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STEADY-STATE COUNTER-DIFFUSION OF GASES IN POROUS SOLIDS.

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ILLUSTRATIONS

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established at a temperature of nearly 75 degrees. If the bed is too hot, the Wood's metal will flow through it too rapidly and uniform distribution of metal around the particles cannot be achieved. If the temperature of the bed is below 75 degrees, the metal will solidify in the bed and again a uniform metal distribution is not achieved. A bed temperature of from 75 to 80 degrees can be tolerated, but above 80 degrees, uniformity is difficult to obtain.

The metal is heated in a porcelain heating dish until it melts. The hot liquid is then introduced to the heated salt bed, and a moderate vacuum is applied to the lower suction flask. It is also important that the vacuum established be just enough to pull the metal through the bed, since high vacuum will cause the liquid to flow too fast and channeling will occur. By keeping about one-half inch of liquid metal above the surface of the salt bed, the liquid seeps down into the salt crystals. When the Wood's metal flows into the suction flask, the vacuum is disconnected, and the heating of the nichrome wires is discontinued. The bed is then allowed to cool, and the metal will then solidify around the salt particles.

When the bed is a solid, the mold is removed from the heating apparatus, and the glass tubing around the metal-salt pellet is broken. The mixed solid is then machined to the desired length by either cutting it on a suitable saw or by sanding down the surface with an electric sander. The
solid used in this study is 1 inch in diameter and was cut to a length of one and one-fourth inches. Visual inspection shown no air bubbles in the lattice with the liquid metal filling the entire salt free volume.

The Wood's metal pellet containing the salt crystals is weighed, and the combined weight is 69.5339 grams. The pellet is then placed in a flowing water stream for removal of the salt. Distilled water is allowed to flow around and through the pellet for several hours or until the outlet water stream gives no chloride test when a drop of silver nitrate is added to the effluent solution. This indicates that all of the salt has been dissolved and that only the porous Wood's metal plug remains. The pellet is then dried for several hours and weighed. The final weight is 50.0389 grams, so it is concluded that there were 19.4950 grams of salt present in the pellet or 5.3265 x 10⁵ grains. Figure 15 shows the pore structure of a small area of the surface of the pellet. From a measurement of the diameters or equivalent diameters of the pores in the photograph an average diameter is found to be about 289 micros for 32 pores measured in two directions (perpendicular diameters). This is within about 5 per cent of the estimated diameters from the screen analysis.

A study of the effect of a possible salt-metal interaction was made by comparing photographs of the pores made over a period of time. No deterioration of the pores was
Figure 15.—Porous Wood's metal surface.
noted when the porous Wood's metal pellet was stored in a dessicator.

9. Compressed powder plug

Two compressed powder plugs are prepared from alumina powders supplied by the American Cyanamid Company. The first powder, Sample 2 (American Cyanamid Code Number 1-233-1225B), has a surface area of 246 square meters per gram before compression and has a pore volume of 0.46 cubic centimeters per gram before compression. The size distribution of these particles is as follows: 98 per cent less than 90 microns, 90 per cent less than 70 microns, 65 per cent less than 50 microns and 21 per cent less than 30 microns. The stainless steel mold, as shown in Figure 16, is filled with about one inch of this powder and the entire mold is placed in a hydraulic press. About 40,000 pounds of force is applied to the piston and the powder is compressed to about a one-half inch thick pellet. The American Cyanamid Company again measured the specific surface area and pore volume of the compressed sample and analysis shows that the surface area per gram of the compressed pellet is 202 square meters per gram, and the pore volume is 0.38 cubic centimeters per gram. However, since the American Cyanamid Company crushed the samples before determining the total pore volume, analysis of the uncrushed samples shows Sample 2 to have at total pore volume of 0.5025 cm^3/gm. Two samples are prepared under
Figure 16.—Pellet mold for powder.
identical conditions, one for analysis by American Cyanamid Company and the other for use in diffusion measurements. This sample is gray in color.

The second solid (white in color) was prepared in the same manner. This powder, Sample 1 (American Cyanamid Code Number 1-233-1225A), has, before compression, a surface area of 246 square meters per gram as obtained from nitrogen adsorption data and a pore volume of 1.04 cubic centimeters per gram. About one inch of this powder is introduced to the mold as shown in Figure 16, and a force of 6000 pounds is applied to the piston. The final pellet which has a length of about one-half inch has a nitrogen surface area of 199 square meters per gram and a pore volume of 0.61 cubic centimeters per gram (crushed) as determined by the American Cyanamid Company. The white solid in compressed form (uncrushed) has a total pore volume of 1.219 cm$^3/gm$ as measured by the present study.

The surface area and pore volume measurements of the crushed pelleted samples are performed by grinding the pellets to about 50 mesh before subsequent nitrogen surface area and water titration pore volume measurements are made by the American Cyanamid Company. The uncrushed measurements are made by the California Research Corporation and by the present study.

Particle size distribution by micromesh sieves of the white sample is as follows: 55 per cent less than 90 microns,
20 per cent less than 70 microns, 6 per cent less than 50 microns and 1 per cent less than 30 microns.

The pore-size distribution of these two samples has been measured by the Gulf Research and Development Company and this data is discussed in Section X.

10. Tooled alumina plug

Solid chunks of aluminum oxide are obtained from the Aluminum Company of America in the form of one to one and one-half inch pieces. This Tabular Alumina T-71 is prepared for diffusion studies by cutting a right circular cylinder of one inch in diameter from a piece of rough alumina of sufficient size. The rough chunk is placed in a core-drilling apparatus and by means of a one inch (inside diameter) diamond core drill, a cylinder of the desired shape is obtained. The rough ends are cut off by means of a diamond saw (see Figure 17) until the desired length is obtained.

The sample used in this study has a diameter of 0.9891 inches and a length of 0.3737 inches.

