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1314 KINNEAR ROAD

COLUMBUS, OHIO 43212

KNUDSEN AND MOLECULAR DIFFUSION OF GASES
IN CAPILLARIES AND POROUS SOLIDS OVER
LARGE PRESSURE RANGES

Dr. Christie J. Geankoplis

Department of Chemical Engineering

January 1, 1972

U. S. ATOMIC ENERGY COMMISSION
Chicago Operations Office
Argonne, Illinois 60439

Contract No. AT(11-1)-1675

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Report No. C00-1675-10

FINAL

REPORT

By

THE OHIO STATE UNIVERSITY
RESEARCH FOUNDATION

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COLUMBUS, OHIO 43212

To..... U. S. ATOMIC ENERGY COMMISSION
Chicago Operations Office
9800 South Cass Avenue
Argonne, Illinois 60439
Contract No. AT(11-1)-1675

On..... KNUDSEN AND MOLECULAR DIFFUSION OF GASES
IN CAPILLARIES AND POROUS SOLIDS OVER
LARGE PRESSURE RANGES

For the period 1 April 1967 - 31 December 1971

Submitted by Dr. Christie J. Geankoplis
Department of Chemical Engineering

Date January 1, 1972

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ABSTRACT

The diffusional transport of gases in porous media or relatively undefined geometry and in straight capillaries is important in many areas of the physical and biological sciences. Some of these areas include diffusion in porous catalysts and molecular sieves, separation of gases in porous barriers and membranes, diffusion in porous biological structures, diffusion through barriers in high vacuum such as outer space, and diffusion in capillaries or other types of equipment. At present, there are few theories and models available for predicting this diffusion at constant total pressure in these cases. The effects of many variables such as pressure, pore geometry, and the number of individual gases present, are still somewhat uncertain in these predictions.

Prior to the present research program initiated in this laboratory several years ago, previous experimental data in the literature covered only a 50/1 range of pressures in porous solids, which did not cover the entire three-mechanism range of Knudsen, transition, and molecular diffusion. Most of the diffusion in industrial catalysts at one atmosphere pressure is in the transition region. No experiments have been done by others in true straight capillaries to test the recently derived equation for binary gases in the transition region.

Experimental data have been recently obtained in this laboratory with a novel vacuum apparatus for diffusion of binary gases in different synthetic porous structures of compressed alumina powder. Solids made and used were one which contained one micropore size and many macropore sizes, several solids where the micropore structure was constant but the macropore radius was varied, and a solid where some of the micropores were blocked off by glass powder particles. Theoretical equations derived in this study for these cases checked the experimental data. The data covered a 1300/1 pressure range which included the Knudsen and most of the transition region.

A method was devised to make a plug containing 644 straight glass capillaries in parallel. Binary experimental diffusion runs using helium and nitrogen were made which covered essentially the entire transition region and which checked closely the theoretical transition region equation. This work is the first experimental confirmation of the theoretical binary transition diffusion equation for straight capillaries. Further experiments could be made to further check this equation using various size glass capillaries and metal capillaries with very rough walls. With this novel vacuum apparatus large capillaries can be used while still reaching the Knudsen region.

A high-pressure apparatus has been designed and constructed to extend the range of pressures covered to 345,000/1. Preliminary binary experimental diffusion runs made on this high-pressure apparatus using a solid with collimated hole structures have produced experimental flux

ratios which check theoretical values. Absolute flux values are as yet undetermined because of uncertainty in the radii of the collimated holes. The highest pressure run thus far has been 250 psia.

An analytical solution to the differential equations for diffusion of a three-component gas mixture was obtained for the complete transition region in an open system. A numerical solution for the mixture of helium, neon, and argon showed the fluxes of helium and neon approaching constant values at high pressures as expected. The flux of argon indicated that osmotic diffusion occurs even though there is no concentration gradient. Under certain conditions the binary flux equations can be used to approximate the fluxes in a ternary mixture and reduce the trial and error computational time in the digital computer. An additional numerical method was devised using nonlinear optimization techniques to drastically reduce computation time. An interesting conclusion is that the flux ratios can change with pressure in the transition region. This could possibly be the basis for a separation process.

Several experimental ternary diffusion runs were made with the vacuum apparatus using the 644-capillary diffusion plug which covered essentially all of the transition region. The gases used were helium, neon, and argon. Preliminary unrefined results check the theoretical transition region equations for a ternary system. This work is the first experimental confirmation of the theoretical ternary transition diffusion equations for straight capillaries.

LIST OF SYMBOLS

Symbol

D_{AB}	Molecular diffusivity for system A-B, cm^2/sec
D_e	Diffusion coefficient defined by Eq. (5), cm^2/sec
D_{KA}	Knudsen diffusion coefficient defined by Eq. (2), cm^2/sec
$\bar{D}_K$	Mean Knudsen diffusion coefficient in pores, cm^2/sec
D_{NA}	Diffusion coefficient defined by Eq. (1) in a tube, cm^2/sec
F	$Q_{\text{experimental}} / Q_{\text{Hagen-Poiseuille}}$ predicted flow
g_c	Conversion factor, 1.33
L	Actual length of porous solid, cm
M	Molecular weight
N_A	Diffusion flux, g mol A/sec-cm ²
N_K	Knudsen number, $\lambda/2\bar{r}$
P	Pressure, mm Hg
P_{mean}	Average pressure in flowmeter, micron Hg
Q	Volumetric flow rate, micron-cm ³ /sec
R	Gas constant
r	Radius of flowmeter, cm
$\bar{r}$	Mean pore radius, cm
T	Temperature, °K
X_A	Mole fraction A
X	Correlation parameter for F , $\mu/(P_{\text{mean}}\bar{r}[\rho_1 g_c]^{1/2})$
α	Flux ratio, $1 + N_B/N_A$
ϵ	Void fraction
λ_A	Mean free path of A, cm

ρ_1 Density of gas at 1 micron Hg, g/cm³-micron

μ Viscosity at atmospheric pressure, poise

Subscripts

a, b, i Macro-, semimacro-, and micropores, respectively

A, B Nitrogen and helium respectively

O, L Nitrogen and helium sides of solid, respectively

s Solid

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I. INTRODUCTION AND PREVIOUS RESEARCH WORK DONE BY OTHERS

The transport of gases by diffusion in porous media of relatively undefined geometry and in straight capillaries is important in many areas of the physical and biological sciences. Some of these areas include diffusion in porous catalysts and molecular sieves, separation of gases in porous barriers and membranes, diffusion in porous biological structures, diffusion through barriers in high vacuum such as outer space, and diffusion in capillaries or other types of equipment. At present there are few theories and models available for predicting this diffusion at constant total pressure in these cases. The effects of many variables such as pressure, pore geometry, and the number of individual gases present, are still somewhat uncertain in these predictions. Following is a discussion of the work of others which includes the pertinent experimental results, theoretical equations, and physical models for diffusion over a range of pressures. The studies presented in this discussion consider mainly diffusion in the gas phase and in cases where indicated combined surface diffusion or combined adsorbed layer flow is also considered. Also, diffusion plus combined forced or hydrodynamic flow is discussed to some extent.

A. THEORETICAL DERIVATIONS FOR DIFFUSION IN CAPILLARIES BY OTHERS

In those studies that have been presented by others the data for a given solid did not cover the entire three-mechanism range of Knudsen, transition, and molecular diffusion. The works of Wakao and Smith¹ and Rothfeld² showed, that in many industrial catalysts, the diffusion at one atmosphere is in the transition region.

The theory for diffusion in the three-mechanism range was first given by Wheeler³ who used an intuitive approach. He also assumed a structure of equivalent parallel pores for diffusion in porous structures. This is the simplest model but requires a tortuosity correction which must be determined experimentally and which may vary with pressure.

Rothfeld,² Scott and Dullien,⁴ and Evans et al.⁵ developed similar theoretical equations for the transition region. They^{2,4} made a momentum balance of molecules A in a straight capillary by considering the total momentum transferred of gas A to be the sum of momentum transferred to the walls and to molecules B in the gas phase. Their equations for the effective diffusion coefficient D_{NA} and flux are

$$D_{NA} = \frac{1}{(1-\alpha X_A)/D_{AB} + 1/D_{KA}} \quad (1)$$

and

$$N_A = - \frac{D_{NA} P}{RT} \left(\frac{dx_A}{dL} \right) = \frac{D_{NA} P}{RTL} (x_{AO} - x_{AL}). \quad (2)$$

Several assumptions are made in this derivation: The square of the drift velocities is $\ll$ the mean square of the thermal velocities. The gas-wall viscous terms or shear stresses are negligible. The momentum lost by molecule A with the walls and by collisions with B is the same as that lost when $D_{AB}/D_{KA} = \infty$. The last two assumptions are crucial indeed and should be tested. No experiments have been reported in the literature to test this equation for diffusion of two components in a straight capillary with no total pressure difference or forced flow. Spiegler⁶ also derived Eq. (1) using a friction factor analysis instead of the detailed kinetic theory of gases.

