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MASTER

TECHNICAL PROGRESS

REPORT

By

THE OHIO STATE UNIVERSITY
RESEARCH FOUNDATION

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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 1969 - 31 March 1970

Submitted by Dr. Christie J. Geankoplis

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Date 28 November 1969

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ABSTRACT

The diffusional transport of gases in porous media or relatively unde-fined 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 capil-laries 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. These studies do not consider surface diffusion or ad-sorbed layer flow.

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 were recently obtained in this laboratory for diffu-sion 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 equa-tions derived 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 272 straight glass capil-laries in parallel. Two preliminary experimental diffusion runs were made in the transition region and checked the theoretical transition region equation reasonably well. Further experiments will 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. The high pressure apparatus has been designed and constructed to extend the range of pressures covered to 345,000/1.

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 diffu-sion 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 interesting conclusion is that the flux ratios can change with pressure in the transition region. This could possibly be the basis for a separated process.

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LIST OF SYMBOLS

I. INTRODUCTION AND PREVIOUS 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 pertinent experimental results, theoretical equations, and physical models for diffusion over a range of pressures. The studies presented in this discussion consider only diffusion in the gas phase and not surface diffusion or adsorbed layer flow.

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 Smith[1] and Rothfeld[2] 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 Wheeler[3] 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,[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_A} and flux are

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

$$N_A' = -\frac{D_{N_A} P}{RT} \frac{dX_A}{dL} = \frac{D_{N_A} P}{RTL} (X_{A_0} - X_{A_L}) \tag{2}$$

Several assumptions are made in this derivation: The square of the drift velocities is $<<$ 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.

1

Integration of Eq. (2) gives

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

Equations (1) and/or (3) are the main theoretical equations for a straight capillary tube for the entire transition region. Rothfeld[2] showed that the transition from Knudsen to molecular diffusion covers a 1000-fold range of mean free paths or pressures. Previously it had been supposed[5] that this region extended from values of $\bar{r}/\lambda$ of 0.1 to 10. Evans et al.[6] and Scott and Dullien[12] 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

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

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. Rothfeld[2] and Scott and Dullien[5] 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_{N_A} by

$$D_e = D_{N_A}\,\frac{\alpha(X_{A_0} - X_{A_L})}{\ln\left[\dfrac{1-\alpha X_{A_L}}{1-\alpha X_{A_0}}\right]} \qquad (5)$$

Combining Equations (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

$$D_e = \frac{D_{AB}}{\ln\left[\dfrac{1-\alpha X_{A_L}}{1-\alpha X_{A_0}}\right]}\,\ln\left[\frac{1-\alpha X_{A_L} + D_{AB}/D_{KA}}{1-\alpha X_{A_0} + D_{AB}/D_{KA}}\right] \qquad (6)$$

Wakao and Smith[1] 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 Vycor[9] deviated markedly.

2

The random pore model of Wakao and Smith[1] 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

$$
D_e = \frac{D_{AB}}{\ln\left[\frac{1-\alpha X_{AL}}{1-\alpha X_{A0}}\right]} \left[\epsilon_a^2 \ln\left[\frac{1 - \alpha X_{A_L} + D_{AB}/\bar{D}_{Ka}}{1 - \alpha X_{A_0} + D_{AB}/\bar{D}_{Ka}}\right] + \epsilon_i^2 \frac{\alpha(X_{A_0}-X_{A_L})}{1 - \frac{\alpha}{2}(X_{A_0}+X_{A_L}) + D_{AB}/\bar{D}_{Ki}} \right.
$$

$$
\left. + \frac{4\epsilon_a(1-\epsilon_a)}{1 + \frac{(1-\epsilon_a)^2}{\epsilon_i^2}} \frac{\alpha(X_{A_0} - X_{AL})}{1 - \frac{\alpha}{2}(X_{A_0}+X_{A_L}) + \frac{D_{AB}/\bar{D}_{Ki}}{1 + \epsilon_i^2/(1-\epsilon_a)^2}} \right] \tag{7}
$$

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

Johnson and Stewart[7] 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 Schwartz[8] 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 Butt[10] 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 work[4] 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 <u>Chemical Engineering Science</u> (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[15,16]. Wicke and Kallenbach[17] 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.

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 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 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.

Fig. 1. Process Flow Diagram

T   Throttle Valve

V   Open or shut valve

F   Capillary flow meter (calibrated by soap film burette meter)
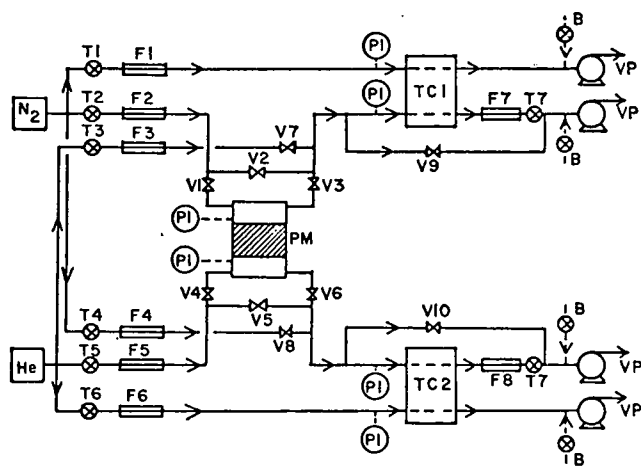
PI   McLeod gage, Pirani, or Hg manometer

B   Bleed for pressure control

VP   Vacuum pump

TC   Thermal conductivity cell

PM   Porous medium

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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 600 psia or a new range of 51.7/1. Hence, the new over-all range would be 200,700/1. 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 determined that glass capillaries, each one-inch long, and having 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.

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_O} and X_{B_L}. A trial and error solution will then 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]

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IV. WORK DONE ON CONTRACT NO. AT(11-1)-1675,
APRIL 1, 1967 TO PRESENT, NOVEMBER 28, 1969.

The work done during the three years of the proposed three-
year study on the present contract is discussed below. Each of the
sub-divisions below conform to the same subdivisions in Section III,
Proposed Research Program for Three-Year Period. The work done pri-
marily in the last year of this contract is covered in Sections IV-A
and IV-B below.

A. Diffusion of Gases at High Pressures

At present the design and construction of the high pressure diffu-
sion 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 pres-
sures. 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 psia or a range of 345,000/1.

The equipment shown schematically in Fig. 2 is to be used to con-
duct gaseous diffusion experiments at pressures in the range of about
1 to 70 atmostpheres. The sections represented by the dark lines on
the flowsheet are constructed of $\frac{1}{4}$-inch, 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; therefore, they are
fabricated from copper.