The sample was submitted to the American Cyanamid Company for surface area and pore volume analysis, and they reported that the nitrogen surface area is 2 square meters per gram and that the pore volume by water titration is 0.03 cubic centimeters per gram. These measurements indicate a
Figure 17.—Tooling of solid alumina.
large average pore radius which is not too suitable for our studies.

11. Plastic ordered plug

The ordered plug is formed by casting a styrene fortified polyester resin about a set of special geometry copper screens. In this manner, a porous solid of known pore structure (pore diameter and flow path) can be accurately constructed. A known pore structure is extremely important in that it eliminates the need for using the "average pore diameter" concept, and therefore experimental measurements should correspond to theoretical values much more closely.

Once the solid is cast and shaped, the bulk of the copper is removed by electroplating using the copper within the solid as the anode. The remaining copper is removed using a concentrated alkaline ammonium hydroxide-carbonate solution.

The screens used in this study are shown in Figure 18. They are prepared commercially by the Buckbee Mears Company (Saint Paul, Minnesota) using a very accurate etching process. The screens are etched to the intricate pattern shown from a pure copper sheet 0.01 inch thick. The rate of etching is controlled as a function of the depth of the etching in order to produce a roughly circular cross-section for each member of the screen network. The screen is cleaned
Figure 18.--Special geometry screen.
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of surface grease from handling by rinsing with acetone and is then cut into one and a half by two and a half inch rectangles. The cutting is done with a machine shear using paper as a protective mask on both sides of the screen. The rectangles of screen are then separated by 0.04 inch wire spacers located at the outside edges. The entire "sandwich" of screens and spacers is clamped between two aluminum plates and the open edges of this "sandwich" are sealed with plastacene modeling compound. The "Laminac" polyester (American Cyanamid Company) is mixed with 1 per cent of methyl-ethyl ketone peroxide which acts as a catalyst. This catalyzed mixture is then poured into the spaces between the confined screens, care being taken to avoid entrapped air bubbles. After the resin has set and cured, the block of resin and screens is machined on a lathe and sander. The plug formed is a right circular cylinder one inch in diameter and slightly over two inches in length. One end of this cylinder is not machined. This end then corresponds to the open side into which the resin is poured, and which has protruding from it about a quarter of an inch of exposed copper screen for each layer. The protruding screens then are soldered to a 10 gage copper wire which acts as the anode during the electroplating process.

The electroplating is carried out in a slightly basic electrolyte which contains approximately 5 grams per liter of copper sulfate to avoid damage to the resin matrix. It
is found that a slightly acid solution will not damage the plastic, but if at all possible it is better to avoid this possible source of error. The bulk of the copper is then removed by electrolysis in about eight to twelve weeks. The power source to this process is a portable General Electric generator and it is run continuously at maximum current.

The copper which remains in the plug after the electroplating process is found in two main areas. First, the small side pieces of the screen which are isolated from electrolysis as the main grid is removed remain, and secondly, a small central core of copper close to the anode connections also remains. It is believed that eventually even this second amount could have been removed by electrolysis, but it would take considerably more time.

The partially completed plug is then machined to remove the soldered anode connection at the top and to open the channels which result from the copper removal.

The porous plug, now partially completed and machined to size is placed in a continuously recycling stream of concentrated ammonium hydroxide-carbonate solution (about 4 N in ammonium hydroxide and containing about 100 grams per liter of ammonium carbonate). After about four months of continuous leaching, no discernible copper is visible from the sides or the bottom of the plug. A slight amount of copper is visible from the top in the center 10 per cent of cross-section. This is due to the fact that the formation
of the copper-ammoniura complex is extremely slow and that the resistance for diffusion through the plug is large. This central amount could be removed in a considerably longer leaching process, but the slight amount of remaining copper is not enough to merit such a long extraction process.

After removal and rinsing with distilled water until no more basic solution was observed as the effluent, the flow of water across the face of the plug through the pores was observed and found to be uniform. It is therefore assumed that nearly all of the flow channels are open and available for diffusion.

Stahel (55) determined the void fraction of this porous solid as 5.64 per cent from measurements of the water-filled plug and the same plug when dried under vacuum. This compared favorably with his value of 5.84 per cent as determined by the original amount of copper screen employed in fabricating the porous plug. This agreement also indicates that the pores within the medium are not closed by any swelling or changes in the plug's pore structure during the basic leaching process and that the very slight amount of unleached copper remaining does not have a noticeable effect on the pore volume.

It should be noted that the experimentally determined 5.64 per cent void fraction takes into account the fact that the plastic lattice absorbed some water during the long leaching process. The plastic plug cracked when dried under
vacuum and this is also due to the rapid removal of the water from the lattice, however, the crack was easily repaired with little or no injury to the original structure. It should be stressed that future preparations of known porous media in this manner should be dried very slowly at room temperature and at atmospheric pressure when possible.

The plug is pictured in Figure 19 and a detail photograph of the screen pattern is shown in Figure 20. The diffusion or flow path of a simple repeating unit of this solid is shown in Figure 21.
Figure 19.—Ordered porous plug.
Figure 20.—Ordered screen detail.
Figure 21.—Detailed flow path.
VII. EXPERIMENTAL PROCEDURES

A. Samples studied

Two porous solids are studied in this work. They are prepared for their consequent subjection to diffusion measurements as described in Part B. 9. of Section VI, Equipment and Experimental Materials. The two compressed powder samples are mounted in the system as described in Part B. 3. of Section VI. Diffusion coefficients are measured as a function of the absolute total pressure of the system that is studied, in this work, the nitrogen-helium counter-diffusion system.

B. Leak test

It is absolutely essential to this study that there be no leaks in the system. Even though this may not cause appreciable error in the nitrogen system other than the difficulty in establishing low pressures, it will give totally erroneous values in the helium system since the coefficients are determined by measuring the small amount of nitrogen contaminant in the flowing helium gas.

