is rather similar to an equation derived by Hewitt and Sharratt (*22*). Their method, however, is limited to mixtures in which all components have nearly the same molecular weight.

Recently Hawtin, et al. (*57*) have reported data for the counter-diffusion of argon-helium and of nitrogen-helium binaries in porous nuclear-grade graphite.

EXPERIMENTAL MEASUREMENTS

Apparatus

The method used to measure mass transport rates in the present work was apparently first employed by Buckingham (*4*). This method has been used subsequently by several investigators (*12, 21, 24, 37, 47, 48, 50, 52*). A discussion of experimental methods can be found in these references. In addition, Rothfeld (*42, 43*), who also employed the apparatus, has given a more complete review of experimental methods for measuring gaseous diffusivities.

The apparatus consists of a diffusion cell with two sides separated by the porous body. Two gas streams of different composition flow into either side of the diffusion cell. Composition changes between gases entering and leaving the cell are related to diffusion rates through the porous body. This apparatus is also easily adapted to permeability measurements.

Figure 2 is a sketch of the apparatus in which all experiments were made. Gas flows from high pressure cylinders through a pressure regulator, and a low flow controller (A). This device maintains a constant flow rate and minimizes pressure fluctuations. The gas next flows through a capillary flow meter (C). From the flow meters the gases flow to a diffusion cell, consisting of two glass cups flanged together. An aluminum plate (P) separates the two sides of the diffusion cell. A hole cut in this plate, 0.300 in. thick, is filled with the porous medium (E). Pressure plates (D) hold the porous body in place. The dark triangles in the plate represent the beveled entrance to the hole in the plate (P). The beveled space is filled with a sealant such as rubber cement or paraffin. The magnetic fans (F) provide good mixing and reduce the effect of boundary layer resistance to mass transfer at the surface of the porous material. The outlet streams flow through gas sampling bottles (G), and portions of the gas flows are shunted through thermal conductivity cells (H) operated by a power control.

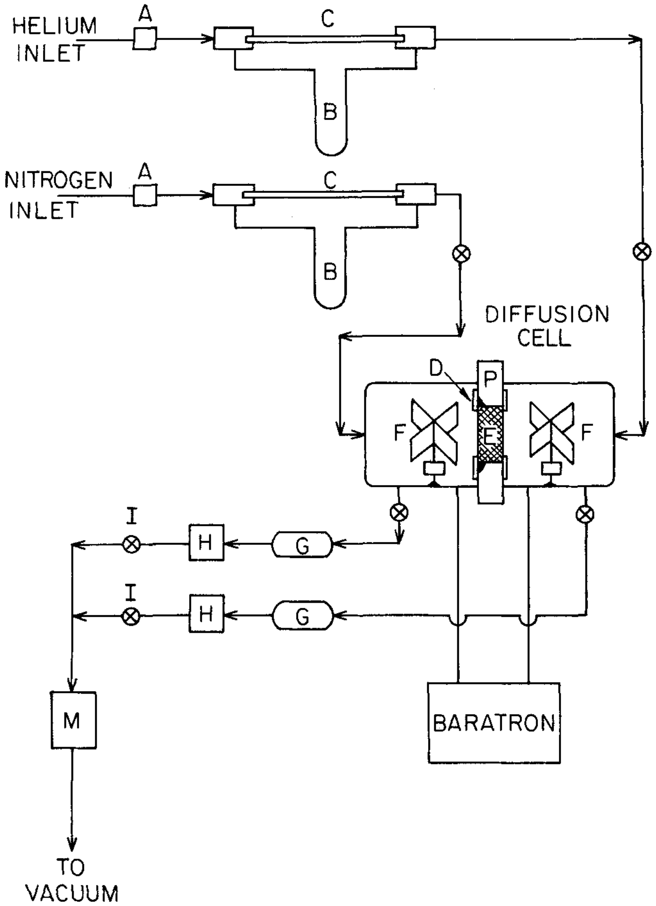

Fig. 2. Diagram of experimental apparatus.

After passing through metering valves (I), the two outlet streams are joined and pass to a mercury manostat (M), which maintains the desired level of vacuum on the system. The gases then flow to a vacuum pump or are exhausted to the atmosphere. Clear vinyl or Tygon tubing (5/16 in. I.D. with 3/32 in. wall) was used for gas lines. Although the plastic tubing has the advantage of great flexibility, it caused inconvenience at low pressures because of the tendency of the tubing to outgas for long periods of time. It was necessary to limit measurements to pressures above 0.5 mm. of Hg. so that the degassing of the tubing would not distort measured gas flow rates by more than 1 or 2%.

