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

For the period..... 1 April 1967 - 31 March 1968

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ABSTRACT

The diffusion of gases in small, straight capillaries or in porous media in the range of very low to high pressures is important in many areas. These areas include diffusion in porous catalysts, separation of gases in porous barriers, 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, as pressure, pore geometry, and the number of individual gases present, are still very uncertain in these predictions.

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.

Experimental data were recently obtained in this laboratory for diffusion of binary gases in different synthetic porous structures. One solid contained one micropore size and many macropore sizes, while another contained one macropore and two micropores. Theoretical equations were derived for these cases using a modified random pore model and the experimental data checked the predicted data. The data covered a 1300/1 pressure range which included the Knudsen and most of the transition region.

A high pressure apparatus has been designed and is being constructed to extend the range of pressures to 345,000/1 which will allow all three regions to be studied. A method has been devised to make a plug containing 100 straight capillaries in parallel. Preliminary experiments are being carried out to test the theoretical capillary equation.

A solution to the differential equations for diffusion of a three-component gas mixture was obtained for the complete transition region in an open system. The equations indicate that a maximum or minimum can occur in the concentration plot and that under certain conditions a diffusion barrier can exist.

LIST OF SYMBOLS

Symbol

D_{AB}	Molecular diffusivity for system A-B, cm^2/sec
D_e	Diffusion coefficient defined by Eq. (4), 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_N	Diffusion coefficient defined by Eq. (1) in a tube, cm^2/sec
L	Actual length of porous solid, cm
M	Molecular weight
N_A	Diffusion flux, g mol A/sec- cm^2
N_K	Knudsen number, $\lambda/2r$
P	Pressure, mm Hg
R	Gas constant
\bar{r}	Pore radius, cm
T	Temperature, $^{\circ}\text{K}$
X_A	Mole fraction A
α	Flux ration, $1 + N_B/N_A$
ϵ	Void fraction
λ_A	Mean free path of A, cm

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

I. INTRODUCTION AND WORK DONE BY OTHERS

The diffusion of gases in fine, straight capillaries or in porous structures in the range of very low to high pressures is important today in many areas, as diffusion in porous catalysts, separation of gases by porous barriers, diffusion in capillaries and high vacuum equipment. At present, there are few models and theories available for predicting the diffusion in these situations. Following is a discussion of the pertinent experimental results, theoretical equations, and physical models for diffusion over a wide range of pressures.

In those studies that have been presented 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.

Rothfeld,² Scott and Dullien,⁵ and Evans et al.⁶ developed similar theoretical equations for the transition region. They^{2,5} 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_N and flux are

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

$$N_A = - \frac{D_N P}{RT} \frac{dX_A}{dL} \quad (2)$$

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.

Integration of Eq. (2) gives

$$N_A = \frac{D_{AB}P}{\alpha RTL} \ln \left[\frac{1 - \alpha X_{A_L} + D_{AB}/D_{KA}}{1 - \alpha X_{A_0} + D_{AB}/D_{KA}} \right] \quad (3)$$

Equation (1) is the main theoretical equation for a tube for the entire transition region. Rothfeld² showed that the transition from Knudsen to molecular diffusion covers a 1000-fold range of mean free paths or pressures. Previously it had been supposed⁵ that this region extended from values of \bar{r}/λ of 0.1 to 10. Evans et al.⁶ and Scott and Dullien¹² 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

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

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 Vycor⁹ 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

$$D_e = \frac{D_{AB}}{\ln \left[\frac{1 - \alpha X_{A_L}}{1 - \alpha X_{A_0}} \right]} \left[\epsilon_a^2 \ln \left[\frac{1 - \alpha X_{A_L} + D_{AB}/\bar{D}_{Ka}}{1 - \alpha X_{A_0} + D_{AB}/\bar{D}_{Ka}} \right] + \epsilon_i^2 \frac{\alpha(X_{A_0} - X_{A_L})}{1 - \frac{\alpha}{2}(X_{A_0} + X_{A_L}) + D_{AB}/\bar{D}_{K_i}} \right. \\ \left. + \frac{4\epsilon_a(1-\epsilon_a)}{1 + \frac{(1-\epsilon_a)^2}{\epsilon_i^2}} \frac{\alpha(X_{A_0} - X_{A_L})}{1 - \frac{\alpha}{2}(X_{A_0} + X_{A_L}) + \frac{D_{AB}/\bar{D}_{K_i}}{1 + \epsilon_i^2/(1-\epsilon_a)^2}} \right] \quad (4)$$

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

Johnson and Stewart⁷ assumed a model similar to others for porous solids^{2,5,6} 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 Schwartz⁸ 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 Butt¹⁰ 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.¹¹ 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.

All of the previous experiments covered only a limited 50/1 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.