With reference to Figure 2, the system is leak-tested as follows: (1) With the outlet valves from the gas cylinders closed, stopcocks 22, 23, and 21 opened, valves V-6 and V-7
open, and valves V-1, V-2, V-3, and V-4 closed, the vacuum pumps are turned on. The bleed valves, V-8 and V-9 are also closed so that the pumps will use their full capacity in evacuating the system.

2) When the system pressure reaches 1 centimeter mercury absolute or lower, a Tesla coil is passed over each glass section of the entire system. A spark from the coil indicates the presence of a pin-hole leak in the glass. When such a leak is discovered it may be sealed in either of two ways. Either the system pressure can be raised to atmospheric pressure by shutting off the pumps and by opening valves V-8 and V-9 to allow air to bleed into the system, and when the system is at atmospheric pressure, a glass seal may be established over the pin-hole, or when the system is at low pressure, hot beeswax can be applied to the leak area and the leak will be at least temporarily sealed as the wax cools over the hole. For permanence, the glass seal is much more desirable.

3) When all apparent leaks have been found, a check of the system pressure at total vacuum should show the pressure to be no higher than about 20-40 microns. A lower value may be reached but to attain very high vacuums (low pressures) other valves than needle valves of the type used in this study would have to be used to shut off the gas cylinders from the system. Even a small leak across any of the valves would cause an appreciable pressure rise.
4) If the system reaches 20-40 microns pressure absolute, then further leak checks need not be made, but if the system will not attain this low pressure, then a systematic check must be made of several parts of the system until the leak is located. This can be done by opening and closing any of the stopcocks or stopcock combinations and isolating any part of the system from the vacuum pump. The entire system may be isolated from the pumps by shutting stopcocks 4, 5, 16, and 15. A leak can be determined by watching the gradual rise in pressure indicated in the Pirani gauges that can be opened to any desired position in the apparatus. The actual value of the leak may be determined by noting the pressure rise as a function of time, and this will give the decrease in the original volume of gas present in the system due to the high atmospheric pressure air leak.

5) If a leak is noted, it is most probable that it will occur in the sample mounting system. A check of this possible leak area may be made by shutting stopcocks 8, 9, 16, 6, 12, 2, 17, and 1 and opening stopcock 30 when the system has been pumped to as low a pressure as possible. Stopcock 5 is open to the pump to enable the system pressure to be reduced. When the lowest possible pressure is reached, as noted on the Pirani gauge, P-1, stopcock 5 is closed, and the rise in pressure of the system (due to the leak) is noted on P-1. The rise can be timed to give the actual rate of
I. ABSTRACT

A study of the transition region of diffusion in porous solids is made with emphasis placed upon the change from Knudsen diffusion to transition diffusion. The experimental technique employed is one which allows the faces of a cylindrical porous plug to be exposed to different gases while the sides of the cylinder are sealed so that diffusion occurs along the cylinder axis only. A nitrogen-helium system is studied, and the counter-diffusing fluxes are measured as a function of the system pressure. The entire system is at constant total pressure so that the transport mechanism is one of diffusion due to an existing concentration gradient.

An examination of existing theories is made and it is shown by this study that the most rigorous present theory can be used to predict mass fluxes over the entire pressure range if three constants can be evaluated experimentally. This work shows that an effective Knudsen coefficient can be measured at low pressures, and the effectiveness factor for the molecular diffusion coefficient can be evaluated at one near-atmospheric pressure measurement. The ratio of the counter-diffusing fluxes can be established from these two
flow of air into the system. If the Pirani gauge remains constant then the sample mount is sealed satisfactorily. When a leak is located it is of course sealed in an appropriate manner. Leaks in the wax mounting of the sample cell may be sealed by touching a hot glass rod to the wax in the suspected leak area and noting whether this melting and resealing will permit the pumps to reduce the system pressure to the desired lowest value.

6) A systematic check of each part of the entire system will eventually show the place where a leak occurs. If possible, the system is then allowed to reach atmospheric pressure, and any glass leaks can be sealed with melted glass rod, and any other leaks can be sealed with either General Electric glyptal enamel or hot beeswax.

7) The actual system pressure is measured with the McLeod gauge, P-10, since the Pirani gauges give only relative pressure readings, and are not too accurate. Their value lies in the fact that they are continuous reading pressure devices, while the McLeod gauge is not continuous.

C. Operating procedure

The object of an experimental determination in this work is to measure a binary counter-diffusion coefficient at a given pressure. It is then desired to study the variation of this coefficient with pressure. Four steps are involved
in making an experimental run, namely:

1) Adjustment of the system pressure
2) Calibration of the helium T/C cell
3) Measurement of the diffusion rates through the sample, and
4) Calibration of the nitrogen T/C cell.

Since the only one of these steps which may be performed separate from the others is the first one, it is usually done the day preceding the other three. It is important that as little time as possible elapses between the performances of steps two, three and four. Steps two, three and four take between 17 and 24 hours to complete, and once begun, it is advisable to complete the entire run.

Aside from the pressure of the system and the temperature of the room, only four principal measurements are taken. They are the flow rates of the pure gases to the diffusion cell, and the final effluent concentrations. Knowing these quantities, a material balance will establish the relative rates of diffusion.

D. Pressure and flow adjustment and cell warm-up

Since pressure is the important parameter in this study, its establishment and invariant maintenance is critical. If an absolute pressure can be maintained constant throughout the calibration of the T/C cells and the actual experimental run without any adjustment from its
Initially set value, accuracy can be increased because a considerable amount of time can be cut from the period between calibration and the actual measurement. It has been found that the calibration of T/C cells drifts with time, so it is important to keep this calibration-run interval at a minimum. If the pressure seems to drift through a calibration or a run, one must continually adjust the air bleeds to the pumps to establish the desired pressure, and this not only makes the calibrations considerably more difficult, but also increases the time factor.