Integration of Eq. (2) gives

$$N_A = \frac{D_{AB} P}{\alpha RTL} \ln \left[\frac{1 - \alpha x_{AL} + D_{AB}/D_{KA}}{1 - \alpha x_{AO} + D_{AB}/D_{KA}} \right]. \quad (3)$$

Equations (1) and/or (3) are the main theoretical equations for a straight capillary tube for the entire transition region. Rothfeld² showed that the transition from Kundsens to molecular diffusion covers a 1000-fold range of mean free paths or pressures. Previously it had been supposed⁴ that this region extended from values of $\bar{r}/\lambda$ of 0.1 to 10. Evans et al.⁵ and Scott and Dullien⁷ proved that the theoretical flux ratio in a binary gas for all three of the diffusion mechanisms in an open system where gases flow past both ends of the capillary or porous solid is

$$N_B/N_A = -(M_A/M_B)^{1/2} = \alpha - 1. \quad (4)$$

Various physical models other than Wheeler's have been proposed for predicting diffusion through porous media at uniform total pressure throughout the solid. All of them depend upon assumptions as to the physical geometry and interconnections of the pores. Rothfeld² and Scott and Dullien⁴ modified Eq. (3) for porous solids and found that predicted values from Eq. (3) and experimental values checked well over pressure ranges of 4/1 and 50/1, respectively. However, it should be noted that to predict the fluxes, two experimental runs must be made first with the porous solid.

Many investigators define an effective diffusivity D_e which is related to D_{NA} by

$$D_e = D_{NA} \frac{\alpha(X_{AO} - X_{AL})}{\ln \left[\frac{1 - \alpha X_{AL}}{1 - \alpha X_{AO}} \right]} \quad (5)$$

Combining Eqs. (2) and (5) and equating the resulting value for N_A to that in Eq. (3), the final theoretical expression for D_e for all three regions is

$$D_e = \frac{D_{AB}}{\ln \left[\frac{1 - \alpha X_L}{1 - \alpha X_{AO}} \right]} \ln \left[\frac{1 - \alpha X_{AL} + D_{AB}/D_{KA}}{1 - \alpha X_{AO} + D_{AB}/D_{KA}} \right]. \quad (6)$$

B. DIFFUSION IN POROUS SOLIDS

Wakao and Smith¹ developed a random pore model for bi-dispersed porous solids which allowed for parallel and interconnected diffusion through the micro- and macropores. The experimental data for a 10-fold pressure range covered part of the transition region. The data and theory for compressed alumina powder pellets checked very well but data for porous Vycor⁸ deviated markedly.

The random pore model of Wakao and Smith¹ assumes that a compressed powder solid is bi-dispersed. The probability that the macro- and/or micropores line up is assumed proportional to the square of the void fraction of the pores. Using the above model and Eq. (1), the integrated value of D_e is

$$D_e = \frac{D_{AB}}{\ln \left[\frac{1 - \alpha X_{AL}}{1 - \alpha X_{AO}} \right]} \left[\epsilon_a^2 \ln \left[\frac{1 - \alpha X_{AL} + D_{AB}/\bar{D}_{Ka}}{1 - \alpha X_{AO} + D_{AB}/\bar{D}_{Ka}} \right] + \epsilon_i^2 \frac{\alpha(X_{AO} - X_{AL})}{1 - \frac{\alpha}{2}(X_{AO} + X_{AL}) + D_{AB}/\bar{D}_{Ki}} \right. \\ \left. + \frac{4\epsilon_a(1 - \epsilon_a)}{1 + \frac{(1 - \epsilon_a)^2}{\epsilon_i^2}} \frac{\alpha(X_{AO} - X_{AL})}{1 - \frac{\alpha}{2}(X_{AO} + X_{AL}) + \frac{D_{AB}/\bar{D}_{Ki}}{1 + \epsilon_i^2/(1 - \epsilon_a)^2}} \right]. \quad (7)$$

In this derivation it is assumed that there is no tortuosity correction factor for each powder particle in the compressed pellet.

Johnson and Stewart⁹ assumed a model similar to others for porous solids^{2,4,5} with a tortuosity of $\sqrt{3}$ and integrated over the pore size range. Experimental fluxes were 45 to 125% of predicted at one atmosphere pressure.

Weisz and Schwartz¹⁰ developed a theory for a simple random pore model in the Knudsen region. They predicted the flux to be proportional to ϵ^2 . For certain mono-dispersed solids, the predicted and experimental results showed reasonable agreement.

Foster and Butt¹¹ proposed a pore model to take into account effects of mixing and dead-end pores. However, certain parameters are needed to test the model. Flood et al.¹² neglected micropore contributions to diffusion and considered the macropores to be a system of bottlenecks in series. The actual geometry of the pores is needed for flux predictions.

Satterfield and Cadle¹³ used a pore model which assumes parallel paths as did Wheeler.³ They used Eq. (3) with the right hand side multiplied by the factor (total void fraction/tortuosity factor). The tortuosity factor was obtained by a diffusion experiment at high pressure. They obtained data over a pressure range of 65/l. Foster et al.¹⁴ also measured diffusion in porous pellets over a pressure range of 14.6/l.

Horak and Schneider¹⁵ studied several binary systems in a tridispersed aluminum oxide pellet at one atmosphere. They compared experimental results with various models such as the random pore model of Wakao and Smith¹ and the model of Johnson and Stewart.⁹

Verhoff and Strieder¹⁶ did numerical studies of combined Knudsen diffusion and chemical reaction in capillaries of finite length.

Cadle and Satterfield¹⁷ found that the effective diffusivity in pellets of pressed boehmite powder varied by a factor of as much as 3 or 4 with axial distance through the compact. They discuss the reasons for this and how to prepare more uniform solids.

All of the previous experiments covered only a limited 65/l pressure range in a given porous solid which included only a part of the transition region. Also, none of the data in a bi-dispersed solid ever reached the true Knudsen region which would require experiments over a wide pressure region.

C. DIFFUSION PLUS COMBINED FORCED FLOW

When the total pressures on both sides of the porous solid pellet or both ends of a straight capillary are different and a binary gas is present, diffusion plus combined forced or hydrodynamic flow can occur. The diffusion of a component occurs because of a partial pressure gradient of this component. The combined forced flow of the bulk stream occurs because of a total pressure gradient and the flow can be Poiseuille, transition (often termed slip flow), or Knudsen. Equations describing this type of diffusion plus forced flow in the entire transition region from Knudsen to molecular are complex and uncertain.

Wakao, Otani, and Smith^{18,19}; Evans, Watson, and Mason⁵; Scott and Dullien²⁰; and Gunn and King²¹ derived different equations for diffusion plus forced flow of binary gases, which include a number of assumptions as to the use of the proper expression for the slip flow term in a binary gas and to the method of combining the diffusion plus forced flow terms to get the total flux of each component. No experimental data are available to test these equations for combined forced flow plus diffusion of a binary gas in a straight capillary. However, some experimental data for binary systems in porous solids are available^{13,19,21}. Also, no derivations have been made for a multicomponent mixture in a straight capillary or porous solids.

D. DIFFUSION PLUS COMBINED SURFACE FLOW

In cases where the total pressure is relatively high and/or readily adsorbable gases are present, such as hydrocarbons, diffusion plus combined surface or adsorbed layer flow may occur in porous solids. Satterfield and Cadle¹³ state that surface diffusion may be small at low pressures but may make a significant contribution to the total flux at higher pressures. However, the extent of this surface diffusion at higher pressure remains unresolved and further work is needed in this area.