For isobaric diffusion experiments the pressure is maintained equal on the two sides of the cell by adjustment of the metering valves (I). Any pressure imbalance is detected with a Baratron, a capacitance differential pressure gauge. The Baratron detects pressure differentials as small as 10^{-6} atm., independent of the total pressure level.

Measurements were made of rates of diffusion of helium-nitrogen mixtures when the porous medium was replaced by two thin sheets of Millipore filter paper. In this way the resistance due to the boundary layers on either side of the diaphragm was ascertained. No significant correction was required for the measurements reported below, but the boundary layer correction was important for the measurement of diffusion in freeze-dried turkey meat, reported elsewhere (*19*). The existence of this boundary layer resistance was not apparent from runs made at varying gas flow rates; hence it is important that direct measurements of boundary layer resistance be made in diffusion cells of this sort.

The diffusion cell is immediately converted for permeability measurements by closing two valves. A known flux of gas is forced to flow through the porous medium and the pressure drop across the porous body is recorded with the Baratron.

RESULTS

Equation (8) contains three terms on the right-hand side. The first is a diffusion term, the second is a drift term, and the third is the D'Arcy flow term. One objective of the experimental program was to verify each term experimentally. The D'Arcy flow term, of course, requires no substantiation because it has been verified already by many investigators (*1, 5, 31, 40*). In addition, the diffusion term has been verified by Scott and Dullien (*48*) and Henry, et al. (*21*) for the isobaric cases. Further investigation was made of this term in the present work. First, the isobaric diffusion flux ratio relationship was verified for the helium-argon system using a Corning pyrex fritted-glass filter. A fine grade filter was used, with a nominal maximum pore size of 4 to 5.5 μ (*6*). The theoretical diffusion flux ratio, $-\sqrt{M_A/M_{He}}$, of -3.16 was confirmed by an experimental value of -3.07. The difference between these two values falls within the range of experimental error. The data were taken at atmospheric pressure, and permeability measurements reported later in this section clearly indicate that Knudsen diffusion at 760 mm. Hg. contributed less than 5% of the total flux in this experiment. This confirms that the diffusion ratio, $-\sqrt{M_B/M_A}$, is valid at pressures far greater than those of the Knudsen regime.

In a second experiment with the fritted-glass filter, isobaric diffusion rates for helium-nitrogen mixtures were measured at different pressure levels ranging from 50 mm. Hg. to atmospheric. Again the agreement with the square-root flux ratio was satisfactory.

If Equation (8) is integrated after setting dP/dx equal to zero, the following equation is obtained:

$$\frac{(y_{AR}\, e^{\Psi} - y_{AL})(1-m)}{e^{\Psi}-1} - 1 = \frac{c_2 D^o_{AB}}{K_A P} = \frac{c_2}{c_1}\,\frac{D^o_{AB}}{P}\sqrt{\frac{M_A}{RT}} \qquad (16)$$

where

$$\Psi = \frac{N_A RT\, L\, (m-1)}{c_2 D^o_{AB}}$$

Subscript R = side of diffusion cell where component A is more concentrated.

Subscript L = side of diffusion cell where component A is less concentrated.

If c_2 is known, experimental data can be substituted into the left-hand side of Equation (16). These numerical values are plotted as functions of reciprocal pressure yielding a straight line which passes through the origin. The slope of this line is equal to $c_2 D^o_{AB}/K_A$, from which K_A can be calculated. If different pairs of gases are to be used for a single porous body, then the left-hand side of Equation (16) should be plotted against $(D^o_{AB}/P)\sqrt{M_A/RT}$. In this case the slope is equal to c_2/c_1. In general c_2 is not known, and in that case several plots are made adjusting c_2 until a straight line is obtained which passes through

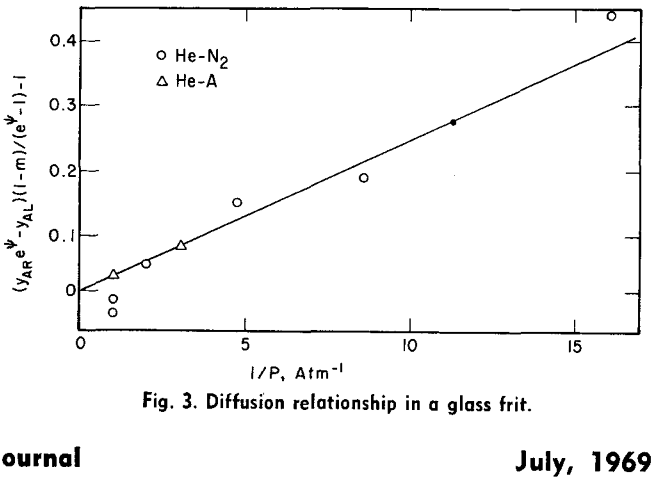

Fig. 3. Diffusion relationship in a glass frit.