Since the pressure of the system is a direct function of the capacity of the pumps in a vacuum flow system, two flow streams are used to establish any desired pressure. The first stream is an air bleed to the five gallon surge tanks which removes part of the capacity of the pumps from the actual evacuation of the apparatus by by-passing the system with a large volume of atmospheric air. This bleed is accomplished by adjusting valves V-8 and V-9 to the sample systems and similar valves set up for the reference pump. Actually V-8 and V-9 (and the reference bleed) consist of two needle valves each. One 1/8 inch valve is for very low pressure adjustment and control (to about 30 cm of mercury absolute), and the other 1/4 inch valve for higher pressure (to atmospheric pressure). For low pressure runs the 1/4 inch valve is closed completely and all of the adjustment is made with the 1/8 inch valve. For high pressure runs, the
1/4 inch valve is for rough settings and the 1/8 inch valve is for the final fine pressure control.

The second stream to the vacuum pump is the actual flow stream through the diffusion or by-pass cell, S-l or B-l. Since this flow is very small, however, it seems to effect the pressure adjustment only slightly in the very low pressure ranges, and not at all in the range above about 5 centimeters mercury absolute.

Since both streams are fed to the pumps simultaneously however, it is easier to adjust both at the same time on the day before a run is actually made. Also, since the T/C cells require a considerable length of time to warm-up (before a constant emf is noted at a constant pressure), the pressure adjustment and the flow adjustment provide a good warm-up period for the cells.

It is important that both thermal conductivity cells be warmed up for the run, therefore, an auxiliary power circuit has been established for the nitrogen cell so that the nitrogen T/C, T-l, cell can be utilizing a small current through its sensing probe while the helium cell is being heated with full operating current (see Figure 8).

The flow rate of the gases through the diffusion system is a function of the pressure of the system itself and of the pressure at the outlet of the feed cylinders. Since too high an outlet pressure from the gas cylinders would drain the cylinders too fast, a two-step reduction
valve is used as described in Part B. 1. of Section VI. The first step reduces the tank pressure to about 20 psig, and the second step reduces the pressure to a sub-atmospheric level. The second valve is only actuated when the pressure at the outlet is below 760 millimeters of mercury absolute. A reasonably good "rule of thumb" is to maintain the outlet of the second reduction valve at a pressure approximately 150-200 millimeters above the actual desired system pressure. At very low pressures, one may desire to use a 100 millimeter delivery pressure in order to make flow control easier.

1. Low pressure adjustment

In the range of pressure from 0.5 mm mercury absolute to 10 mm mercury absolute, the McLeod gauge, P-10, is used to measure the pressure. Since this gauge can only measure point pressures it must be used in conjunction with the Pirani gauges which record pressure continuously. However, since the Pirani gauges are not too accurate they are used as a relative measurement, and their absolute value is established by checking them with the McLeod gauge. It must be remembered that in moving the mercury piston of the McLeod gauge up the gauge to trap a sample of gas at the unknown pressure, a surge is being introduced to the system by virtue of the fact that the mercury is compressing the gas in the external "legs" of the McLeod gauge and, these "legs" are part of the over-all system. This is not
important in the higher pressure range, but may be important in the extremely low pressure range.

A stepwise account of a low pressure adjustment is as follows:

a) Close valves V-8 and V-9 (also bleed to reference pump).

b) Make sure valves V-6 and V-7 are open to prevent the pressure surge from blowing the oil out of manometers P-8 and P-9.

c) Close stopcocks 5, 6, 7, 8, 9, 16, 11, 1, 12, and 13 if these last two have not already been closed to maintain the McLeod gauge under vacuum (desirable if possible). Open all others.

d) Open valves V-1 and V-4 about one to one and one-half full turns (just enough to allow a small amount of gas to pass through the reference cells at all times).

e) Open valves V-2 and V-3 about two full turns, and open by-pass stopcocks 22 and 23.

f) Open outlet from reduction valves from gas cylinder source.

g) Check to see that V-5 is closed and that stopcocks 25 and 26 are closed when 24, 27, and 21 are open. This latter check is to see that the calibration bleed capillary is ready to bleed nitrogen into
the helium stream during the initial helium T/C cell calibration.

h) Turn on all three vacuum pumps.

i) Adjust the outlet reduction valve (0-760 mm) to read about 100-150 millimeters of mercury absolute. This valve controls the delivery pressure of the gases from the cylinders.

j) Close stopcocks 22 and 23 when delivery pressure is set in (i). This activates flowmeters P-6 and P-7.

k) Making sure that stopcock 31 is open, open the small needle valve of V-9 (1/8") until the pressure on Pirani gauge P-2 indicates the approximate system pressure desired (from 0.5 mm absolute to 10 mm absolute).

l) Open valve V-3 until P-7 shows a mercury height differential of about 10 centimeters. A differential of about 5-10 centimeters of mercury across P-6 and P-7 will give a suitable bulk flow rate for calibration of the gauges in the pressure range from 0.5 mm absolute to 10 mm absolute. The actual flow rate of gases through these capillaries, P-6 and P-7, can be calculated from their calibration curves (see Figures 10 and 11).
m) When the approximate flow rate of 5-10 centimeters differential of mercury is observed, and P-6 and P-7 are about the same, and the approximate pressure is indicated on the Pirani gauge, open stopcock 13 to the McLeod Gauge. Check the system pressure.

n) Adjust V-9 in desired direction to give desired pressure and reread McLeod gauge. Continue until desired pressure is established and note Pirani gauge reading for later reference. Note that the Pirani gauge readings will vary as the composition of the gas to which they are exposed varies, so this noted reading is applicable to only pure helium.

o) Adjust V-3 to give the desired pressure drop across P-7. This adjustment will affect only the very lowest pressure readings, so generally the flow rate can be finally established after the pressure of the system is set. At the lowest pressures, a continued adjustment of V-9 and V-3 is made until both the pressure and the flow rate, P-7 are established at their desired values.