The diffusion cell shown in Fig. 2 is the main part of the equip-
ment. 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, will
each contain a different gas. When binary diffusion studies are to be
made, a pure gas such as nitrogen or helium will be 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 to be attached to each of the gas storage cylinders. The
regulators will 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 will flow through separate, but identi-
cally constructed, branches of the system. Considering only the upper
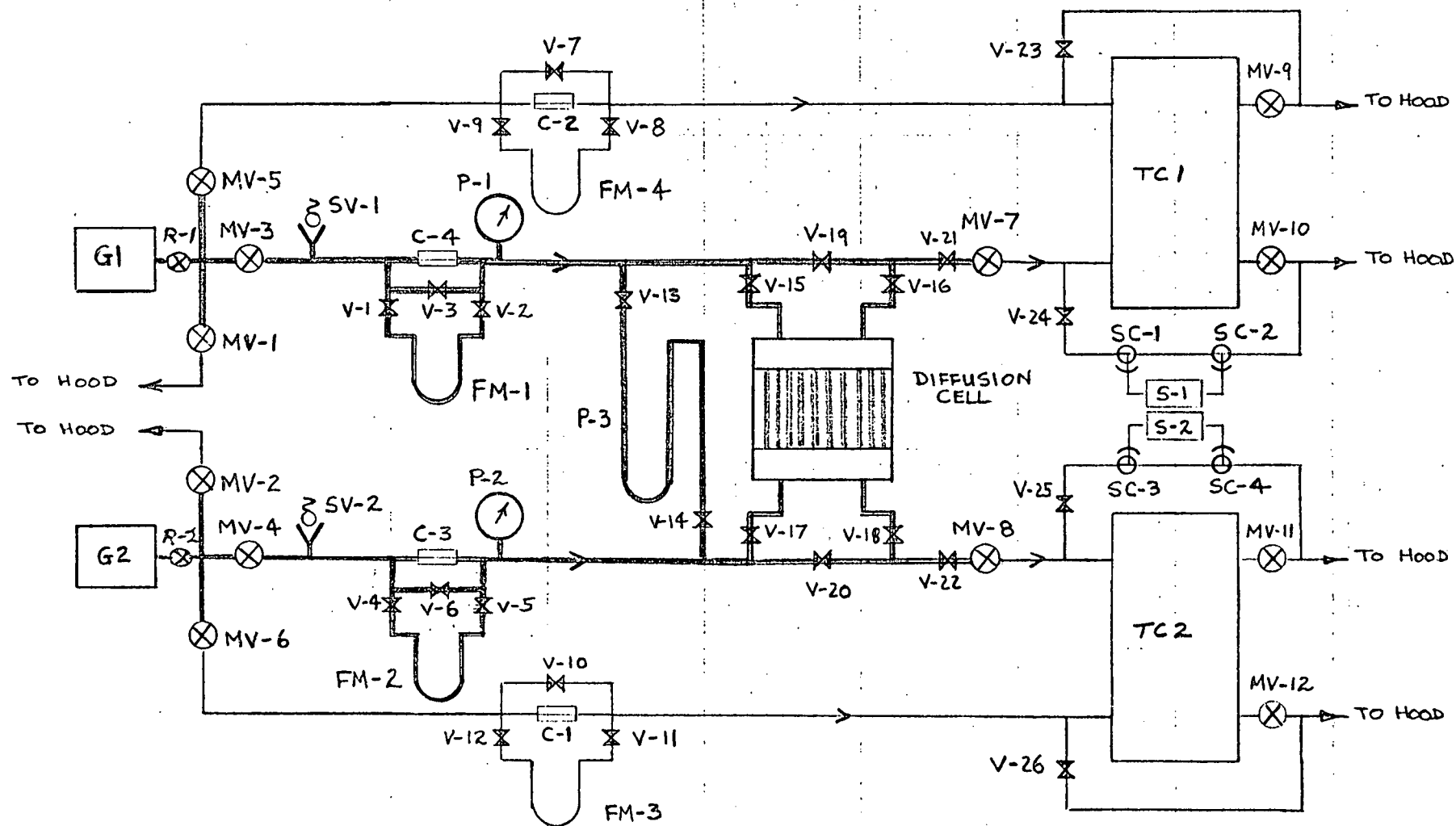branch: the valves MV-1, MV-3, and MV-5 are Nupro Type M fine metering

FIG. 2 HIGH PRESSURE DIFFUSION EQUIPMENT

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valves with micrometer handles and are used to reduce the pressure and direct the flow of gas entering the branch. Valve MV-3 will reduce the pressure to the final value desired in the system and will help control the gas flow rate to the diffusion cell. Valve MV-5 will throttle a portion of the incoming gas to atmospheric pressure and will direct 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 will be required.

After passing valve MV-3 in the upper branch (or MV-4 if the lower branch is considered) the gas will proceed on to the diffusion cell if the system pressure does not exceed about 80 atmospheres. If the system pressure is too high, the safety valves, SV-1 and SV-2, will exhaust the gas to the hood. The gas flow rates to the diffusion cell will be 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, will be used for pressure drop measurement. The line pressure will be 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 to be 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 will indicate any pressure difference across the diffusion cell. Should a pressure difference exist, gas will flow as well as diffuse 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 will be 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 pressure will be 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 measurement 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.

B. Diffusion of a Binary Gas Mixture
    In Straight Capillaries

A number of different types of capillaries have been purchased for use in diffusion experiments. In Fig. 4 photomicrographs are shown for the three sizes of glass capillaries at a magnification of 125X. The inside walls appear relatively smooth. In Fig. 5 titanium, brass, and 304 stainless steel capillaries are shown for sizes of 0.0034″ I.D., 0.0036″, and 0.0033″ respectively. This shows how jagged and rough the inside metal walls are compared to the glass. Experiments on the two 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. In Fig. 6 a photomicrograph is shown of a solid containing collimated hole structures approximately 0.0018″ I.D. Two other such structures are available for diffusion experiments of 0.00051″ and 0.0041″ I.D.

The novel vacuum apparatus in Fig. 7 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. New lines were installed to allow samples of the two outlet gas streams to be taken for mass spectrometer analyses. In this way mas spectrometer analyses could be compared with the analyses from the TC cells. 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 range of 0.15 mm Hg to 1 atmosphere. All flow lines shown in Fig. 7 are constructed from ¼″ glass tubing, except for the capillary flowmeters (designated FM), which are fine-bore glass capillaries. All metering valves for flow control (except MV-12 and MV-13), denoted as MV, are Nupro Type M needle valves, some of which are equipped with vernier handles for fine adjustment. Valves MV-12 and MV-13 are standard regulating valves attached to gas storage cyclinders G1 and G2, respectively. These valves are used to reduce cylinder pressures down to almost atmospheric pressure. Valves marked V are glass stopcocks, and those marked SC are 3-way glass stopcocks.

The cylinder G1 and G2 each contain a different gas. For binary diffusion studies He and N_2 gases are used as shown in Fig. 7. For 3-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.