II. PREVIOUS RESEARCH DONE IN THIS LABORATORY

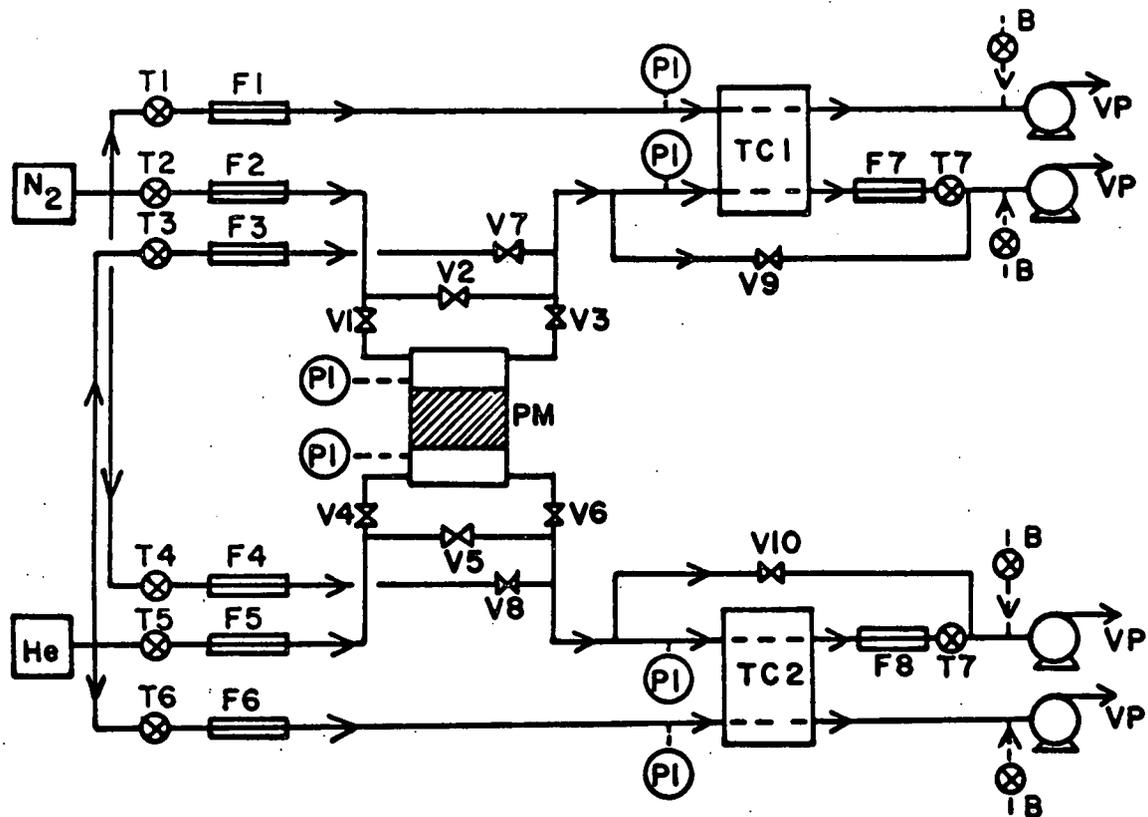
The following work⁴ was done in this laboratory just before the United States Atomic Energy Commission's Contract No. AT(11-1)-1675 was obtained. The financial aid for this work was provided mainly by the Department of Chemical Engineering, The Ohio State University, and by several industrial fellowships. This research was published in Chemical Engineering Science (1967) Vol. 22, pp. 11-20. Six reprints are included with this progress report under separate cover.

The process flow and diffusion apparatus to measure experimentally both of the countercurrent fluxes are shown in Fig. 1 and described in detail elsewhere.^{15,16} Wicke and Kallenbach¹⁷ originally described this type of apparatus. For a diffusion run, valves V2, 5, 7, and 8 were closed and V1, 3, 4, 6, 9, and 10 were opened.

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.

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



After each diffusion run, a calibration of the thermal conductivity cells was made at the same pressure by opening valves V2, 5, 7, 8, 9, and 10 and closing valves V1, 3, 4, and 6. The outlet sample stream was bypassed and a known mixture of N₂-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/l range of pressures which included the Knudsen and most of the transition region. Previous data covered only a 50/l 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 due to 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. PROPOSED RESEARCH PROGRAM FOR THREE-YEAR PERIOD (April 1, 1967 - March 31, 1970 for Contract No. AT(11-1)-1675)

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 three-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/l 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/l range.

It is proposed to also construct a new high pressure apparatus to expand the top pressure from 600 mm to 600 psia or a new range of 51.7/l. Hence, the new over-all range would be 200,700/l. This would enable all

experiments to reach the true molecular region even in a bi-dispersed solid. In the micropores of the alumina solids at 600 mm, the N_{K_i} was 0.1 in solid 1. Using this new pressure range and capillaries, the Rothfeld capillary Eq. (1) can also be tested. At high pressures in bi-dispersed solids, the per cent flow through the micropores will be about 50% instead of the 10% at 600 mm.

B. Diffusion of a Binary Gas Mixture in Straight Capillaries

Diffusion experiments will be performed to make a direct experimental test of Eq. (1) 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.

It has been calculated that 10 glass capillaries, each one-inch long, and having a radius of 0.010 mm, and arranged in a parallel bundle, are needed. This will give sufficient diffusion rates so that accurate measurements can be made in the present apparatus. These capillaries can easily be made by drawing out glass tubes. The bundle 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.