p) Close stopcock 13, and check to see that stopcock 30 is open. Adjust V-8 until desired pressure is indicated on Pirani gauge P-1 in the nitrogen
Adjust V-2 and V-8 until the desired pressure and flow rate, P-6, in the nitrogen system is achieved. This pressure should be within 1-2 per cent of the helium system pressure. The absolute pressure are measured by opening stopcock 12 to the McLeod gauge.

q) Recheck pressure in the helium and nitrogen systems by opening appropriately stopcocks 12 and 13 separately until the pressure is equal and constant. This establishes the operating pressure of the run. Note: the pure gases are flowing through B-1 and B-2 during this adjustment.

r) Close stopcock 18 and 30. See 17 is open.

s) Open stopcock 1 and adjust reference bleed valve until a pressure of about 3-4 centimeters of mercury absolute is noted on absolute manometer, P-3. This reference pressure will be noted and maintained for both helium and nitrogen systems for all reference pressures from 0.5 mm mercury absolute to 10 mm absolute. It has been observed that a change in reference system pressure does not affect the voltage output of the T/C cells significantly. However, it is desirable to eliminate the possibility of this pressure effect upon the T/C cell output by maintaining the reference cell pressure at some approximately constant
value. During low pressure calibrations and the run, the nitrogen system is so arranged that the pressure in P-3 can be noted continuously with the cathetometer while the helium and nitrogen sample systems pressure can be adjusted and noted on the McLeod gauge by opening either 12 or 13. (Both are never open at the same time.)

t) When the system pressures are at a constant desired value the power to the helium cell is turned on and the auxiliary power unit to the nitrogen cell is turned on. The current to the helium cell is established at about 140 milliamperes, while the current to the nitrogen cell (for its initial warm-up) is about 40 milliamperes.

u) The system is allowed to run several hours, usually over night to establish good steady state conditions.

2. Higher pressure adjustment

In the pressure range of from 10 millimeters of mercury absolute to atmospheric pressure, the absolute manometers, P-3 and P-4 are used for pressure measurements. The use of these manometers is somewhat easier than using the McLeod gauge since these are continuous pressure indicators where the McLeod gauge indicated only point value pressures. The height of the mercury differential in these manometers,
measurements, and the equation for the entire pressure range can be determined.

Two samples are studied, and the effect of the pore-size distribution of each sample on the mass flux is noted.

Using the pore-size distribution data and established Knudsen diffusion measurements, it is shown that the effective tortuosity for the macro-pores is considerably smaller than the micro-pore tortuosity. It is established that the macro-pores contribute to at least 70 per cent of the mass flux through the studied solids, which the macro-pores contribute only 20-30 per cent of the total pore volume. The solids studied are typical of catalyst carrier samples employed in present day research.

Since the micro-pores contribute most to the surface area available for chemical reaction, it is concluded that the macro-pores act as "feeder pores" to the micro pore network.

The flux ratio is observed to be constant over the entire pressure range studied, but is different from the theoretical ratio predicted by a momentum balance on the system.

A chemically inert system is constructed to enable pressures in the order of 0.5 mm Hg absolute to be established and fluxes are measured from this value to atmospheric pressure. It is shown that for typical commercial porous solids, Knudsen flow is not achieved until the ratio
the absolute pressure, is measured with a cathetometer which is accurate to the nearest 0.005 centimeter. Since the nature of the second valve from the gas cylinder is such that it will not open except at sub-atmospheric pressure, the highest attainable pressure in the present apparatus without actually removing this delivery valve is about 600 millimeters of mercury absolute. Above this value, the proper pressure differential for utilizing the bleed technique of calibration through P-5 cannot be established.

A stepwise account of a high pressure adjustment is as follows:

a) Close valves V-8 and V-9 (also bleed to reference pump) and check to see that V-6 and V-7 are open.
b) Close stopcocks 5, 6, 7, 8, 9, 16, 11, 1, 12, and 13. Stopcocks 12 and 13 should be closed at all times during the high pressure adjustments, and the McLeod gauge should be kept under vacuum at all times.
c) Open valves V-1 and V-4 about one to one and one-half full turns (just enough to allow a small amount of gas to pass through the reference cells at all times).
d) Open Valves V-2 and V-3 about two full turns, and open stopcocks 22 and 23.
e) Open the outlet from the reduction valves from the gas cylinder.

f) Check to see that V-5 is closed and that stopcocks 25 and 26 are closed when 24, 27, and 21 are open as in the low pressure adjustment.

g) Turn on vacuum pumps.

h) Adjust the outlet reduction valve (0-760 mm) to read about 100-200 millimeters of mercury absolute above the desired established pressure. This is the delivery pressure from the gas cylinders.

i) Close stopcocks 22 and 23, and note gas flow rates as indicated on manometers P-6 and P-7.

j) Making sure that stopcocks 30, 31, 17, 18, 19, and 20 are open, adjust the larger needle valve (1/4") of V-8 and V-9 until the desired pressures are nearly reached as noted on manometers P-3 and P-4. Complete the adjustment with the fine needles valves of V-8 and V-9 until the exact pressure is established. Pressure measurements are made with the cathetometer.

k) Adjust V-2 and V-3 until a 10-12 centimeter differential is noted on P-6 and P-7. They should be nearly equal. This will establish the desired flow rates of the bulk gas stream.
1) Adjust V-8, V-9 and V-2 with V-3 until the desired pressure and flow rates are established.

m) Close stopcocks 18 and 30 and open stopcock 1 (stopcock 17 should already be open). This will enable one to establish the pressure in the reference cells of the system.

n) Open the bleed valves to the reference vacuum pump's surge tank until the pressure of about 10-20 centimeters of mercury absolute is established and read on manometer P-3, with the cathetometer. This will be the reference pressure, and reasonable care should be taken to maintain this value throughout the entire experimental run, but the maintainance of this pressure value does not seem to be critical. The reference pressure can be any determined value, but it should be maintained reasonably constant throughout a run.

o) When the reference pressure has been established, close stopcock 1, and open stopcock 30. This will permit P-3 to be used for the nitrogen sample system pressure's measurement.

p) Note: The nitrogen sample pressure and the systems reference pressures cannot be read simultaneously. One must switch back and forth during an experimental run to check these systems for a constant pressure value.
q) When the desired equal pressures are reached in the sample systems (P-3 and P-4) the T/C cells are turned on as in the "low pressure" establishment.

r) Allow the system to run for several hours so that steady state can be reached.