Diffusion plus surface diffusion in porous solids has been measured experimentally by a number of investigators. Satterfield and Cadle¹³ measured the surface diffusion flux of N_2 gas in a mixture of He- N_2 in various porous solids. They correlated the surface diffusion empirically by a "Fickian" type law with Henry's law relating the surface and gas phase concentrations. They used nitrogen adsorption data reported by others²² for values of Henry's law constants. For the solids experimental tortuosities were used.¹³

Barrer and Barrie²³ measured diffusion plus surface flow of a number of gases in porous glass in the region where Knudsen diffusion occurs in the gas phase because of the small pore sizes. Miller and Kirk²⁴ investigated the kinetics of the catalytic dehydration of primary alcohols and pointed out the possibility of surface flow being the predominant mass transfer mechanism in their catalyst system. Masamune and Smith²⁵ conducted experimental studies of adsorption of ethyl alcohol on silica gel. They attributed the majority of mass transfer to surface flow at the temperatures and pressures investigated. Pore diffusion was almost negligible. Others also measured surface diffusion of hydrogen on nickel,²⁶ hydrocarbons on molecular sieves,²⁷ hydrocarbons on vycor glass,²⁸ CO_2 in alumina,²⁹ and hydrocarbons on porous glass.³⁰ Several different theories have been derived to explain surface diffusion³⁰⁻³² but it is difficult to test these series alone in porous solids because of complicating factors such as unknown pore geometries, interactions of a binary gas mixture on the surface adsorption, effect of the presence of a second adsorbed component on the surface diffusion of the first component, etc. Experimental data are needed in pores of known geometries such as straight capillaries to eliminate the pore geometry effects.

II. PREVIOUS RESEARCH DONE IN THIS LABORATORY

The following work³³ was done in this laboratory just before the United States Atomic Energy Commission's Contract No. AT(11-1)-1675 was obtained. The financial aid for this work was provided mainly by the Department of Chemical Engineering of The Ohio State University, and by several industrial fellowships. This research was published in Chemical Engineering Science (1967) Vol. 22, pp. 11-20, by J. P. Henry, R. S. Cunningham, and C. J. Geankoplis. Six reprints were sent to the Atomic Energy Commission in 1967.

The process flow and diffusion apparatus to measure experimentally both of the countercurrent fluxes are shown in Fig. 1 and described in detail elsewhere.^{34,35} Wicke and Kallenbach³⁶ originally described this type of apparatus. For a diffusion run, valves V 2, 5, 7, and 8 were closed and V 1, 3, 4, 6, 9, and 10 were opened.

Fig. 1 - Process Flow Diagram

- T Throttle valve
- V Open or shut valve
- F Capillary flow meter (calibrated by soap film burette meter)
- PI McLeod gage, Pirani, or Hg manometer
- B Bleed for pressure control
- VP Vacuum pump
- TC Thermal conductivity cell
- PM Porous medium

The system was allowed to reach steady state with pure nitrogen flowing past one side of the porous solid and helium past the other side at constant and equal pressures. The pressures were controlled with a system of vacuum pumps, surge tanks, and bleed lines, and were measured by McLeod and Pirani gages and mercury manometers. The streams were analyzed in Gow-Mac thermal conductivity cells with pure nitrogen or pure helium to the reference side of each cell. Pressures from 0.46 to 600 mm were used in the runs.

After each diffusion run, a calibration of the thermal conductivity cells was made at the same pressure by opening valves V 2, 5, 7, 8, 9, and 10 and closing valves V 1, 3, 4, and 6. The outlet sample stream was bypassed and a known mixture of N_2 -He was added to the cell to match the emf.

The porous solids studied were made by compressing alumina powder to pellets having a diameter of 2.6 cm and lengths of 1.25 to 1.66 cm.

Experimental data were obtained for diffusion of gases at constant total pressure in bi-dispersed porous alumina solids and mono-dispersed porous Vycor. The data covered a 1300/1 range of pressures which included the Knudsen and most of the transition region. Previous data covered only a 50/1 range.

Experimental diffusivities of the alumina compared closely with those predicted by the Wakao and Smith random pore model. Data on the Vycor also checked the predictions contrary to the findings of others. A possible explanation may be the differences in pore structure. Modified equations were derived to extend the random pore model to special cases for diffusion of gases and for liquids in porous media.

III. COMBINED PROPOSED RESEARCH PROGRAMS FOR TWO THREE-YEAR PERIODS (April 1, 1967 -- March 31, 1970; April 1, 1970 -- March 31, 1973; actual funding was only up to December 31, 1971)

It is proposed to continue the experimental studies in this laboratory in straight capillaries and porous solids and to further derive theoretical equations for multicomponent diffusion of gases in capillaries and of gases in porous solids. Listed below is a summary of the number of important programs which are in need of investigation and which could be undertaken. Unfortunately, all of these cannot be undertaken in the proposed six-year period. Specifically, these programs will involve studies as follows.

A. DIFFUSION OF GASES AT HIGH PRESSURES

The present experimental apparatus has been used from 0.45 to 600 mm Hg or a 1330/1 range of pressures. With the purchase of new vacuum

pumps, this range can be extended to 0.15 mm or less and the flow rates can still be metered accurately. This will give at least a 4,000/1 range.

It is proposed to also construct a new high-pressure apparatus to expand the top pressure from 600 mm to 1000 psia. Hence, the new over-all range covered in the vacuum apparatus and high-pressure apparatus would be 345,000/1. This would enable all experiments to reach the true molecular region even in a bi-dispersed solid and in some of the smaller size capillaries. In the micropores of the alumina solids at 600 mm, the N_{K_1} was 0.1 in solid 1 used by Henry, Cunningham and Geankoplis.³³ Using this new pressure range and capillaries, the Rothfeld capillary Eq. (3) can also be tested. At high pressures in bi-dispersed solids, the percent flow through the micropores will be about 50% instead of the 10% at 600 mm.

Additional effects which must be considered in using the theoretical Eq. (3) or other theoretical diffusion equations at high pressures are the deviations from the ideal gas law. This equation will be studied and possibly rederived or modified to take into account these deviations. Experimental diffusion data will help confirm the type of equation to use.

B. DIFFUSION OF A BINARY GAS MIXTURE IN STRAIGHT CAPILLARIES

Diffusion experiments will be performed to make a direct experimental test of Eq. (3) for straight capillaries which has not been done previously. As stated earlier, there are several crucial assumptions which were used in this derivation and which may not be completely valid. The tests will be made over a wide pressure range to reach all three regions of diffusion.

It is necessary to completely establish the mechanism of diffusion first in a capillary so that these results can be used in porous solids to determine the pore geometry effects. First, the diffusion experiments will be carried out in straight glass capillaries of different diameters over a wide pressure range of about 0.15 mm Hg abs to about 1 atm abs using gases with little or no surface diffusion.

It has been determined that glass capillaries, each one-inch long with a radius of 0.010 mm and arranged in a parallel bundle, can be used. This will give diffusion rates so that measurements can be made in the present apparatus. The bundle of capillaries can be encased in plastic or beeswax to form a cylinder one inch long by one inch in diameter to fit into the present apparatus.

Then, various metal capillaries with seemingly rough walls compared to the smooth glass will be used to elucidate any differences in the mechanism of Knudsen diffusion where f is the fraction of the

molecules striking the walls which are reflected diffusely or randomly. This fraction f has been assumed constant in Eq. (3) but may actually vary with the type of capillary surface. The different size capillaries will be used so that experiments can be performed in the pure Knudsen region all the way up to the pure molecular region using both the vacuum and the high-pressure apparatus.

Also, experiments will be performed measuring the flow of a single gas in the pure Knudsen region using the above capillaries. This will be compared with the diffusion data and should give data to corroborate the assumption made of each gas specie in a binary system diffusing in the Knudsen region with no interactions occurring between the two gases. Knudsen's original experiments³⁷ were done using pure gases and not binary mixtures. Hence, as far as is known, no experiments have been reported in the literature where actual diffusion of binary mixtures has been studied in the Knudsen or transition region in true capillaries where the geometry is known exactly.

The experiments with straight capillaries are probably the most important ones in this program. The novel vacuum apparatus used required extensive development in this laboratory. It can be used at low pressures while still reaching the Knudsen region with relatively large capillaries. At atmospheric pressure capillaries too small to be made must be used to reach the Knudsen region.

C. DIFFUSION OF A MULTICOMPONENT GAS MIXTURE IN STRAIGHT CAPILLARIES

1. Theoretical Derivation

The derivation for a multicomponent mixture will be done in the following manner.³⁸ The equation for the total momentum lost by A in a gas mixture of A, B, and C will be the sum of the momentum transferred by A to the walls plus the momentum transferred by A to B and A to C. This can be converted to an equation relating dX_A to N_A , N_B , N_C , X_A , X_B , X_C , D_{AB} , D_{AC} , and D_{KA} . Similar equations can be written for B and C. These equations can then be combined to yield two differential equations.

These two differential equations will then be solved simultaneously for an exact solution which will relate the fluxes N_A and N_B to the concentrations X_{A0} and X_{AL} at both ends of the capillary. Another equation will relate N_A and N_B to X_{B0} and X_{BL} . A trial-and-error solution will then be necessary to solve for N_A and N_B directly.