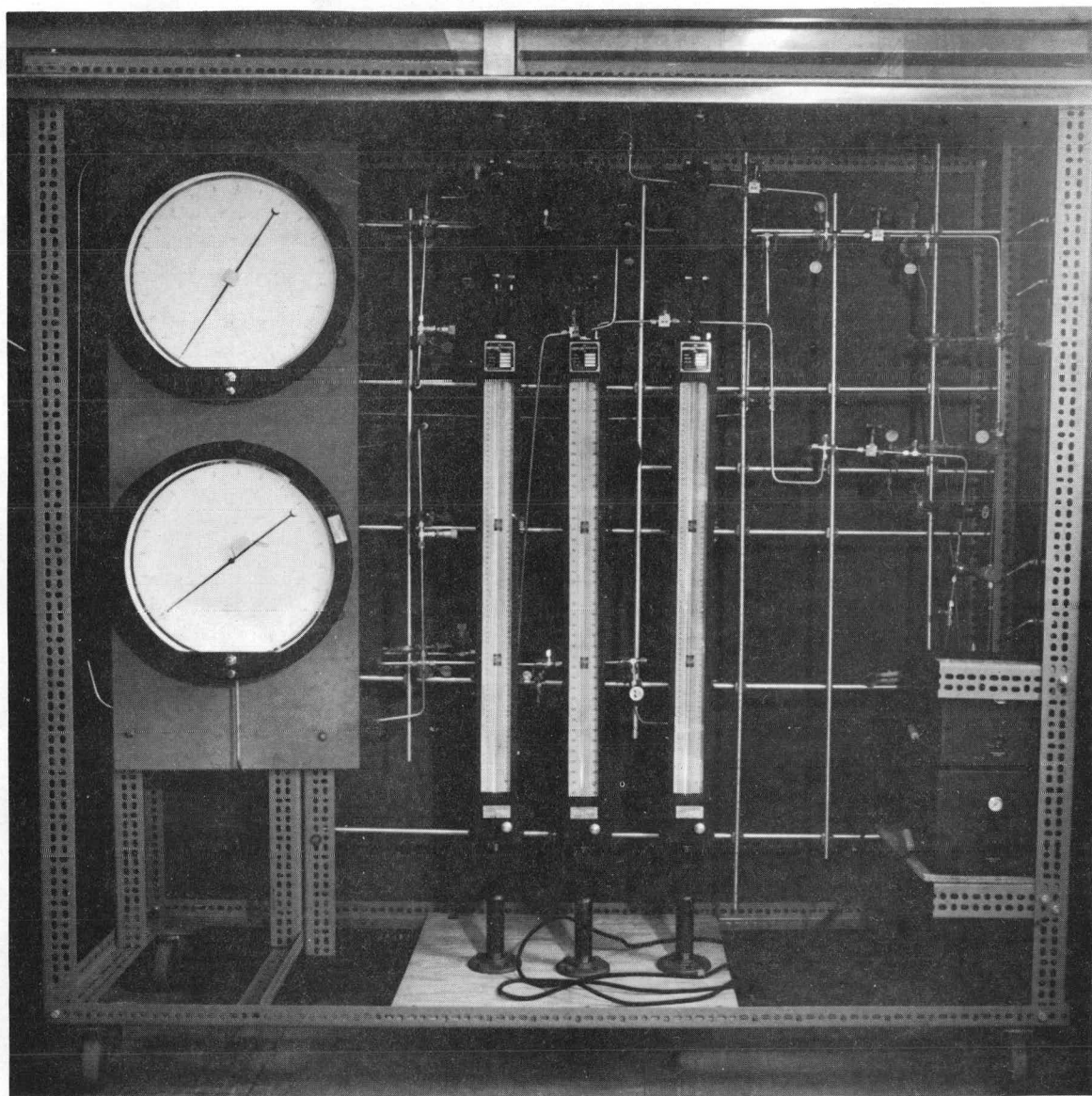Fig. 3. Photograph of High Pressure Apparatus