E. Calibration of the Helium T/C cell

With the pressure of the system established several hours before the run is to be made as in Part D, Pressure and Flow Adjustment and Cell Warm-up, the run is performed in three steps: (1) Helium Cell Calibration, (2) Diffusion Measurement, and (3) Nitrogen Cell Calibration. As stated earlier, it is desirable to keep as little a time lapse between the calibrations and the actual measurement as possible. The T/C cells, which have been turned on several hours before the run is to be made, or when the pressure adjustment is completed should show a 0 per cent emf value of nitrogen on the helium cell output. This value should be constant for 10-15 minutes to indicate that steady state is reached. The constant-current data needed for calibration of the T/C cells is:

1) Reference cell pressure (absolute)
2) System pressure (absolute)
3) Concentration as measured by
   a) The bulk flow of helium, P-7 and
b) The bleed flow of nitrogen, P-5
4) T/C cell output voltage, emf
5) Temperature of the system (room temperature)

Since steady state measurements are to be made, valves V-6 and V-7 are closed throughout the calibration. This eliminates the variable of flow rate through the T/C cell. The flowing gases by-pass the T/C cells and flow through opened stopcocks 28 and 29.

A stepwise calibration of the helium cell is made as follows:

1) When the pressure, P-4, of the system is constant, a check should show that the bleed system is adjusted to permit the bleeding of nitrogen to the helium system through P-5, i.e., stopcocks 24, 21 and 27 are open and 25 and 26 are closed. Valve V-5 is closed.

2) Flow rate P-7 should be constant at between 5-15 centimeters differential.

3) When a constant output voltage from the helium cell is noted (for pure helium), stopcock 4 of the nitrogen system is closed and stopcock 22 is opened. This shuts the vacuum pump from the nitrogen system, and the nitrogen system pressure will rise to the value indicated on the output delivery pressure gauge on the gas cylinders. It is
necessary that this nitrogen system pressure be
higher than the helium system in order to bleed
nitrogen from the nitrogen side, through P-5,
into the helium system.

4) A 0 per cent nitrogen (100 per cent helium) con-
centration value and its corresponding emf can be
noted at the system pressure. Note: Each time a
concentration value is recorded all of the data as
described earlier in this section must be recorded.

5) If the system pressure is found to drift, each
time a concentration-emf value is established,
the pressure must be varied through the range
which include the desired value, and the change in
emf with pressure is noted for that particular
concentration. If the pressure remains constant,
then the direct concentration-emf value may be
taken at the constant pressure. It should be noted
that the T/C cells are extremely pressure sensi-
tive so it is absolutely essential that the pres-
sure be maintained constant. This includes both
the low pressure and the high pressure ranges.

6) Close stopcock 21 and open valve V-5 slightly.
Note the mercury differential established in
manometer P-5. Knowing this bleed differential
and the differential of the bulk flow of P-7, a
rough calculation with Equation (70) can be made
to establish the concentration at the desired pressure. It should be again noted that capillary P-5 is twice as long as capillary P-7 to enable small amounts of nitrogen (or helium) to be bled from one system to the other.

7) The emf-concentration value is noted for at least three different concentrations for a helium cell calibration. These values must all occur at the constant desired pressure, and the emf-concentration relationship should be a nearly linear one.

8) It should be noted that it is also very important that the current to the T/C cells be constant. The current can be adjusted by means of the "current adjust" knob located on the T/C cell control panel.

9) When taking any manometer reading, the legs should be tapped several times to insure that no mercury is held up by sticking to the glass. The McLeod gauge should be tapped whenever a reading is taken.

10) For the helium T/C cells a 0-10 per cent nitrogen concentration curve should be established for low pressure studies. At higher pressures a 10-15 per cent calibration curve should be established, and three carefully measured points should determine a straight line emf-concentration relationship.
11) When the emf-concentration curve nitrogen in helium has been established at constant pressure and constant current conditions, proceed directly to the diffusion measurement.

F. Measurement of the Counter-diffusion rates

The measurement of the actual rate of counter-diffusion of nitrogen and helium through the porous solid sample is made immediately after the helium T/C cell calibration and immediately before the nitrogen T/C cell calibration. The bulk flow rates of nitrogen and helium through the system were established in Part D, Pressure and Flow Adjustment, so these need not be readjusted. The pressures were also established during that time, and were maintained during the preceding section with the exception that at the end of the helium T/C cell calibration, the nitrogen side of the system is shut off from the vacuum pump at stopcock 4. By opening stopcock 4 and closing stopcock 22 (the flow meter by-pass), the nitrogen system will attain its original determined pressure, and desired flow rate as indicated on P-6. The system is allowed to run for about 30 minutes in order that pressure surges be equilized and the system again achieves a steady-state status. When this has been accomplished, proceed as follows:

1) When the helium cell calibration is completed, close valve V-5 and open by-pass stopcock 21. At
this time stopcocks 24 and 27 are closed and stopcocks 25 and 26 are opened to prepare the bleed system for the nitrogen cell calibration.

2) Open stopcock 4 and close stopcock 22. Allow system to reach steady state.

3) Close stopcocks 2, 3, and 4 and open stopcocks 5, 6, and 7. This allows the nitrogen gas to flow across the porous solid sample. At this step, all stopcocks should be open with the exceptions of 22, 12, 1, 2, 3, 4, 24, and 27 in the nitrogen system.

4) Check the nitrogen system pressure and if it is not at the desired value, make the necessary adjustments to establish the pressure that is desired for the run.