Analytical solutions should also be obtained for other systems such as molecular diffusion in an open system, diffusion in the transition region in a closed system where $\sum N_i = 0$, molecular diffusion in an

open system with $N_c = 0$ for a solubility barrier, linearization of the transition region equation for a closed system, etc. It would be useful also to see if the above solutions exhibit osmotic or reverse diffusion. Numerical solutions for the above cases are also needed to give the physical significance of the equations.

2. Experimental Measurements

Using the straight capillary bundle, pure gas C will be passed by one side of the capillary plug and a mixture of A and B by the other side. No modifications to the equipment will be needed since premixed gases of A and B will be purchased and used. Samples of the exit gases will be obtained and analyzed by mass spectrometer. The pressure and the gas compositions will be varied and the results will be a check on the theoretical equations derived. These experiments will be done in the low- and the high-pressure apparatus.

D. DIFFUSION OF A BINARY GAS MIXTURE IN POROUS SOLIDS

1. Theoretical Derivations

An outline of the general method to be used to derive the equation for diffusion in a porous solid with three sharp peaks or pore sizes ($\bar{r}_a$, $\bar{r}_b$, and $\bar{r}_i$) follows. First, $\epsilon_a + \epsilon_b + \epsilon_i + \epsilon_s = 1.0$. It will be assumed that ϵ_i is the void fraction of the micropores in the powder particle and ϵ_a and ϵ_b the macropores between particles. Then taking a length of one powder particle in the compressed solid, the probability that two void areas will line up is proportional to the product of the two void fractions. The macropore, a, the smaller macropore, b, and the micropore, i, will line up in the following parallel paths with each path a series as follows: (a-a), (b-b), (i-i), (a-b), (a-i), and (b-i). Then using Eq. (1), the equation for the flux through each pore can be written. The sum of the individual fluxes and final D_e can be obtained.

For a mono-dispersed solid with a broad pore size distribution having no sharp peaks, it is doubtful that the equation for a mono-dispersed solid will be valid since the average value of D_{K_a} would have little meaning. This case could be treated by assuming the solid to be made up of n-sharp peaks of macropores outside the nonporous powder particles each with a different $\bar{r}$. Then, following the general method given for a tri-dispersed solid, a final equation could be derived for an n-dispersed solid.

These equations primarily utilize the random-pore concept. However, in other types of solids or in the same solids at higher pressures the random-pore model may not be applicable. Satterfield and Cadle¹³ found that the parallel pore model with an experimental

tortuosity gave better results with various catalysts than the random pore model. Hence, derivations should be tried utilizing some aspects of the tortuosity model alone or possibly in partial combination with the random-pore model.

2. Experiments with Various Porous Solids

A systematic study of the following porous solids over a large pressure range should help in testing models derived for various special cases, such as sharp-peak mono-dispersed, broad-peak mono-dispersed, bi-dispersed, and tri-dispersed solids. Also, the question of whether a small tortuosity correction factor is needed is unanswered in the case of porous solids.

A tri-dispersed alumina solid can be made from the same powder by using a very fine and a very coarse size of the powder compressed together. This should give two macropores and micropore. Such a solid has not yet been studied.

An alumina solid made from very fine powder particles will give a small macropore size somewhat larger than the micropores. This will mean that the micropore flow will be closer to 50% of the total instead of 10%. This will be a severe test of the models.

A solid made of nonporous powder particles such as ground glass or ground hard plastic could be compressed to a porous solid. Difficulties might be encountered in getting the powder to adhere. This solid would contain only macropores similar to those in the bi-dispersed solid. Hence, the true molecular region could be reached at lower pressures and the special equations for mono-dispersed solids would be tested.

A broad-peak mono-dispersed solid could be made by using a wide spectrum of sizes of nonporous powder particles. This would allow a check to be made on the theory derived for such a solid.

Finally, various combinations could be tried, such as a mixture of nonporous and alumina powder to give a special bi-dispersed solid. Solids such as molecular sieves could be used in the experiments; naturally occurring solids such as sandstone, etc., could be tried. Other solids such as compressed powder particles of Vycor, silica, or metals can also be used.

Since the data on Vycor are still uncertain, various types of heat-treated Vycor will be tried to see the effect of structure on diffusion rates. Also, grinding up the Vycor and compressing the powder would give a special bi-dispersed solid. Again, the particles may not adhere well.

To further check the theoretical models, experiments will be performed at high pressures also using the proposed high-pressure apparatus. These data will be obtained for binary mixtures and also for multicomponent mixtures.

E. DIFFUSION OF A MULTICOMPONENT GAS MIXTURE IN POROUS SOLIDS

No derivations exist for multicomponent diffusion in the transition region for porous solids. Such equations should be derived using the random pore model and other models. Numerical solutions of the differential equations will probably be needed. Experimental diffusion runs will be made in porous solids described in Section D2 to check validity of the predictions.

F. DIFFUSION PLUS COMBINED FORCED FLOW

Experiments will be performed using straight capillaries and a binary gas mixture where the total pressure on both ends of the capillary is different so diffusion plus combined forced flow will occur. The results will be used to test the various equations and assumptions proposed by others^{5,18,19,21} which have not been tested experimentally in capillaries. Various types of capillaries such as glass and metal will be used to see the effect of the type of surface on the forced flow term and its interaction with the straight diffusion term (which will be obtained by diffusion experiments). These experiments will be done in the present vacuum apparatus and proposed high-pressure apparatus.

After the results for the straight capillary have been obtained and adequate theories selected, modified, or rederived, then diffusion plus combined forced flow experiments can be done using porous solids to see the effects of different pore geometries and types of solid surfaces on the results. Equations will be derived for the effects of geometry on diffusion plus combined forced flow using some modifications of the tortuosity or random pore model.

New equations will be derived for multicomponent diffusion plus combined forced flow in capillaries and compared with experimental results at low and high pressures. Numerical solutions of these derived equations using the digital computer will probably be necessary.

G. DIFFUSION PLUS COMBINED SURFACE FLOW

To experimentally determine the amount of combined surface layer flow when diffusion is also occurring, straight diffusion experiments must first be performed in the Knudsen and transition regions. This is done by using He or another relatively nonadsorbable gas. Next, an

experiment is done with He and an adsorbable gas such as methane. Then the diffusion flux of the adsorbable gas is subtracted from the total flux for diffusion plus surface flow. However, it is not at all certain that the Knudsen equation is valid here because it is derived on the basis that a certain fraction of the molecules strike the wall and are reflected randomly. When a large adsorbed layer of an adsorbable gas is present on the walls, it is apparent that this could affect the Knudsen diffusion in the gas phase. Also, when this occurs in small pores of a porous solid of about 50 Å size, it is difficult to determine the proper diameter to use because of the thickness of the adsorbed layer which will reduce the open area for gas diffusion.

Experiments will be done using straight capillaries where the radius is relatively large compared to the adsorbed layer thickness. Adsorbable gases such as hydrocarbons will be used and studies will be made in the vacuum apparatus and the high-pressure apparatus using different capillary sizes and glass and metal capillaries. These different solid surfaces will be used to study their effect on the adsorbed layer flow.

Various porous solids will be used as mentioned in Section III.D. Also, the effect of a total pressure difference causing combined forced flow, surface layer flow, and diffusion will be studied.

H. EXPERIMENTS WITH LIQUIDS

Some of the equations derived for gases with the Knudsen contribution removed could be used for molecular diffusion of dilute liquids in solids. Solids made of Vycor or made from compressing powdered porous particles could be used in a diffusion cell similar to the one in use in this laboratory and described in papers by Perkins, Bidstrup, and Geankoplis.^{39,40,41}

IV. WORK DONE ON CONTRACT NO. AT(11-1)-1675 (April 1, 1967 to December 31, 1971)

The work done during the period of funding (April 1, 1967 to December 31, 1971) on the present contract is discussed below. Each of the sub-divisions below conforms to the same sub-division in Section III, Combined Proposed Research Programs for Two Three-Year Periods. The work done primarily in the last year and nine months of this contract is covered essentially in Sections A, B, and C below.

A. DIFFUSION OF GASES AT HIGH PRESSURES

At present the design and construction of the high-pressure diffusion apparatus is completed. The apparatus is designed to go to 1000 psia, which is higher than the 600 psia originally proposed. This

higher pressure is possible since a new method was devised to use the thermal conductivity cells at atmospheric pressures and not at operating pressures. The system is also designed for possible use under some vacuum. The pressure range which can be studied now in the present high-vacuum glass apparatus and the high-pressure apparatus will be from 0.15 mm to 1000 psia or a range of 345,000/1.