Fig. 4. Photomicrographs of Glass Capillaries

0.0035" I.D.   0.0055" I.D.   0.0016" I.D.
                          125X

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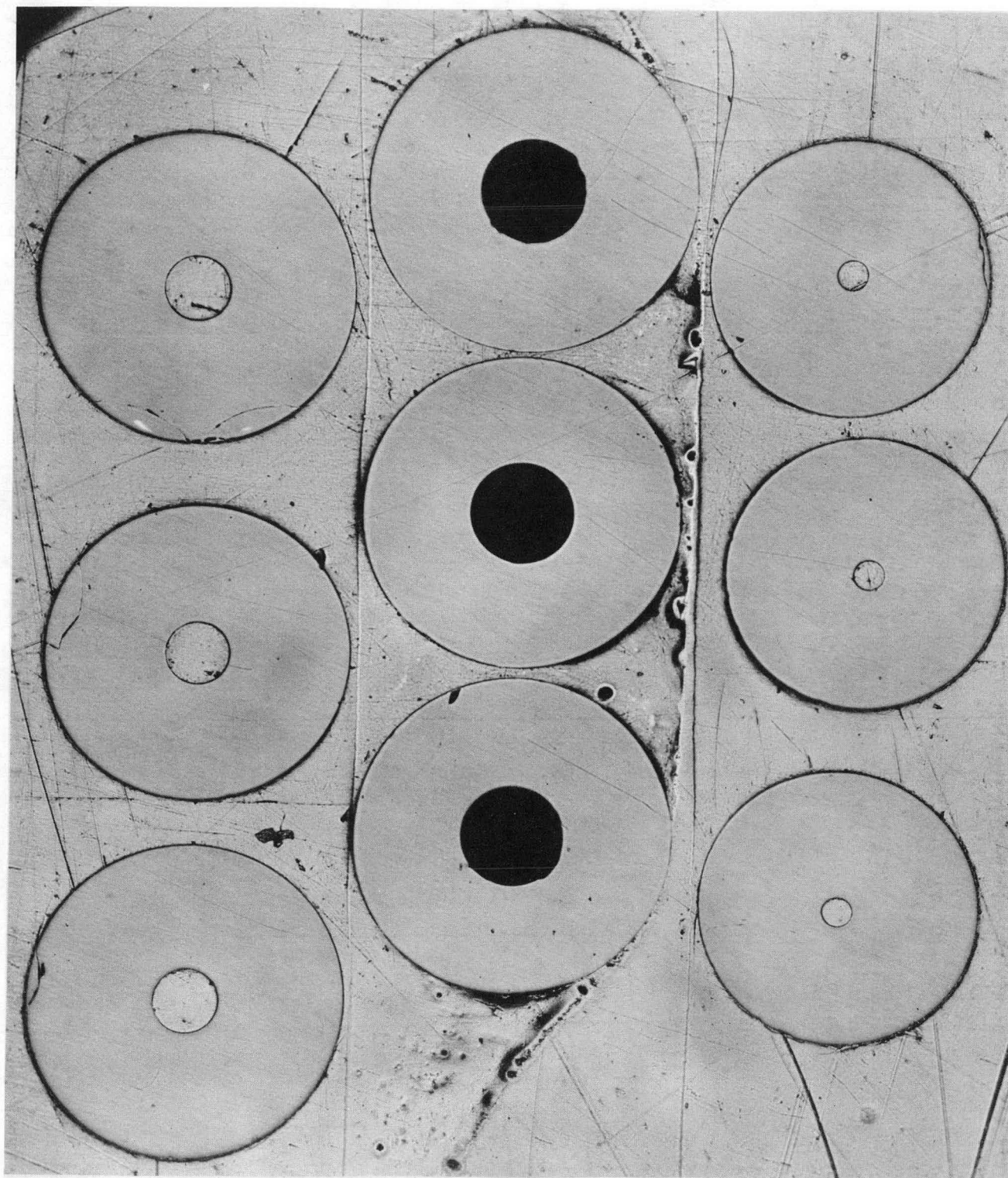
Fig. 5. Photomicrographs of Metal Capillaries
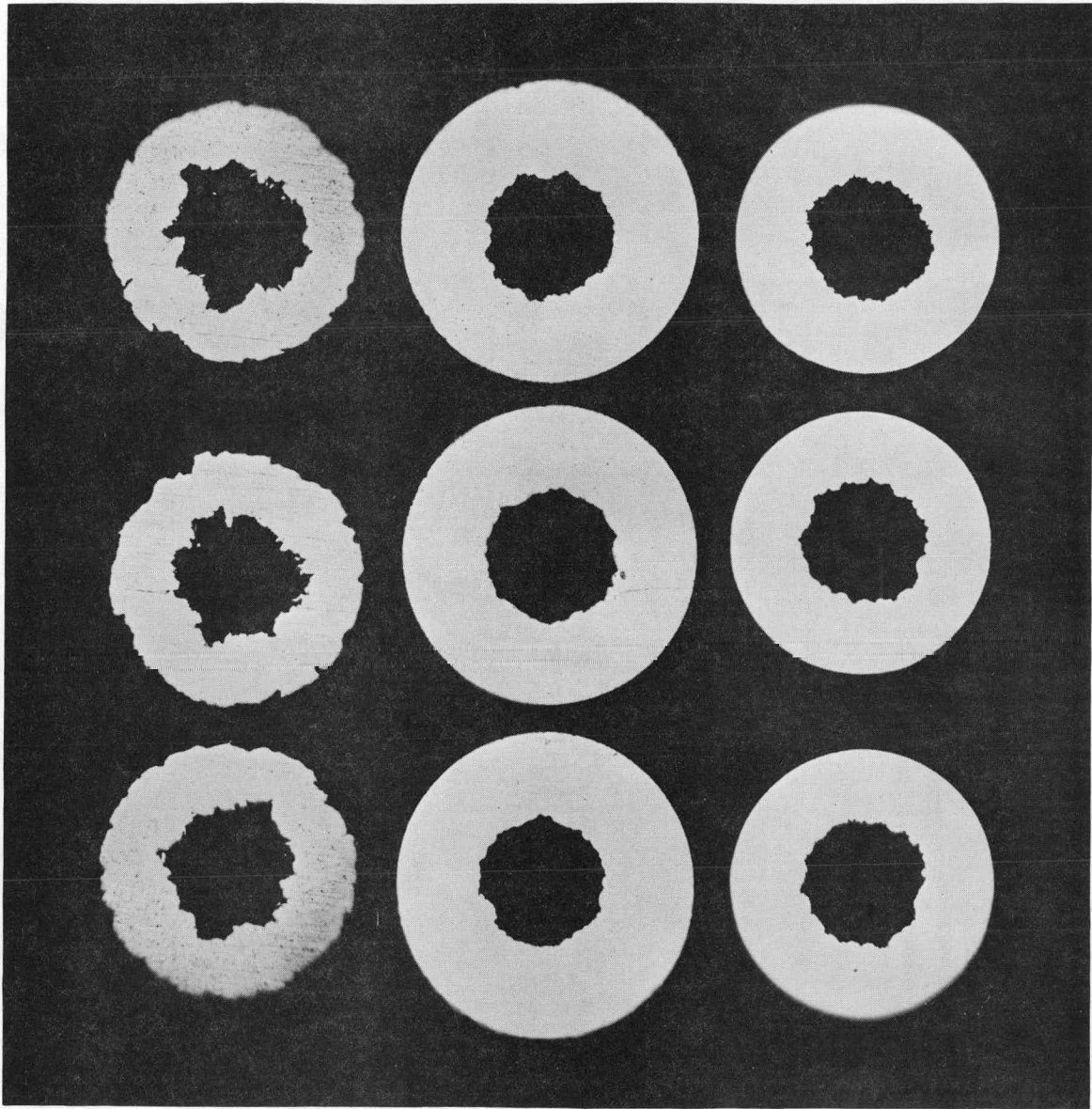
Titanium	Brass	304 Stainless Steel
0.0034" I.D.	0.0036" I.D.	0.0033" I.D.
	200X	

Fig. 6. Photomicrograph of Collimated Hole Structure

0.0018" I.D.
200X

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Fig. 7. Vacuum Diffusion Equipment Schematic