5) Close stopcocks 10, 14, and 15, and open stopcocks 8, 9, and 16. Helium now flows across the porous solid. At the step, all of the stopcocks in the helium system should be open except 10, 11, 14, 15, 23, and 13. The system pressure can either be checked with the manometer, P-4, or McLeod gauge, P-10, depending upon the pressure range at which the run is to be made.

6) When equal pressures are established in the helium and the nitrogen systems, and the helium system
pressure is the same as that at which the calibration was made, the system is allowed to run until a steady-state voltage is recorded from the T/C cells on the potentiometer. Note: The system pressure must be exactly the same as the calibration pressure, and ample time must be allowed for the system to reach steady-state, i.e., a constant voltage recorded on the potentiometer for at least 15 minutes, since a very small voltage change is to be examined in the helium system.

7) When steady state is reached, the bulk flow rate is measured in the helium system at P-7 making sure that the manometers are tapped before readings are taken. The pressure is recorded as well as the current at which the T/C cells are operated (same as calibration). V-7 is closed. Note the room temperature and record this value. By means of the potentiometer, record the steady-state emf of the helium T/C cell, and from the calibration curve initially prepared, the concentration can be recorded directly. The pressure of the nitrogen reference side is also recorded, and this should be nearly the same pressure as was established during the calibration procedure.
of the mean free path to the mean pore diameter is 100 to 1000 times the ratio calculated assuming the Wheeler mean pore radius based upon total porous solid properties of total surface area and total pore volume. The pore-size distribution is needed to estimate diffusion coefficients. Use of the Wheeler mean pore radius concept for diffusion coefficient estimation can lead to serious error in predicting the mass fluxes through the porous solid.
8) When the helium concentration (per cent nitrogen) has been noted by means of T-2, the power supply is switched to the pre-warmed nitrogen cell, T-1, and the current adjusted at about 140 milliamperes. A constant current will have to be supplied to T-1 during this part of the run and during the calibration of this T/C cell, so this value should be noted.

9) When steady-state is reached by noting a constant emf from T-1 for about 10-15 minutes, the bulk flow rate of nitrogen as measured by P-6 is noted. Valve V-6 is closed. Room temperature, system pressure, and reference pressure is also recorded, together with the sample emf value. When this is completed, proceed immediately with the nitrogen cell calibration.

G. Calibration of the nitrogen T/C cell

The calibration of the nitrogen T/C cell, T-1, must immediately follow the measurement of the counter-diffusion rates, since the cell calibration may drift with time. The procedure is exactly the same as the calibration of the helium T/C cell except that P-5 is now used to bleed helium into the nitrogen system. A stepwise procedure is as follows:
1) When the steady-state nitrogen sample emf has been recorded, close stopcocks 5, 6, 7, 8, 9, 16, and open stopcocks 2, 3, 4, 10, 14, and 15. This bypasses the sample cell, S-1 and S-2, and the pure gases flow through B-1 and B-2.

2) Open stopcock 23 to allow a large flow of helium to purge its system of the previously diffused nitrogen gas.

3) After the pure gases have flowed for about 15 minutes, close stopcock 15, which shuts the helium system from its vacuum pump. The system pressure will then rise to the pre-established value set on the cylinder outlet valve.

4) Close stopcock 21, the bleed-capillary by-pass.

5) Open V-5 slightly until a small mercury height differential is noted at P-5. Helium is now flowing into the nitrogen system. It should be noted here that the diffusion rates of helium into nitrogen are about twice those of the nitrogen into the helium system. The calibration range of the nitrogen T/C cell is therefore about twice that of the helium cell.

6) A rough estimate of the desired concentrations can be made by applying the laminar flow equation, Equation (70), through the capillary, or by remembering that the capillary, P-5 is twice the
length of capillary P-6, so a direct estimate of the concentration can be made at any established P-6.

7) A desired differential can be established at P-5 so that the nitrogen cell can be calibrated from 5-15 per cent helium at the low pressures, and as high as 23 per cent at the higher pressures. The advantage that the nitrogen T/C cell calibration has compared to the helium T/C cell calibration is that the sample emf of the nitrogen system is known, and enough helium can be bled to establish an output voltage from T-1 to nearly equal that of the pre-recorded sample emf. In this way, the sample emf value can be surrounded by three concentrations directly, and the calibration performed.

8) V-6 should be closed when any emf-concentration value is established to eliminate the flow variable of the T/C cells.

9) Three values of emf-concentration are established about the sample emf value at the sample pressure. If the pressure of the calibration system is found to vary, then a study of each concentration emf versus pressure must be made to establish the proper voltage for any given concentration at the pre-established sample pressure.
10) For any concentration the data are recorded as:
   a) Room temperature
   b) Reference pressure
   c) System pressure
   d) Bulk flow rate, P-6
   e) Bleed flow rate, P-5
   f) Cell output, emf
   g) Concentration (from d. and e.)

11) When the straight-line relationship is established between concentration and output from T-1, the sample concentration is noted.

H. System shut-down

   At the end of any run, the system is shut down before another one can be made, and the following steps must be taken in this shut down:

   1) Open V-6 and V-7 or the pressure surge will blow the oil out of the flow rate manometers across the cell flow lines.
   2) Close V-5, and open stopcock 21.
   3) Close stopcocks 25 and 26 and open 24 and 27 to prepare the system for the next helium calibration.
   4) Open by-pass stopcocks 22 and 23 (if not already open), and open the helium stopcock 15 if it has not already been opened.
   5) Allow the pure gases to flow through the system for a few minutes.
6) Shut off the power to the T/C cells, and adjust the switches so that the power will be applied to T-2 when turned on.

7) Open cylinder outlet sub-atmospheric reduction valve completely.

8) Shut off vacuum pumps.

9) Check water level in two batteries which supply power to the T/C cells.