The equipment, shown schematically in Fig. 2, is to be used to conduct gaseous diffusion experiments at pressures in the range of about 1 to 70 atmospheres. The sections represented by the dark lines on the flowsheet are constructed of $\frac{1}{4}$ " 22-gauge, Type 304, stainless steel tubing. These sections are easily capable of withstanding the planned operating pressures. The sections represented by the lighter lines are not required to withstand high pressures and are fabricated from copper.

The diffusion cell shown in Fig. 2 is the main part of the equipment. It will contain either a porous-solid plug, or a plug comprised of a number of small, parallel capillaries imbedded in a nonporous matrix material. The second possibility is shown in an exaggerated form in the figure. The diffusion cell is a pressure chamber which permits exposure of the two faces of the plug to different gas streams flowing past the faces under high pressure.

Gas storage cylinders, designated G1 and G2 in the figure, each contain a different gas. When binary diffusion studies are to be made, a pure gas such as nitrogen or helium is contained in each cylinder. If measurement of three-component diffusion is the objective, one of the cylinders will contain a chemically analyzed mixture of two gases and the other a pure gas. Standard bottled-gas regulators R-1 and R-2 are attached to each of the gas storage cylinders. The regulators reduce the pressures of the gases admitted to the system from the high cylinder pressures to valves slightly above the system operating pressure.

The gases from G1 and G2 flow through separate, but identically constructed, branches of the system. Considering only the upper branch: the valves MV-1, MV-3, and MV-5 are Nupro Type M fine metering valves with micrometer handles and are used to reduce the pressure and direct the flow of gas entering the branch. Valve MV-3 reduces the pressure to the final value desired in the system and helps control the gas flow rate to the diffusion cell. Valve MV-5 throttles a portion of the incoming gas to atmospheric pressure and directs the gas to the reference side of the thermal conductivity cell TC-1. Valve MV-1 can be used to eject part of the incoming gas to the hood; thus, providing a damping action for the upstream pressure on MV-3 and MV-5. As a consequence of the use of valve MV-1, less frequent adjustment of valves MV-3 and MV-5 is required.

After passing valve MV-3 in the upper branch (or MV-4 if the lower branch is considered) the gas proceeds on to the diffusion cell if the system pressure does not exceed about 80 atmospheres. If the system

Fig. 2 - High Pressure Diffusion Equipment

pressure is too high, the safety valves, SV-1 and SV-2, exhaust the gas to the hood. The gas flow rates to the diffusion cell are calculated from measurements of their pressure drop through mechanically shielded lengths of precision bore capillary glass tubing, C-3 and C-4. Meriam Model 30 EL 120 high pressure manometers, FM-1 and FM-2, are used for pressure drop measurement. The line pressure is measured with calibrated Heise Model C pressure gages, P-1 and P-2.

Measurements of the thermal conductivity cell reference gases flow rates are also facilitated by measuring the pressure drop across precision bore capillary tubing (see C-1 and C-2). However, the manometers FM-3 and FM-4 used for this purpose are simple U-tube glass manometers since they need not withstand high pressures.

Another Meriam Model 30 EL 120 high-pressure manometer, P-3, is located between the two branches of the system just upstream of the diffusion cell. This manometer indicates any pressure difference across the diffusion cell. Should a pressure difference exist, gas flows as well as diffuses through the plug contained in the cell. Because bulk flow is undesirable since diffusion is being measured, corrective action must be taken to equalize the pressures in the two branches if a pressure difference is noted. Corrections are made by adjusting valves MV-1, MV-3, MV-5, and MV-7 for the upper branch or valves MV-2, MV-4, MV-6, and MV-8 for the lower branch.

After the gases in each branch flow by the faces of the diffusion cell, their pressures are reduced to slightly greater than atmospheric by valves V-21 and MV-7 (or by V-22 and MV-8). Valves MV-7 and MV-8 are Nupro Type BM extremely fine metering valves. Valves V-21 and V-22 are Nupro Type H bellows valves.

The gases from MV-7 or MV-8 can be directed either to the sample side of their respective thermal conductivity cells for measurements of the gas concentration or they can be by-passed. The thermal conductivity cells are Gow-Mac Model TR II B cells with hermetically sealed tungsten filaments. The cells are thermostated to operate at a constant temperature of 75°F. Although operation of the cells at high pressures is not planned, the cells are capable of operation at pressures up to 34 atmospheres. If the gases are by-passed around the thermal conductivity cells they can be sampled for mass spectrographic analysis by use of the "flow-through" type gas sampling vials, S-1 and S-2, and the three-way glass stopcocks, SC-1 through SC-4. A photograph of the high-pressure apparatus is shown in Fig. 3.

Some preliminary binary diffusion experiments have been conducted on the high-pressure apparatus using He and N₂ with mass spectrometry analyses. For these test runs, a solid containing collimated hole structures approximately 0.0018" I.D. was purchased and installed. A photomicrograph of this solid is shown in Fig. 4. Two other such structures of 0.00051" and 0.0041" I.D. are available for diffusion experiments. Results show that the experimental flux ratio calculated by

Fig. 3 - Photograph of High Pressure Apparatus

Fig. 4 - Photomicrograph of Collimated Hole Structure (200X), 0.0018" I.D.

material balance is within $\pm 5\%$ of the theoretical calculated by Eq. (4). Accurate deviations of experimental fluxes from predicted values are undetermined as yet because of uncertainty in the radius to be used in the theoretical flux Eq. (3). All runs to date have been primarily in the molecular region with a maximum run pressure of 250 psia. Present plans for future work, if funding is obtained, are to make runs from atmospheric pressure to 1000 psia in this collimated hole structure first. Then, a plug of multiple straight glass capillaries of smaller diameter will be used so that a broader range of the transition region at high pressures can be covered. These results should show the effects of nonidealities on the transition region equation.

B. DIFFUSION OF A BINARY GAS MIXTURE IN STRAIGHT CAPILLARIES

1. Types of Capillaries to be Used

A number of different types of capillaries have been purchased for use in diffusion experiments. In Fig. 5 photomicrographs are shown for the three sizes of glass capillaries at a magnification of 125X. The inside walls appear relatively smooth. Smaller glass capillaries have been ordered with I.D.'s of 0.0005" and 0.001". Also titanium, brass, and 304 stainless steel capillaries have been obtained with I.D. of 0.0034", 0.0036", and 0.0033", respectively. Photomicrographs of these metal capillaries are shown in Fig. 6. These inside walls are jagged and rough compared to the glass. Experiments on the varied types of metal and glass surfaces should elucidate any differences in the mechanism of Knudsen flow where the molecules primarily strike the walls in diffusing.

2. Vacuum Apparatus for Diffusion Runs

The novel vacuum apparatus in Fig. 1 has been modified considerably to obtain data for capillaries. Since the fluxes with capillaries are quite small, all large dead spaces in measuring lines to manometers had to be reduced in volume to reduce the excessive time needed to reach steady-state. A new oil manometer to indicate the pressure differences, if any, between the two sides of the diffusion cell was installed. This manometer can also be used to detect significant pressure drop between the point of measurement of absolute pressure (immediately downstream of FM-1 and FM-2 in flow diagram, Fig. 7, which will be described below) and the immediate vicinity of the capillary diffusion cell. This enables a correction to be made to the measured pressure in order to predict a theoretical flux as in Eq. (3). New lines were installed to allow samples of the two outlet gas streams to be taken for mass spectrometer analyses. In this way mass spectrometer analyses could be compared with the analyses from the TC cells if desired. Details are given below.

The equipment shown schematically in Fig. 7 is used to conduct gaseous diffusion experiments in fine pores in the approximate pressure

Fig. 5 - Photomicrographs of Glass Capillaries (125X)

0.0035" I.D.

0.0055" I.D.

0.0016" I.D.

Fig. 6 - Photomicrographs of Metal Capillaries (200X)

Titanium
0.0034" I.D.

Brass
0.0036" I.D.

304 Stainless Steel
0.0033" I.D.

Fig. 7 - Vacuum Apparatus Flow Diagram

range of 0.15 mm Hg to 1 atmosphere. The more thickly drawn lines in Fig. 7 indicate the main flow during a diffusion experiment. All flow lines shown in Fig. 7 are constructed from $\frac{1}{4}$ " glass tubing, except for the capillary flowmeters (designed FM), which are fine-bore glass capillaries. All metering valves for flow control (except MV-7, MV-8, MV-9, MV-10), denoted as MV, are Nupro Type M needle valves, some of which are equipped with vernier handles for fine adjustment. Other metering valves are needle valves made by Consolidated Vacuum Corporation. Valves MV-1 and MV-2 are standard regulating valves attached to gas storage cylinders G1 and G2, respectively. These valves are used to reduce cylinder pressures down to almost atmospheric. Valves marked V are high-vacuum hollow glass stopcocks, and those marked V-25, V-29, V-26 and V-30 are 3-way high-vacuum hollow glass stopcocks. Vacuum pumps are designated by VP in Fig. 7.