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.¹³ 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_{A_0} and X_{A_L} at both ends of the capillary. Another equation will relate N_A and N_B to X_{B_0} and X_{B_L} . A trial and error solution will then probably be necessary to solve for N_A and N_B directly.

2. Experimental Measurements

Using the straight capillary bundle, pure C will be passed by one side of the plug and a mixture of A and B by the other side. The equipment will be modified to meter the third component. Samples of the exit gas streams will be analyzed by the mass spectrometer or gas chromatograph. The pressure will be varied in these diffusion experiments.

D. Diffusion of a Multicomponent Gas Mixture in Porous Solids

The random pore model equation will be rederived and modified for porous solids and multicomponent gases using the derivation for capillaries. Experimental diffusion runs will be made in alumina and Vycor solids to check these predictions.

E. 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.

2. Experiments with Various Porous Solids

A systematic study of the following porous solids over a large

pressure range should help in testing the 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 a 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.

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.

F. Experiments with Liquids

As discussed previously, many of the equations derived should hold for molecular diffusion of dilute liquids but no adequate experimental data are available. Some of the solids mentioned, as Vycor and those made from nonporous solids, could be tried with liquids. A diffusion cell, similar to the one used in previous work in this laboratory, will be used.¹⁴

IV. WORK DONE ON CONTRACT NO. AT(11-1)-1675, APRIL 1, 1967 TO PRESENT

The work done during the first year of the proposed three-year study on the present contract is discussed below. Each of the subdivisions below conform to the same subdivisions in Section III, Proposed Research Program.

A. Diffusion of Gases at High Pressures

At present the design and process flow diagram 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 to possibly be used under some vacuum. The new 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 psi absolute or a range of 345,000/l.

The system will be primarily stainless steel on the high pressure region with some brass in the low pressure region of the apparatus after the diffusion cell (Fig. 1). All valves on the high pressure side will be bellows-type and capillaries with special manometers will be used as in the low pressure apparatus, to measure small flows. The selection of all the components and various pieces of equipment has been completed and purchase orders issued. Upon arrival of all the components the apparatus will be assembled, tested for leaks, and the various capillary flow meters calibrated. Experiments at high pressures will be conducted as discussed in Section III and in the following subsections.

B. Diffusion of a Binary Gas Mixture in Straight Capillaries

Satisfactory and uniform glass capillaries, having an I.D. of 0.002, 0.003 and 0.004 inch, were purchased. Also purchased was a stainless steel capillary of 0.002 inch and a brass capillary of 0.003 inch. Under the microscope the inside surfaces of the glass capillaries were very smooth while those of the metal capillaries were quite jagged and rough.

A method has been devised to encase 100 glass capillaries in parallel in a plug of beeswax which can be inserted in the vacuum apparatus (Fig. 1) in place of the porous medium plug.

Preliminary diffusion runs are now being made on the capillary plug. It is intended to carry out these experiments with binary gases

using several sizes of glass capillaries at low pressures. These experiments will be carried out using the metal capillaries to see the effects, if any, of the roughness of wall on the diffusion. A method will be devised to make these same types of plugs which will withstand high pressures. Diffusion data will be obtained up to 1000 psia, which will reach the true molecular region. These data will be a check on the theoretical Eq. (1) which covers the Knudsen, transition, and molecular regions.

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. Geankoplis¹⁸ and has been forwarded to the Industrial and Engineering Chemistry Fundamental Journal for publication. Six preprints of this paper were sent to the United States Atomic Energy Commission in September, 1967.

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 Toor²⁰ 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.

Unlike 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 computer is needed. Complete parametric-type curves should be obtained since the physical significance of these equations is not readily apparent because of their extreme complexity.

2. Experimental Measurements

Using the capillary bundle, pure C will be passed by one side of the capillary plug and a mixture of A and B by the other side of the plug. 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 gas chromatograph or sent out for analysis by mass spectrometer. The pressure and the gas compositions will be varied and the results will be a check on the theoretical equations derived.

D. Diffusion of a Multicomponent Gas Mixture
in Porous Solids

After experimental measurements are made for multicomponent mixtures in capillaries, these mixtures will also be used in porous solids. The random pore model equation will be rederived and modified for porous solids using multicomponent gases. Both alumina and Vycor solids will be used in the experiments.

E. 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. Geankoplis¹⁹ has been sent to the Industrial and Engineering Chemistry Fundamentals Journal for publication. Six preprints of this paper were sent to the United States Atomic Energy Commission in October, 1967.

In this research paper, theoretical equations were derived for a pore structure containing one micropore and many sizes of macropores and for a structure containing one macropore but two micropores. Synthetic porous solids were made of these two types of pore structure and the experimental data checked the predicted data.

Hence, the phase of the work for theoretical derivations for porous solids using the random pore model has 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.

2. Experiments with Various Porous Solids

In this same paper¹⁹ experimental data were 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 structure constant, the macropore radius and bulk density were varied over a wide range. This gave a solid where over 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.

At present many other types of porous solids remain to be investigated as discussed in Section III-E.

F. Experiments with Liquids

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

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