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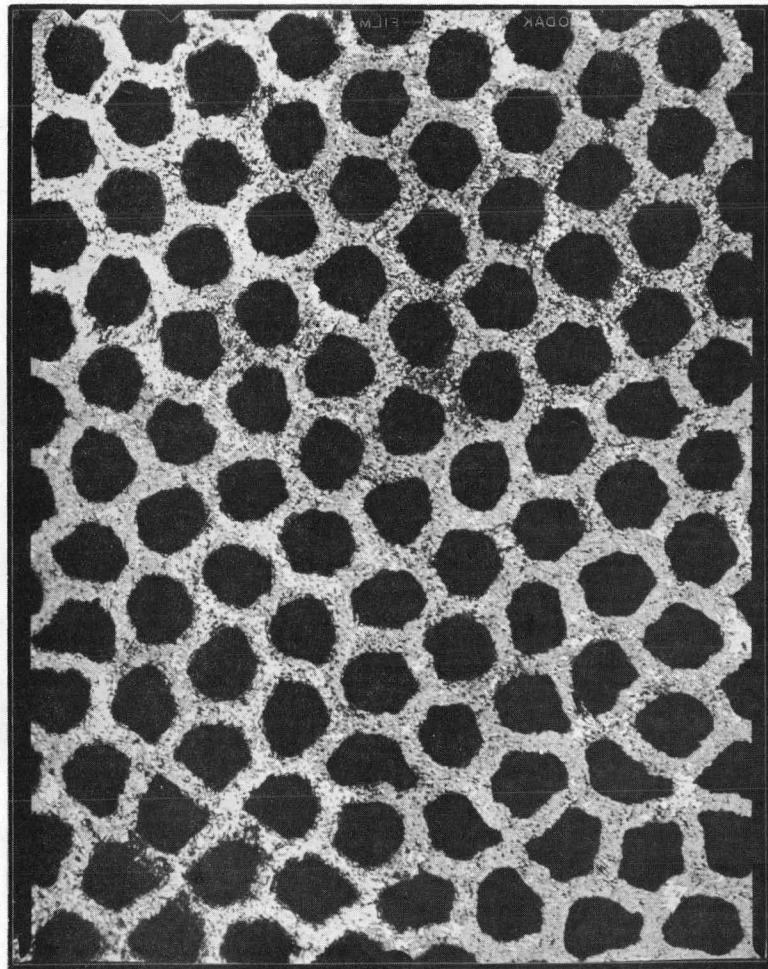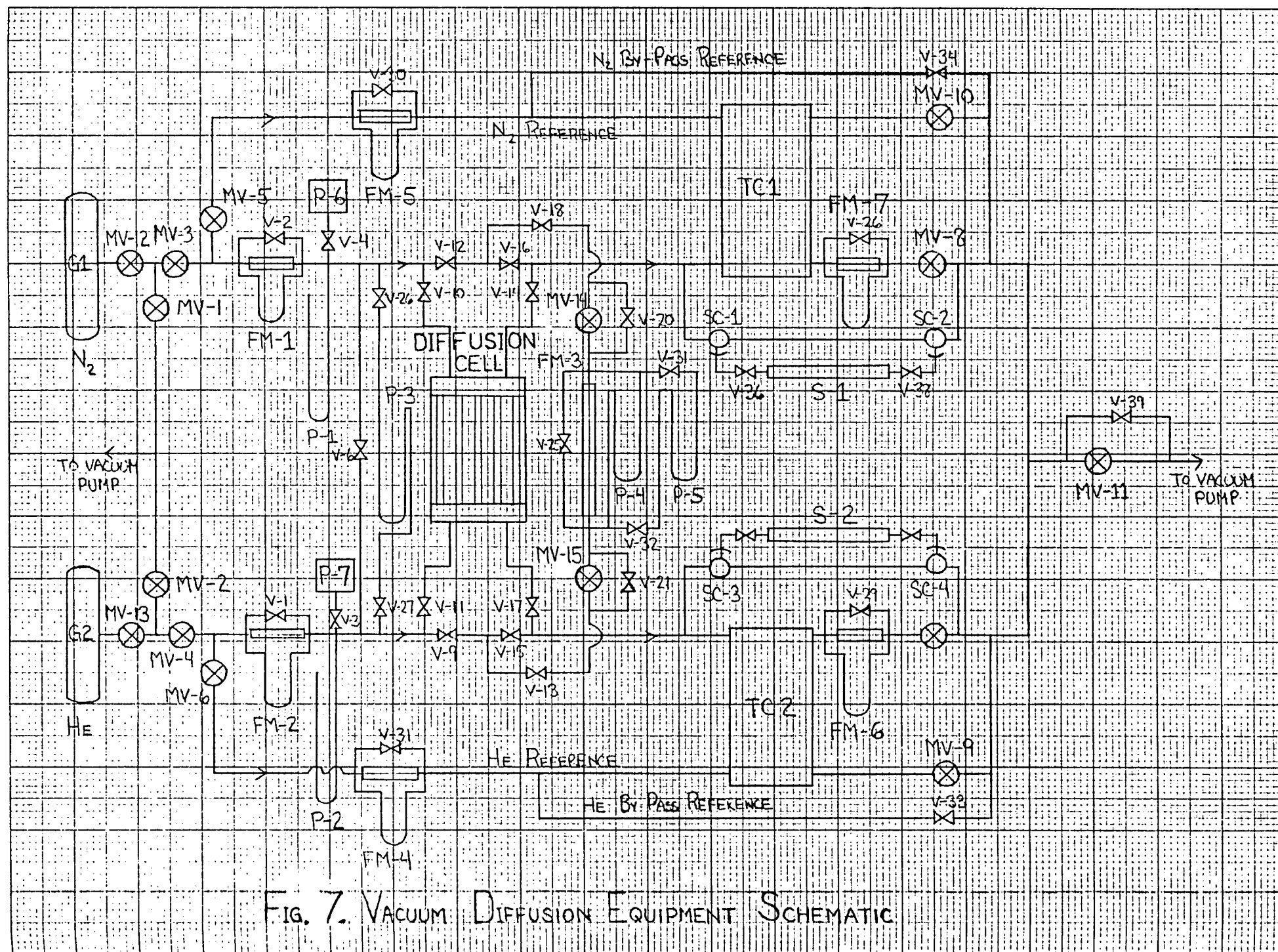
The diffusion cell shown exaggerated in Fig. 7 is the most important part of the apparatus. It is the device through which gases diffuse countercurrently at various levels of low pressure. For the case of binary diffusion, N_2 flows past the ends of the cell through V-10 and out V-14 (at this point the stream contains some diffused He) on the N_2-rich side, and 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 a single cell in order to obtain measurable amounts of gas diffusing through the cell. Fig. 7 shows a schematic of a capillary 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 H_2 and He sides of the diffusion cell, respectively. They are capable of measuring pressures from 2μ to 10 mm Hg. Indicators P-1 and P-2 are absolute mercury manometers for use on the N_2 and He sides, respectively, when the system pressure is above the range of the McLeod gauges. Indicator P-3 is an oil manometer used to detect overall pressure differences between the N_2 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-1, MV-3 and MV-5 are used to throttle the flow to the indicated sections. Valve MV-5 directs pure N_2 gas to the reference side of the thermal conductivity cell TC1 using FM-5 as the flowmeter. A major portion of the gas by-passes TC1 to allow for a slow flow in the reference side. Valve MV-1 in combination with MV-3 and MV-5 helps to insure steady flow from G1 in which the pressure continuously decreases slowly. It also diminishes periods of unsteady-state following a change of gas flow rate to the diffusion cell. Valve MV-3 reduces pressure to the desired sub-atmospheric level for flow of N_2 past the diffusion cell. This flow is metered by the pressure drop across FM-1 which contains a fine bore glass capillary. Absolute pressure measurements of the N_2 side are made using either P-1 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 TC1, or it can be physically sampled for mass spectrographic analysis by use of the "flow-through" type gas sampling tube, S-1. Flow out of TC1 is metered by FM-7, which aids in eliminating the flow velocity dependency in the thermal conductivity cell.

For a particular diffusion experiment, 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-14 and MV-15 into the N_2 stream (with V-10 and V-14 closed) to calibrate TC1. 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 completed vacuum apparatus is shown in Fig. 8.

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

The first plug made used 0.00155" I.D. glass capillaries 0.747" long and is shown in Fig. 9. Two diffusion experiments have been completed so far using this capillary plug and the binary gas mixture N_2-He. One run at 310 mm pressure gave an experimental value of D_e which is within 9% of the theoretical calculated using Eq. 6. Another run at 0.535 mm pressure gave a value within 12% of the value from Eq. 6. This latter run should be regarded as preliminary since some difficulty was encountered in metering the flows at this low pressure. The two experimental points are plotted in Fig. 10 and agree reasonable well with the theoretical curve, Eq. 6. The pure Knudsen diffusion limit and molecular diffusion limit are also shown on the graph. Experimental diffusion runs will be made at other pressures in the vacuum apparatus. The experimental fluxes and flux ratio will be measured in this vacuum apparatus using the binary gases helium and nitrogen.