the origin. This procedure simultaneously yields values for c_1 and c_2. Figure 3 is a plot of this type for the fritted glass filter at 25 ± 1°C. for the helium-nitrogen binary and 19°C. for the helium-argon binary. Both sets of binary data can be presented on a plot such as Figure 3 because by coincidence $D^o_{\text{He-A}}$ and $D^o_{\text{He-N}_2}$ are virtually identical in value, and because M_A is the same in each case. The data show an experimental uncertainty of about ± 5% in the experimental flux. The value for the Knudsen diffusion coefficient for helium at 25°C. is 4.9 sq.cm./sec. as compared to a value of 5.5 sq.cm./sec. based on permeability tests with pure helium (see Figure 4). The difference between the two values falls within the range of experimental uncertainty.

D^o_{AB} was taken to be 0.697 for helium-nitrogen at 25°C. and 0.695 for helium-argon at 19°C., both values in atm.-sq.cm./sec. In the Knudsen regime, therefore, D_{AB} will be substantially greater than K_A, as is necessarily true.

The unidirectional flow of a pure gas through a porous body is considered next. Equation (8) is integrated after setting dy_A/dx to zero and rearranging to give

$$\frac{N\sqrt{M\,RT}}{\Delta P} = \frac{c_1}{L} + \frac{c_o}{L^2}\left(\frac{\bar{P}L}{\mu}\sqrt{\frac{M}{RT}}\right) \tag{17}$$

where $\bar{P}$ = arithmetic average pressure.

Equation (17) shows that a plot of the dimensionless flow rate, $N\sqrt{M\,RT}/\Delta P$, vs. dimensionless pressure, $\bar{P}L\sqrt{M}/\mu\sqrt{RT}$, yields the same straight line independent of the gas flowing or the temperature. The intercept of this line with the ordinate gives the Knudsen coefficient, c_1/L, and the slope of the line gives the D'Arcy permeability, c_o/L^2. It can be shown that the dimensionless pressure on the right-hand side of Equation (17) is proportional to a modified Knudsen number (λ/L).

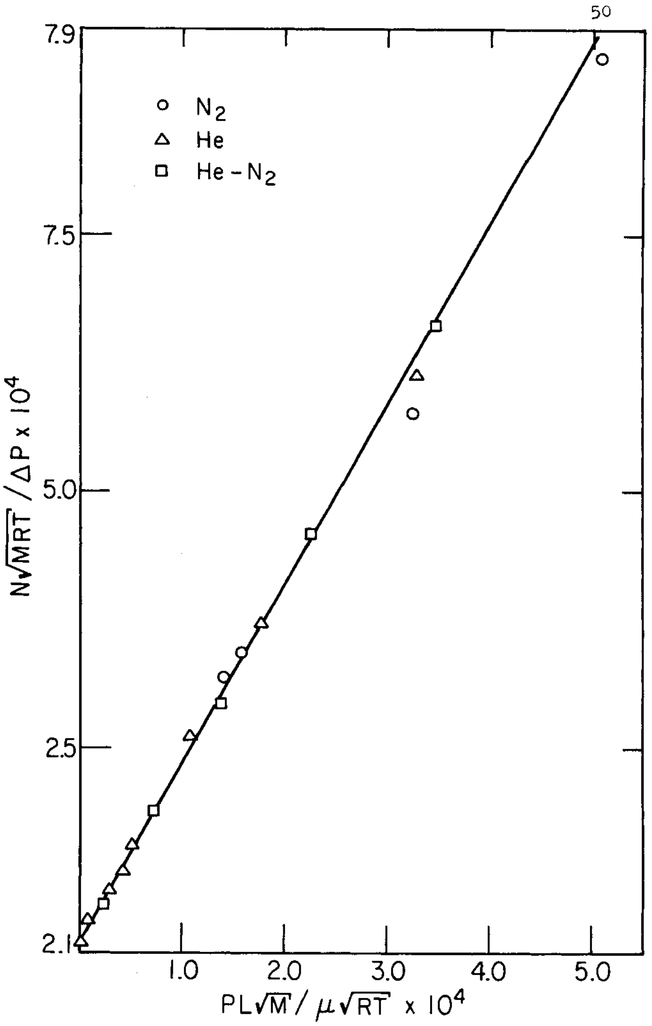

Fig. 4. Permeability of a glass frit.