The cylinders G1 and G2 each contain a different gas. For binary diffusion studies He and N₂ gases are used as shown in Fig. 7. For three-component diffusion one storage cylinder would contain a chemically analyzed mixture of two gases and the other cylinder a pure gas.

Thermal conductivity cells included in this experimental apparatus, TC1 and TC2, are the same type as used in the high-pressure apparatus. Their use is identical to that described for the high pressure experimental work in Section A.

The diffusion cell shown exaggerated in Fig. 7 is the most important part of the apparatus. It is the device through which gases diffuse countercurrently at various levels of low pressure. For the case of binary diffusion, N₂ flows past the end of the cell through V-12 and out V-18. At this point the stream contains some diffused He on the N₂-rich side. He flows past the other side of the cell through V-11 and out V-17.

There are basically two types of cells. One is a nonporous matrix imbedded with many fine bore parallel capillaries (glass or metal). A number of the same size capillaries are used in parallel in a single cell in order to obtain measurable amounts of gas diffusing through the cell. The other type of cell is a plug made of a porous solid material.

The pressure indicators are of three types: mercury manometer, oil manometer, and McLeod gauge. Indicators P-6 and P-7 are McLeod gauges for measuring the absolute pressure on the N₂ and He sides of the diffusion cell, respectively. They are capable of measuring pressures from 2 μ to 10 mm Hg. Indicators P-2 and P-1 are absolute mercury manometers for use on the N₂ and He sides, respectively, when the system pressure is above the range of the McLeod gauges. Indicator P-3 is a new oil manometer used to detect overall pressure differences between the N₂ and He sides of the system. Indicators P-4 and P-5 are mercury and oil manometers, respectively, to measure the pressure drop across

FM-3. Manometers for flowmeters FM-1, FM-2, FM-4, and FM-5 are mercury and those for FM-6 and FM-7 are oil.

Gases from G1 and G2 flow through separate but essentially identical branches of the apparatus. Considering the upper (N_2) branch in Fig. 7, valves MV-4, MV-8 and MV-10 are used to throttle the flow to the indicated sections. Valve MV-8 directs pure N_2 gas to the reference side of the thermal conductivity cell TC2 using FM-4 as the flowmeter. A major portion of the gas by-passes TC2 to allow for a slow flow in the reference side. Valve MV-4 in combination with MV-10 helps to insure steady flow from G2 in which the pressure continuously decreases slowly. Valve MV-4 reduces pressure to the desired sub-atmospheric level for flow of N_2 past the diffusion cell. Fine control is obtained by further throttling with MV-10. This flow is metered by the pressure drop across FM-2 which contains a fine bore glass capillary. Absolute pressure measurements of the N_2 side are made using either P-2 or P-6. As the N_2 flows past the diffusion cell, it picks up some diffused He and enters the sample inlet of the thermal conductivity cell TC2, or it can be physically sampled for mass spectrographic analysis by use of the "flow-through" type gas sampling tube. Flow out of TC2 is metered by FM-6, which aids in eliminating the flow velocity dependency in the thermal conductivity cell.

For a particular diffusion experiment in which mass spectrometry is not used for analyses, the thermal conductivity cells must be calibrated. This is achieved by passing various known mixtures of N_2 and He through TC1 and TC2. The output voltage is recorded, and calibration yields a plot of output voltage versus concentration of N_2 in the He stream or the concentration of He in the N_2 stream. Flowmeter FM-3 is used to meter the flow of one gas into the other during calibration. For example, He can be bled through MV-11 and MV-12 into the N_2 stream (with V-21 and V-22 closed) to calibrate TC2. Indicator P-4 or P-5 is used to measure the pressure drop across FM-3. Indicator P-5 is used for pressure drops less than 1.5 cm Hg and P-4 for those greater than 1.5 cm Hg. A photograph of the vacuum apparatus is shown in Fig. 8.

3. Diffusion Experiments with Capillaries

Earlier calibrations³⁴ of the precision bore glass capillary flowmeters (FM-1 and FM-2 in Fig. 7) were checked experimentally with regard to possible H_2O vapor included in the original calibration technique. Originally, He, for example, flowed through FM-1, then through a small pool of aqueous soap solution, and finally up a 50 cc burette between regularly spaced soap films which were timed to obtain a flow rate. To check for an estimate of water vapor saturation in these earlier runs, the calibration apparatus was modified so as to accept various sizes of burettes (from 1.6cc up to 50cc) and to measure moisture content by means of drierite tubes. An electrical resistance wire was installed to rupture soap films after they had travelled up the burette so the exact time of contact of the gas with the wetted walls of the burette was known. Results showed that the gas streams

Fig. 8 - Photograph of Vacuum Apparatus

were 96% saturated. This is a conservative number because of the physical limitations of the modified calibration apparatus. Assuming 96% saturation resulted in the reduction of predicted flows from the original calibration curves by 3.2%

A method was devised to encase 272 glass capillaries in parallel in a plug which can be inserted in the vacuum apparatus (Fig. 7). Preliminary experiments indicated that this number of capillaries was needed to raise the outlet concentrations to measurable levels.

The first plug made used 0.00155" I.D. glass capillaries 0.747" long (see Fig. 9). Two preliminary diffusion experiments were made using this capillary plug and the binary gas mixture N_2 -He which gave fluxes within 12% of the theoretical calculated using Eq. (3).

It was determined that the flow regime in the precision bore glass capillary tubes used for metering flows (FM-1 and FM-2 in Fig. 7) was that of slip flow.⁴² In this regime the gas is not entirely a continuum, and the Hagen-Poiseuille flow equation is not strictly applicable. Consequently, the correction factor approach of Brown, et al.⁴² was used with the Hagen-Poiseuille equation. In this approach the true or experimental flow is expressed as

$$Q_{\text{experimental}} = (F) Q_{\text{Hagen-Poiseuille predicted flow}}, \quad (8)$$

where

$$F = 1.0 + A (X),$$

$$A = \text{Constant based on curve fit, and}$$

$$X = \frac{\mu}{P_{\text{mean}} r (\rho_1 g_c)^{1/2}}$$

It was felt necessary to more thoroughly investigate the empirical correlation by Brown for the slip flow region because of the importance of this factor in the measurement of flows during diffusion runs. Experimental data sources cited by Brown⁴² were used to construct an F vs. X curve between X = 0.0 and 0.1. Careful study of Todd's data used by Brown indicated these data should not be used because of the uncertainty of the temperatures of the runs. The remaining data were treated by least squares analysis to obtain the best straight line going through F = 1.0 at X = 0.0, the slope of which turned out to be A = 6.6773. Hence, the final equation used for flowmeters FM-1 and FM-2 in the vacuum apparatus is

$$Q_{\text{experimental}} = (1.0 + 6.6773X) Q_{\text{Hagen-Poiseuille predicted flow}} \quad (9)$$

Fig. 9 - Porous Plug with Multiple Capillaries

Figure 10 shows the F vs. X calculated data along with the least squares line.

In order to keep the value of F close to 1.0 and, thus, avoid dependence on a correction factor, higher flows were needed. Consequently, to keep concentrations of diffused components in a reasonable range, the number of capillaries in the diffusion plug had to be increased to produce greater amounts of the components in the outlet streams.

Another capillary plug was made similar to that described above with 272 capillaries. This new plug contained 644 unobstructed capillaries in parallel with an average I.D. of 0.00154" and an average length of 0.378."

Nine diffusion runs were made with the He-N₂ system using the 644-capillary plug in order to cover essentially the entire range between Knudsen and molecular diffusion. Concentration analyses were made by Battelle Memorial Institute with a mass spectrometer. The experimental points are plotted in Fig. 11 as $\ln D_e P$ vs. $\ln P$ with the Knudsen and molecular limits indicated. The data agree well with the theoretical curve calculated from Eq. (6). Table I summarizes the important results.