Experiments will be continued to cover the whole transition region. Also, several different size glass capillaries will be used. 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. (3), 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. Geankoplis[18] 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. A reprint is also included with this present report.
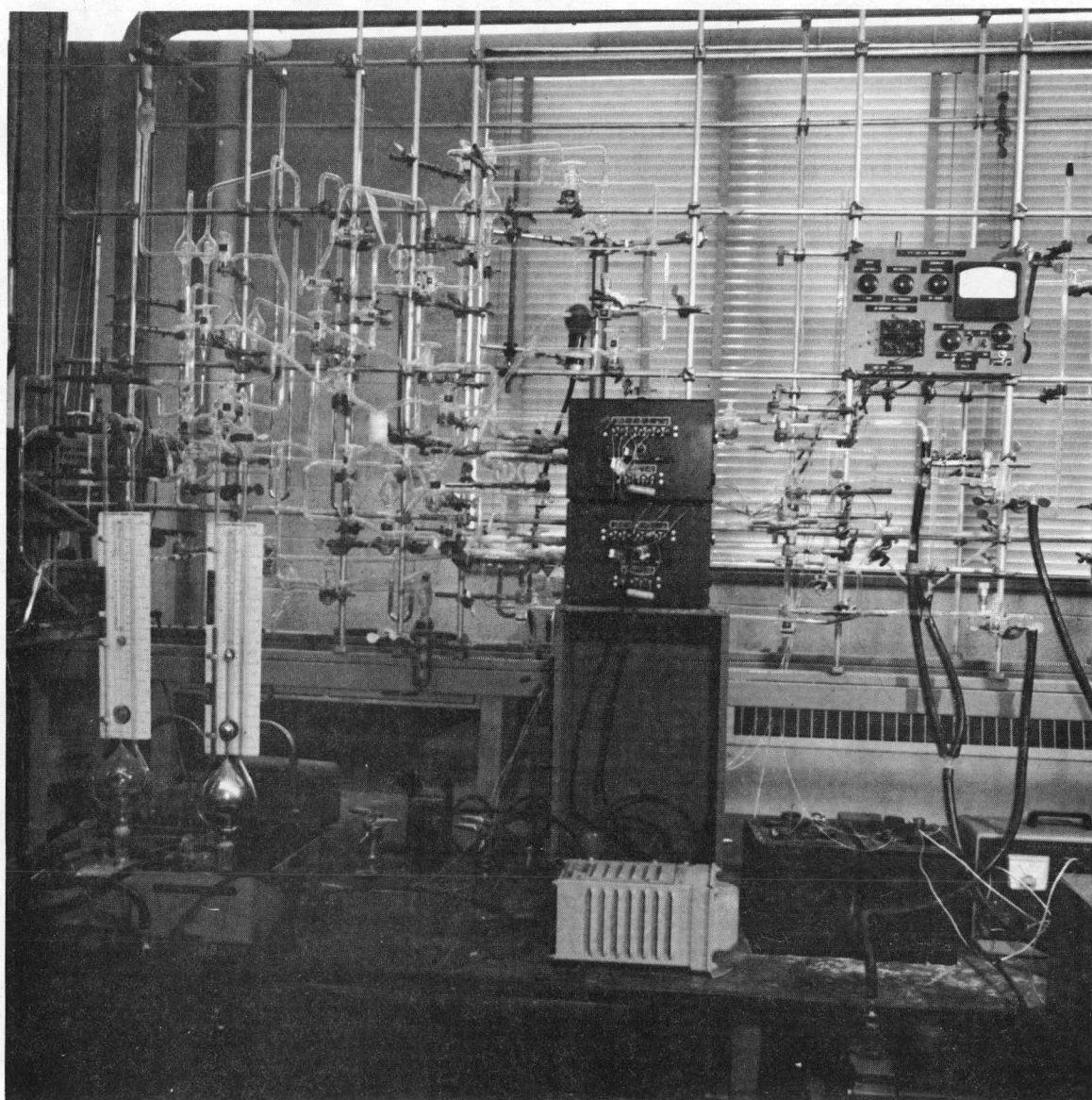
19