For the flow of gas mixtures, Equations (13) and (14) can be combined and rearranged to give

$$(N_A\sqrt{M_A} + N_B\sqrt{M_B})\sqrt{RT} = \left\{c_1 + \frac{c_o}{L}\left[\frac{PL(y_A\sqrt{M_A} + y_B\sqrt{M_B})}{\mu\sqrt{RT}}\right]\right\}\frac{dP}{dx} \tag{18}$$

Equation (18) upon integration at constant composition yields

$$\frac{(N_A\sqrt{M_A} + N_B\sqrt{M_B})\sqrt{RT}}{\Delta P} = \frac{c_1}{L} + \frac{c_o}{L^2}\left[\frac{PL(y_A\sqrt{M_A} + y_B\sqrt{M_B})}{\mu\sqrt{RT}}\right] \tag{19}$$

A comparison of Equation (19) with Equation (17) shows that a plot of permeability data for the flow of either a pure gas or a mixture should fall on the same straight line, provided that for mixtures the following definitions are made:

$$N\sqrt{M} = N_A\sqrt{M_A} + N_B\sqrt{M_B} \tag{20}$$

$$\sqrt{M} = y_A\sqrt{M_A} + y_B\sqrt{M_B} \tag{21}$$

This result, however, is only an approximation because some composition change always occurs through the porous medium, and Equation (19) is obtained through an integration holding the mole fractions constant. However, if the total pressure decrease is only a small portion of the total pressure, this approximation is very good.

Equation (19) is a test primarily of the D'Arcy and drift terms because the diffusion term has been eliminated in the derivation. Figure 4 is a permeability plot for the fritted-glass filter using pure helium, pure nitrogen, and nitrogen-helium mixtures. The data essentially coincide on the same straight line, thus substantiating the validity of Equation (19). The pressure range for this experiment is from atmospheric to a few millimeters of mercury. The intercept of the straight line yields a c_1 value of 0.70×10^{-4} cm.

In addition to the results presented here, a considerable amount of data, which are reported elsewhere (*18, 19*), have been obtained for permeation and diffusion in freeze-dried turkey meat. The equations derived here have been found to apply to these materials as well as to porous media such as the fritted-glass filter.

CONCLUSIONS

An equation predicting gas-phase mass transfer rates in porous bodies with gradients in composition and total pressure has been developed from the dusty gas model. This equation reverts to the necessary limiting forms in all cases. Experimental evidence from the present work and past studies supports the validity of this relationship. The experimental results from the present work also confirm the findings of earlier investigators in support of Equations (1) and (2). The fundamental qualitative differences between mass transport in porous media and in tubes have been discussed, and it has been shown that the equations derived here describe the behavior of porous bodies but not of capillaries.

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NOTATION

C = molar concentration of a component, g.-moles/cc.
c_o = constant dependent only upon structure of porous medium and giving relative D'Arcy flow permeability, sq.cm.
c_1 = constant dependent only upon structure of porous medium and giving relative Knudsen flow permeability, cm.
c_2 = constant dependent only upon structure of porous medium and giving the ratio of bulk diffusivity within the porous medium to the free gas bulk diffusivity, dimensionless
d = diameter of a capillary tube, cm.
D_{AB} = free gas mutual diffusivity in a binary mixture of components A and B, sq.cm./sec.
$D^o_{AB} = D_{AB}P$, dynes/sec.
$\mathrm{erf}(f)$ = error function of f
$F = N_A/N_B$
K_A = Knudsen diffusivity $= c_1\sqrt{RT/M_A}$, sq.cm./sec.
$K_m = y_BK_A + y_AK_B$, sq.cm./sec.
L = length of a porous body in the direction of mass transfer, cm.
$m = \sqrt{M_A/M_B}$
M = molecular weight, g./g.-mole
N = molar flux, g.-moles/sq.cm.-sec.
N_{A0} = molar flux of component A in the absence of a total pressure gradient
N^o = diffusive flux of a component, g.-moles/sq.cm.-sec.
P = total pressure; with a subscript = partial pressure of that component, dynes/sq.cm.
P_o = total pressure at the same position as taken for y_{A0}
R = gas constant, 8.31×10^7 ergs/g.-mole-°K.
T = absolute temperature, °F.
x = distance in direction of mass transfer, cm.
y = mole fraction
y_{A0} = mole fraction of component A at one face of a porous body [Equation (20)]
$\nabla(f)$ = gradient of f, cm.$^{-1}$
λ = mean free path of gas molecules, cm.
μ = viscosity, g./cm.-sec.

Subscripts

A = component A
B = component B
D = dust molecules
i, j = components in a multicomponent mixture
m = mixture

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