Table I. Results of Binary Vacuum Diffusion Runs

	He	N ₂
Average deviation of $(D_e)_{\text{expt'l.}}$ from $(D_e)_{\text{theor.}}$ - (without regard to sign)	5.5%	4.0%
Average deviation of $(D_e)_{\text{expt'l.}}$ from $(D_e)_{\text{theor.}}$ - (with regard to sign)	0.3%	-0.4%
Range of deviations of $(D_e)_{\text{expt'l.}}$ from $(D_e)_{\text{theor.}}$	-9.2 to + 8.6%	-6.4 to + 6.4%
Average experimental flux ratio, $\frac{N_{\text{He}}}{N_{\text{N}_2}}$		-2.666 (compared with -2.645 theoretical)
Range of concentrations in outlet streams (mole fraction)	0.016 - 0.169	0.005 - 0.055
Range of F factors used for FM-1 and FM-2	1.02 - 1.16	1.01 - 1.06

Fig. 11 - $D_e P$ versus P for Binary Diffusion Runs

Temperatures for all nine runs ranged from 26.5°C to 29.8°C with an average temperature of 28.0°C. The theoretical $D_e P$ vs. P curve shown in Fig. 11 is based on an average temperature of 28.0°C and average outlet concentrations of He and N_2 of 0.067 and 0.023, respectively. Two points are shown at a single run pressure because of basing experimental D_e calculations on either the He or N_2 fluxes.

This is the first confirmation of the binary equations for diffusion in an open system in fine capillaries having a well defined geometry. Significant progress thus has been made in understanding the diffusional process in such systems and in confirming the theoretical transition region Eq. (6) for binary gas mixtures in capillaries.

C. DIFFUSION OF A MULTICOMPONENT GAS MIXTURE IN STRAIGHT CAPILLARIES

1. Theoretical Derivation

An exact analytical solution has been obtained to the theoretical differential equations for diffusion of a three-component gas system in a capillary in the transition region. This work has been written as a research paper entitled, "Diffusion in Three-Component Gas Mixtures in the Transition Region Between Knudsen and Molecular Diffusion," by R. S. Cunningham and C. J. Geankoplis⁴³ and has been published by the Industrial and Engineering Chemistry Fundamentals Journal, 7, 429 (1968). Six reprints of this paper were sent to the Atomic Energy Commission in 1968.

Two sets of equations were obtained for an open system in the solutions, with one set being in an exponential form somewhat similar to the molecular diffusion equations of Toor⁴⁴ for three components in a closed system and the other set being in a sine-cosine form. The proper set to be used must be determined by trial and error. These equations are quite lengthy and are given in the paper by Cunningham and Geankoplis.⁴³

Like the equations of Toor, the exponential form may have a maximum or minimum in the concentration versus distance plot and the sine-cosine form may possibly have several maxima or minima. The equations are shown to have two singular points; they also show that a diffusion barrier can exist in this system.

To solve these two sets of equations for the actual fluxes and concentration gradients for given fixed pressures, different capillaries, and different boundary concentrations, a trial and error solution on the digital computer is needed. Complete parametric-type curves are needed since the physical significance of these equations is not readily apparent because of their extreme complexity.

2. Numerical Solution

Such a numerical study (mentioned in 1. above) has been completed for one phase of this theoretical study of diffusion of multicomponent gases. This work is based on the M.S. thesis of R. R. Remick⁴⁵ and has been written as a research paper entitled "Numerical Study of the Three-Component Gaseous Diffusion Equations in the Transition Region between Knudsen and Molecular Diffusion" by R. R. Remick and C. J. Geankoplis. This has been published by the Industrial and Engineering Chemistry Fundamentals Journal, 9, 206 (1970). Six preprints of this paper⁴⁶ were included with this report in 1968 to the Atomic Energy Commission.

In this paper a numerical solution to the equations for steady-state diffusion in a three-component gas mixture of helium, neon, and argon was obtained in the transition region between Knudsen and molecular diffusion in an open system. The fluxes N_i of helium (A) and neon (B) given in Fig. 12 showed the expected trends, increasing with pressure and approaching constant values at high pressures in the molecular region. The flux of argon (C) indicated that osmotic diffusion is occurring even though the concentration at both ends of the diffusion capillary was the same at 0.500 mole fraction. The shape of its flux versus pressure curve was also somewhat similar to that of a binary mixture. Reasons were given for this behavior. Osmotic or reverse diffusion cannot occur in the Knudsen region.

Under certain conditions the binary flux equations can be used to approximate the fluxes in a ternary mixture and reduce computational time. This method is discussed in detail in the paper by Remick and Geankoplis.⁴⁶ Figure 13 shows the ternary line for helium (A) as well as the bracketing lines from the binary flux equations, the form of which is given by Eq. (3). The binary line for A-B was calculated by using the Knudsen diffusivity of A and the molecular binary diffusivity of A-B in Eq. (3). Similarly, the binary line for A-C was calculated by using the same items as for A-B except for replacing the molecular binary diffusivity of A-B with that of A-C. The existence of a maximum or minimum point in the concentration versus distance plot was indicated for argon. Such a point was definitely shown for molecular diffusion in a closed ternary system.

An interesting conclusion is that the flux ratios of A to B and/or A to C can change slightly or markedly with pressure in the transition region depending on the concentration gradient of each component. This could possibly be the basis of a separation process. This is contrary to binary mixtures for diffusion in the transition or molecular regions or multicomponent mixtures in molecular diffusion where the flux ratios are constant.

Equations were derived for maxima and minima in the concentration versus distance plots. A minimum was found in the case of CO_2 in the ternary system CO_2 , H_2O , and H_2 in a closed system in the molecular region.

Fig. 12 - $\frac{N_i P}{P/RTL}$ versus P

Fig. 13 - Comparison of Binary and Ternary Equations

Recent work has shown it is possible to solve the two sets of equations mentioned in Section C.2. above for the fluxes by employing a modification of the nonlinear optimization technique described by Wilde and Beightler.⁴⁷ Calculation time is drastically reduced. As an example, for a given set of physical parameters and concentrations, several points describing an entire transition curve showing fluxes of A, B, and C versus pressure can be obtained in less than 0.5 minute of computing time on the IBM System/370 Model 165.

3. Experimental Measurements

A pre-mixed cylinder of pure neon and argon gases (approximately 55% neon) was purchased from the Matheson Company. In order to ensure that the two gases are well-mixed in the cylinder during an experimental diffusion run, a heating device was constructed to induce convection currents within the cylinder. This consisted of an asbestos-lined box covering roughly the bottom one-fourth of the cylinder, a 300-W incandescent lamp, and two small fans. Another box enclosing the lamp was mounted next to the inlet of the box in which the cylinder bottom was contained. A fan was mounted so as to force ambient air over the lamp in the first box, past the cylinder bottom in the second box, and out through an exhaust, thus heating the cylinder bottom slightly. Simultaneously, a fan was mounted so as to force ambient air over the top of the cylinder for cooling. Tests were made to ensure the gas temperature, after flowing through several feet of copper tubing, was essentially ambient before reaching the flowmeter FM-2 in Fig. 7. In addition to heating, before each multicomponent run, the binary cylinder was rolled on a ball mill in each direction for one-half hour to ensure pre-mixing.

To predict gas flow rates for a binary gas through flowmeter FM-2 in Fig. 7, it is necessary to have a viscosity of the binary mixture and to know how it varies with ambient temperature. A polynomial least squares fit was performed on viscosity-versus-composition data for Ne-Ar mixtures in the Landolt-Boernstein Tables.⁴⁸ The resulting best fit at 20°C is as follows:

$$\mu \times 10^4 = 3.1150073 - 1.134936(x_{Ar}) + 0.24389976(x_{Ar})^2 \quad (10)$$

The same relative change in μ with temperature was evident in the Landolt-Boernstein Tables data, as was seen in the Wilke viscosity equation for gas mixtures, although the absolute viscosity values predicted by the Wilke equation for Ne-Ar as compared with tabular data differed by a few percent. Consequently, a true viscosity of Ne-Ar was estimated by taking the ratio of the Wilke predicted value to the least squares value from Eq. (10), all at 20°C, and applying this factor to the Wilke value estimated at the actual run temperature. A check of this estimated value was made by making a soap bubble calibration run with the Ne-Ar mixture.

The same 644-capillary diffusion plug used in the binary vacuum diffusion runs described in Section B.3 was used to conduct five experimental ternary diffusion runs on the vacuum apparatus. All runs were made with the Ne-Ar mixture flowing on the FM-2 side of the apparatus shown in Fig. 7 and pure He on the other. Outlet concentrations as well as Ne-Ar feed composition were analyzed by Battelle Memorial Institute with a mass spectrometer. The experimental points are plotted in Fig. 14 as $\ln [N_i P / (P/RTL)]$ vs. $\ln P$ with the Knudsen and molecular limits indicated, and they agree reasonably well with the theoretical curves computed as explained in Section C.2. for the given physical system. Table II summarizes the important results.

Temperatures for all five runs ranged from 27.2°C to 28.3°C. The theoretical flux curves in Fig. 14 are based on a temperature of 27.5°C and end concentrations of He of 0.96 and 0.06.