Fig. 8. Photograph of Vacuum Apparatus

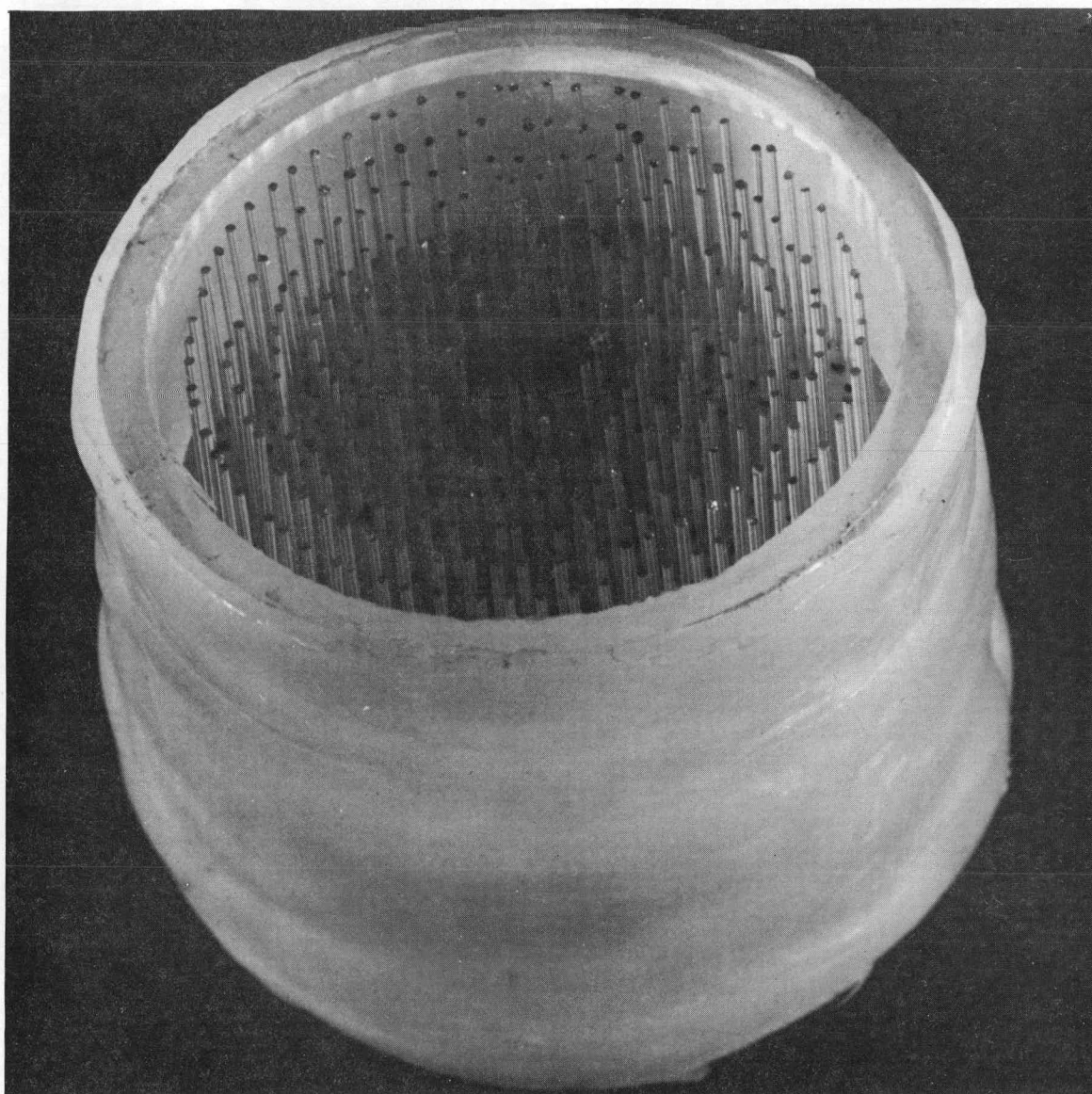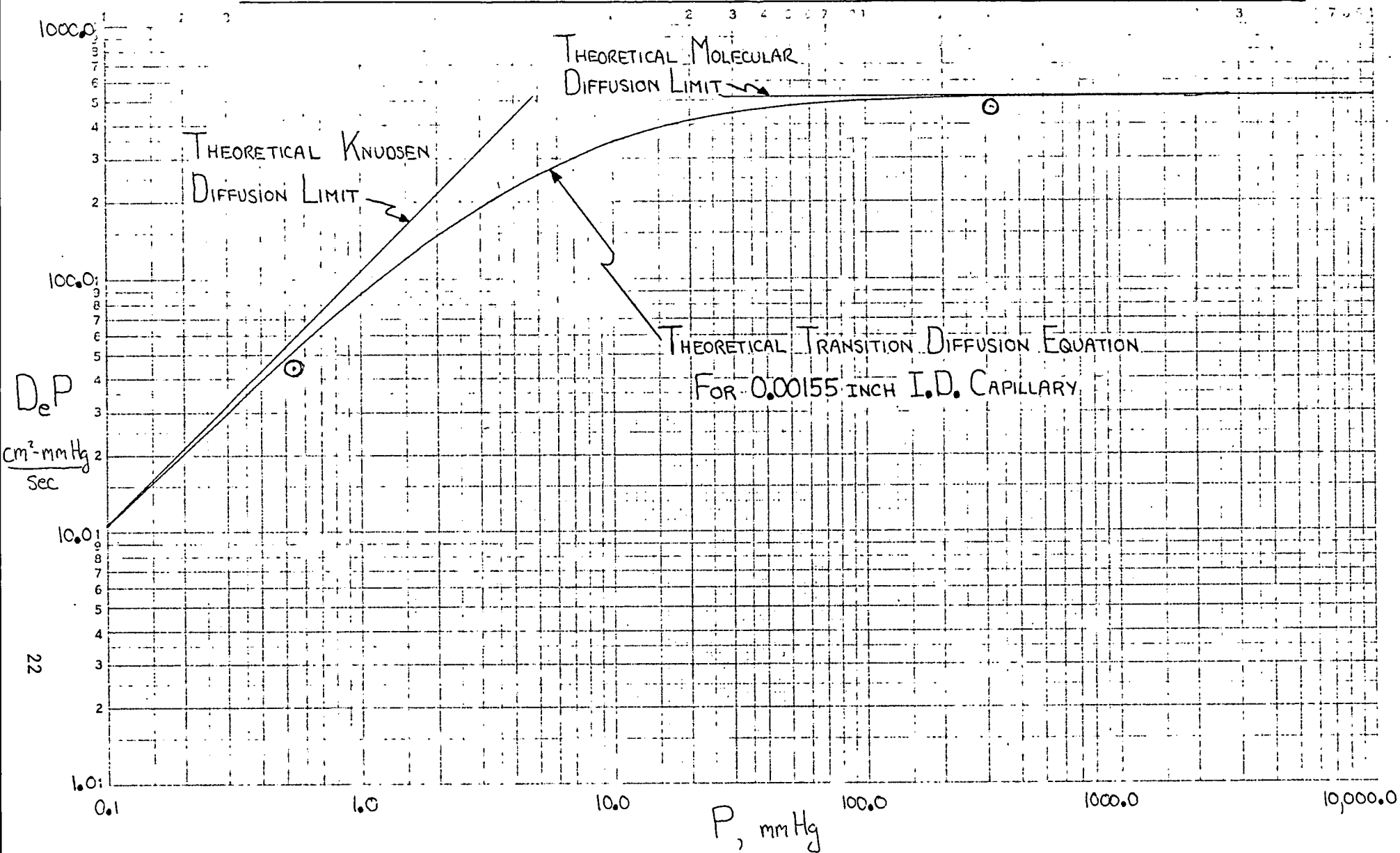Fig. 9. Porous Plug with Multiple Capillaries

FIGURE 10. COMPARISON OF EXPERIMENTAL AND THEORETICAL D_eP vs. P FOR VACUUM DIFFUSION DATA

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 Toor[20] 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[20].

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.

Such a numerical study has been completed for one phase of this theoretical study of diffusion of multicomponent gases. This work is based on the recent M.S. thesis of R. R. Remick[31] 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 accepted by the Industrial and Engineering Chemistry Fundamentals Journal for publication in 1970. Six preprints of this paper[22] were included with this report in 1968 to the Atomic Energy Commission. A preprint is also included with this present report.

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. 11 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 - vs. - 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.[33] The existence of a maximum or minimum point in the concentration - vs. - 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

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Figure 11 $\dfrac{N_iP}{P/RTZ}$ versus P
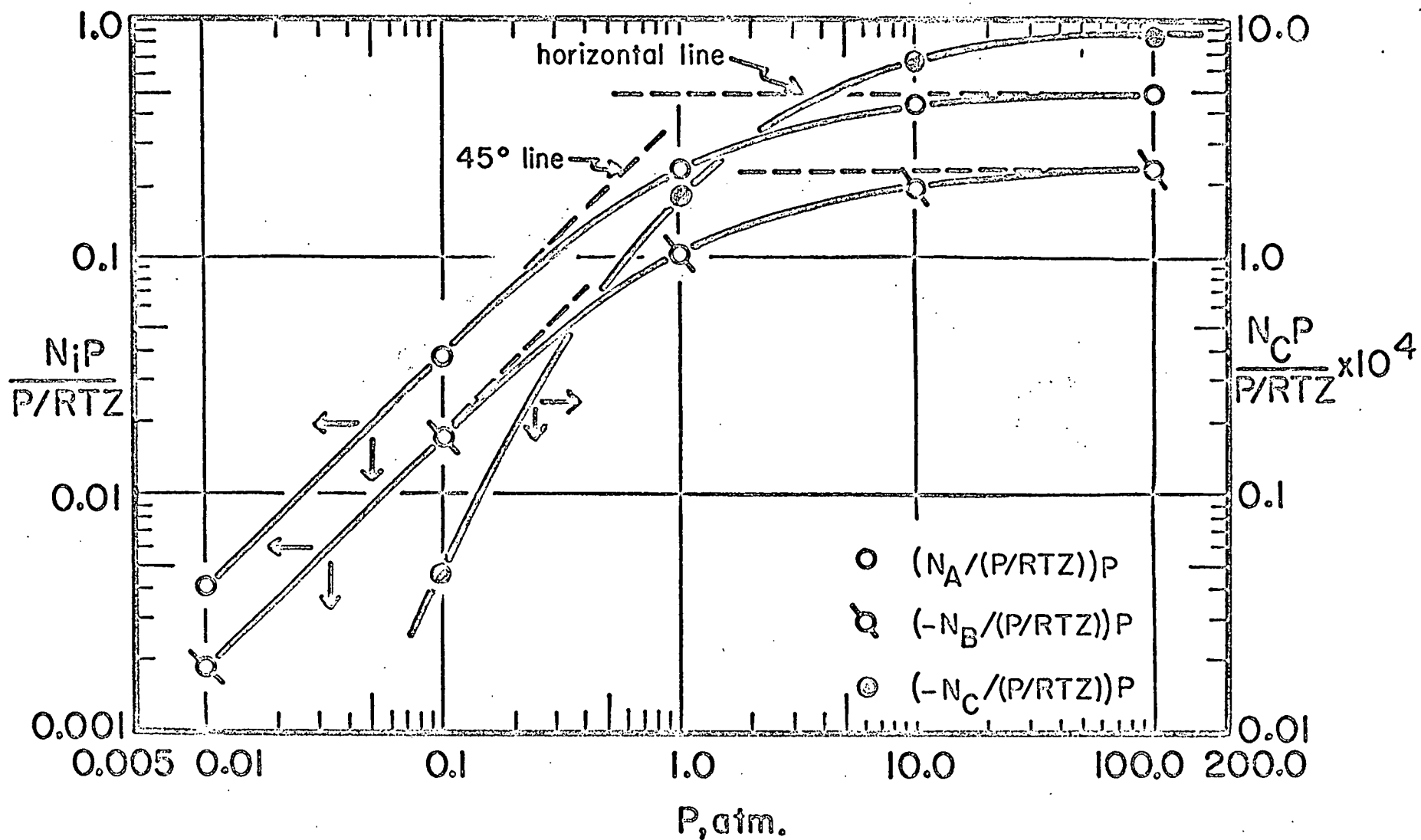
region depending on the concentration gradient of each component. This could possibly be the basis of a separation process. This is contrary to binary mixtures for diffusion in the transition or molecular regions or multicomponent mixtures in molecular diffusion where the flux ratios are constant.

Equations were derived for maxima and minima in the concentration-vs.-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.

2. Experimental Measurements

Using the 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 of the plug. No modifications to the equipment will be needed since pre-mixed 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.

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. Other pore models such as those using tortuosity will also be used.

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 Regions," by R. S. Cunningham and C. J. Geankoplis[19] 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. A reprint is also included with this present report.

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. 12.

The relation between the porosities is

$$\epsilon_a + \epsilon_b + \epsilon_i + \epsilon_s = 1.0 \tag{8}$$

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. 12. If the areas given above are multiplied by the number of paths, the sum is unity. Applying these areas and paths to Equations 1 and 2 and summing, the result is the differential diffusivity. Details are given in the paper.[19]

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

$$D_e = \frac{D_{AB}}{\ln\left[\dfrac{1-\alpha X_{A_L}}{1-\alpha X_{A_0}}\right]} \left[\epsilon_i^2 \frac{\alpha(X_{A_0} - X_{A_L})}{1-\alpha\left[\dfrac{X_{A_0}+X_{A_L}}{2}\right] + \dfrac{D_{AB}}{D_{K_i}}} + \right.$$

$$\sum_n \epsilon_n \sum_j \epsilon_j \left\{ \ln\left[\frac{2(1-\alpha X_{A_L}) + D_{AB}/\bar{D}_{K_n} + D_{AB}/\bar{D}_{K_j}}{2(1-\alpha X_{A_0}) + D_{AB}/\bar{D}_{K_n} + D_{AB}/\bar{D}_{K_j}}\right] \right\} +$$

$$\sum_n \frac{4\epsilon_n(1-\sum_j \epsilon_j)}{1 + [(1-\Sigma\epsilon_j)^2/\epsilon_i^2]} \cdot$$

$$\left. \frac{\alpha(X_{A_0} - X_{A_L})}{1-\alpha\left[\dfrac{X_{A_0} + X_{A_L}}{2}\right] + \dfrac{D_{AB}/\bar{D}_{K_i}}{1 + [\epsilon_i^2/(1-\sum_j\epsilon_j)^2]}} \right] \tag{9}$$

The first term on the right side of Eq. (9) 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.[19] Such a solid was made and experimental data checked the theoretical equation as shown in

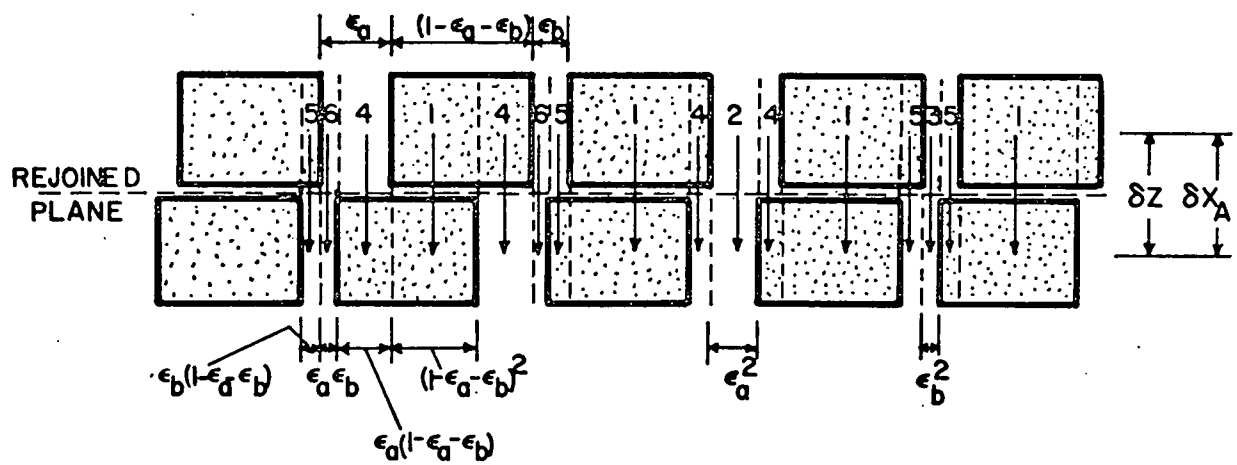Fig. 12 Diffusion Paths in a Tridispersed Medium

Fig. 13. Also, in Fig. 13, a solid with a broad macropore distribution is shown and the data check Eq. 9 quite well for 3 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 paper[19] 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 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.

A 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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Fig 13. Effect of Broad Macropore Size Distribution (Solid 3) and Blockage of Micropores (Solid 4) on D.
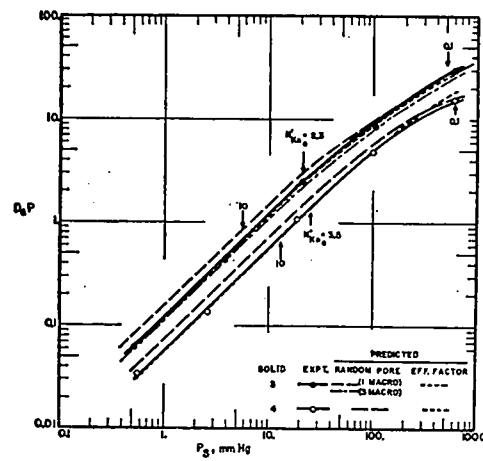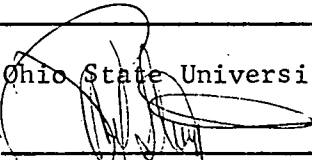
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