It should be emphasized that the results shown in Fig. 14 and given in Table II are preliminary. Further refinements will be incorporated in calculations due to the following: Because of the measurement of more experimental variables in a diffusion run than necessary to make the number of unknowns and equations the same in this ternary system, there are several different ways of computing the same theoretical and experimental fluxes. Consequently, investigation of the various ways of computation is being carried out in order to arrive at the best computation. However, it is expected that the investigation of these various computational methods will give final results which do not vary by more than a few percent from the preliminary results given here.

The fact that the experimental fluxes for Ne and Ar both are apparently relatively high from theoretical at the lowest run pressure may possibly be accounted for by two factors. Because of the low pressure of the run, some difficulty was experienced in making duplicate analyses of the samples, thus making the results for that run somewhat less accurate than for others. In addition, the relatively low flow of He caused the use of a relatively high F correction factor in the flow prediction. Hence, a greater uncertainty exists in these results for the lowest run pressure.

This work is the first confirmation of the ternary equations for transition region diffusion in an open system in fine capillaries. The results confirm the theoretical equations derived by Cunningham and Geankoplis⁴³ and the numerical computational methods presented by Remick and Geankoplis.⁴⁶ For the most part, runs at lower pressures tend to support the theory of independent transport of various species, regardless of the number of species present. This ternary work, together with the binary results given in Section B.3, complete the main goals in the study of diffusion in capillaries. However, other investigations should be carried out to examine the effect of wall roughness, capillary size, adsorbed layer flow, etc. on true Knudsen and transition region diffusion.

Fig. 14 - $\frac{N_i P}{P / RTL}$ versus P for Multicomponent Runs

Table II. Results of Ternary Vacuum Diffusion Runs

	<u>He</u>	<u>Ne</u>	<u>Ar</u>
Average deviation of $(N_i)_{\text{expt'l.}}$ from $(N_i)_{\text{theor.}}$ -(without regard to sign)	6.6%	8.6%	7.0%
Average deviation of $(N_i)_{\text{expt'l.}}$ from $(N_i)_{\text{theor.}}$ -(with regard to sign)	-1.5%	+5.7%	+0.3%
Range of deviations of $(N_i)_{\text{expt'l.}}$	-10.3 to +6.8%	-7.1 to +29.7%	-7.8 to +18.3%
Range of concentrations in outlet streams (mole fraction)	0.047 - 0.065	0.024 - 0.034	0.014 - 0.019
Range of F factors used for FM-1 and FM-2	1.02 - 1.36	1.01 - 1.09	

D. DIFFUSION OF A BINARY GAS MIXTURE IN POROUS SOLIDS

1. Theoretical Derivations

A research paper entitled, "Effects of Different Pore Structures of Porous Solids on the Diffusion of Gases in the Transition Region," by R. S. Cunningham and C. J. Geankoplis⁵⁰ has been published in the Industrial and Engineering Chemistry Fundamentals Journal, 7, 429 (1968). Six reprints of this paper were included with this report in 1968 to the Atomic Energy Commission.

In this research paper, theoretical equations were derived for a pore structure containing one micropore and many sizes of macropores. A synthetic porous solid was made of this type of pore structure and the experimental data checked the predicted data. A discussion of the theoretical derivation follows.

Many industrial catalysts made by compressing powder particles cannot be represented by a model consisting of two sharply defined peaks of one micropore and one macropore. It is possible to have three or more peaks or even a broad pore size distribution. Thus, the bidispersed random pore model should be extended to include multidispersed porous solids.

The following derivation is done for one micropore, i , in the individual powder particle and two macropores, a and b , in the region surrounding the compressed powder particles. The model is given in Fig. 15.

The relation between the porosities is

$$\epsilon_a + \epsilon_b + \epsilon_i + \epsilon_s = 1.0 \quad (11)$$

The unit cell consists of two powder particles with two different macropore sizes separating the particles. The contribution of each particle in a unit cell is $(1 - \epsilon_a - \epsilon_b)/2$ or $(\epsilon_i + \epsilon_s)/2$. There are six combinations of pore alignments in Fig. 15. If the areas given above are multiplied by the number of paths, the sum is unity. Applying these areas and paths to Eqs. (1) and (2) and summing, the result is the differential diffusivity. Details are given in the paper.⁵⁰

Extending the equation to include one micropore and n macropore regions the final equation for the integrated D_e is

Fig. 15 - Diffusion Paths in a Tridispersed Medium

$$\begin{aligned}
D_e = & \frac{D_{AB}}{\ln \left[\frac{1 - \alpha X_{A_L}}{1 - \alpha X_{A_O}} \right]} \left[\epsilon_i^2 \frac{\alpha(X_{A_O} - X_{A_L})}{1 - \alpha \left[\frac{X_{A_O} + X_{A_L}}{2} \right]} + \frac{D_{AB}}{\bar{D}_{K_i}} \right. \\
& \left. \sum_n \epsilon_n \sum_j \epsilon_j \left\{ \ln \left[\frac{2(1 - \alpha X_{A_L}) + D_{AB}/\bar{D}_{K_n} + D_{AB}/\bar{D}_{K_j}}{2(1 - \alpha X_{A_O}) + D_{AB}/\bar{D}_{K_n} + D_{AB}/\bar{D}_{K_j}} \right] \right\} + \right. \\
& \left. \sum_n \frac{4\epsilon_n(1 - \sum_j \epsilon_j)}{1 + [(1 - \sum_j \epsilon_j)^2 / \epsilon_i^2]} \right. \\
& \left. \frac{\alpha(X_{A_O} - X_{A_L})}{1 - \alpha \left[\frac{X_{A_O} + X_{A_L}}{2} \right]} + \frac{D_{AB}/\bar{D}_{K_i}}{1 + [\epsilon_i^2 / (1 - \sum_j \epsilon_j)^2]} \right] \quad (12)
\end{aligned}$$

The first term on the right side of Eq. (12) is the micropore term (i-i), the second includes all the macropore combinations, and the third includes all the micro-macropore series terms.

Also an equation was derived for a solid where some of the micropores were blocked off by glass powder particles.⁵⁰ Such a solid was made and experimental data checked the theoretical equation as shown in Fig. 16. Also, in Fig. 16, a solid with a broad macropore distribution is shown and the data check Eq. (12) quite well for three macropores.

Hence, the phase of the work for theoretical derivations for porous solids using the random pore model has largely been completed for binary gases. However, new equations need to be derived for other kinds of porous solids made by methods other than compressing powders. These equations will use the random pore and/or the tortuosity models in the derivations.

2. Experiments with Various Porous Solids

In this same paper⁵⁰ experimental data were also given for diffusion of gases in porous alumina solids made by compressing a powder in the Knudsen and most of the transition region. Keeping the micropore

Fig. 16 - Effect of Broad Macropore Size Distribution
(Solid 3) and Blockage of Micropores
(Solid 4) on D

structure constant, the macropore radius and bulk density were varied over a wide range. This gave a solid where more than 90% of the flow was in the macropores and also a solid where less than 17% was in the macropores, which should be a severe test of a predicted model. The experimental data compared quite closely with those predicted by the random pore model. In addition, a comparison was made with the so-called effectiveness factor model.⁵⁰ Results are shown in Fig. 17.

At present many other types of porous solids remain to be investigated, as discussed in Section III.D.2.

E. DIFFUSION OF A MULTICOMPONENT GAS MIXTURE IN POROUS SOLIDS

To date no work has been done in this area. However, because of the already proven success of the technique for feeding Ne-Ar to the vacuum apparatus, it remains only to insert various porous solids into the diffusion cell in place of the present capillary plug. The random pore model equation could be rederived and modified for porous solids using multicomponent gases. Both alumina and Vycor solids would be used in the experiments. Other pore models such as those using tortuosity could also be used.

F. DIFFUSION PLUS COMBINED FORCED FLOW

At present no results have been obtained in this area.

G. DIFFUSION PLUS COMBINED SURFACE FLOW

To date no work has been done in this area.

H. EXPERIMENTS WITH LIQUIDS

At present no work has been done on molecular diffusion of dilute liquids in porous solids.

I. SIGNIFICANCE OF THIS WORK FOR FUTURE RESEARCH

Research in the area of diffusion of gases in small capillaries should be continued because of the importance in catalysis and separation processes in general, as well as in applications to environmental problems. Particularly, work should be concentrated in the areas of effects of surfaces of the capillaries on transition region diffusion, interactions between species in multicomponent diffusion in the transition and molecular regions, effects of forced flow and surface diffusion, and the effects of high-pressure nonidealities.

Fig. 17 - Experimental and Predicted Diffusivities for Solids 1, A, and 2.

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