The system will reach atmospheric pressure and will be ready for the pressure adjustment and calibration of the helium T/C cell, T-2, when another experimental determination is to be made.
VIII. EXPERIMENTAL DATA

A. Material balance for experimental system

An over-all material balance for the experimental system can be made with reference to Figure 22. In an actual experimental determination, the quantities $R_A$ and $R_B$ are measured in terms of their molar flow rates, gram moles per square centimeter per second. The actual calculated values are obtained from Equation (70), from the measured pressure differential established across manometers, P-6 and P-7 in Figure 2, and from the capillary calibration curve, Figures 10 and 11. The capillary outlet pressure must be known absolutely, and this is always measured as the actual system pressure.

The outlet concentrations from the diffusion cell are measured by means of the calibrated thermal conductivity cells, T-1 and T-2. The quantities $X_A$ and $X_B$ are the mole fractions of nitrogen and helium in the outlet streams from the diffusion cell, respectively.

An over-all expression for the material balances for both streams A (nitrogen) and B (helium) can be written as:

$$R_A = F_A + N_A^C$$

(71)
Figure 22.—Over-all material balance.
\[ R_B = F_B + N_B^c \]  

(72)

The effluent concentrations, \( X_A \) and \( X_B \) are measured as

\[ X_A = \frac{N_A^c}{(N_A^c + F_B)} \]  

(73)

\[ X_B = \frac{N_B^c}{(N_B^c + F_A)} \]  

(74)

Since \( R_A, R_B, X_A, \) and \( X_B \) are known, it is desired to find the two quantities, \( N_A^c \) and \( N_B^c \), which are the diffusion rates of nitrogen and helium, respectively.

Rearrangement of Equations (73) and (74) show that

\[ N_A^c = \frac{(X_A / (1 - X_A)) F_B}{(X_A / (1 - X_A)) F_B} \]  

(75)

\[ N_B^c = \frac{(X_B / (1 - X_B)) F_A}{(X_B / (1 - X_B)) F_A} \]  

(76)

If \( C_A \) and \( C_B \) are defined as,

\[ C_A = X_A / (1 - X_A) \]  

(77)

\[ C_B = X_B / (1 - X_B) \]  

(78)

then,

\[ N_A^c = C_A F_B \]  

(79)

\[ N_B^c = C_B F_A \]  

(80)
A combination of Equations (79) and (80), and Equations (71) and (72) can be made,

\[
R_A = \frac{N_B^C}{C_B} + N_A^C
\]  

(81)

\[
R_B = \frac{N_A^C}{C_A} + N_B^C
\]  

(82)

and Equations (81) and (82) can be solved for the unknown quantities, \(N_A^C\) and \(N_B^C\), as

\[
N_A^C = C_A \left( R_B - C_B R_A \right) / (1 - C_A C_B)
\]  

(83)

\[
N_B^C = C_B \left( R_A - C_A R_B \right) / (1 - C_A C_B)
\]  

(84)

These latter two equations form the basis of all of the experimental calculations. The experimental values are given in Tables 5 and 6.

B. Calculation of Knudsen diffusion coefficients

In section V, Theory, it is stated that the defined Knudsen diffusion coefficient can be expressed as Equation (11). The implications of this statement include that the diffusing gas is not affected by any counter-diffusing gas, and that the flux is constant over the length of the diffusion path. By the nature of the Knudsen diffusion phenomenon, namely where the resistance due to flow is due to molecular-wall bombardments rather than intermolecular
collisions, it should be noted that the direct integration of this expression can be used to define the Knudsen coefficient, $D_{KA}^e$. The direct integration of this expression can strictly be used only for the Knudsen region, but for the case of equi-molal counterdiffusion, the generalized definition of counter-diffusion as expressed in Equation (20) can be reduced to Fick's first law.

Integration of Equation (11) results in the expression,

$$N_A = -D_{KA}^e c \frac{\nabla X_A}{L}$$  \hspace{1cm} (85)

where $N_A$ is the molar diffusion rate, gm moles/cm$^2$-sec, $D_{KA}^e$ is the Knudsen diffusion coefficient, cm$^2$/sec, $c$ is the total molar concentration, $L$ is the length of the diffusion path, and $\Delta X_A$ is the mole fraction gradient over which diffusion occurs.

Knowing that the gases behave ideally at the studied pressures, an expression for the total molar concentration in terms of the absolute pressure can be shown to be

$$C = \frac{P}{RT}$$  \hspace{1cm} (86)

Substitution of Equation (86) into Equation (85) allows the Knudsen diffusion coefficient to be calculated from steady-state measurements of the diffusion flux, as

$$D_{KA}^e = \frac{N_A RL}{P \Delta X_A}$$  \hspace{1cm} (87)
II. INTRODUCTION

The problem of the diffusion of gases in porous solids is encountered in two major areas, namely, gas separation techniques and heterogeneous catalysis. In gas separation, the effect of the solid’s interaction with the diffusion coefficients must be determined.

In heterogeneous catalysis, the molecules of the reacting gas or of the reacting gas mixture must come into contact with the catalytic surface in order for the reaction to proceed. Since this necessarily involves the movement of these molecules from the bulk gas stream into the catalyst or the catalyst-carrying particles, the study of this movement is important.

If a particular catalyst particle is subject to total pressure gradients throughout, or if the geometrical arrangement of the particle is such that there is an appreciable flow rate change along the surface of the particle, then a physical flow of the gases into the particle takes place. Such a phenomenon might occur in cases where the particle is extremely long or if the ratio of the radius to the length of the particle is very small. The flow of gases in porous solids due to such total pressure gradients has been studied by Carman (4) and (5), Field (13), Goodnight et al (14),
if the flux is measured and the concentration gradient is known.

In the calculation of the data of this study Equation (87) was applied to the total pressure range to determine the range of Knudsen diffusion. One criterion of Knudsen diffusion is that it is pressure independent, so, strictly speaking, Equation (87) can be used until it is shown that the effective diffusion coefficient becomes pressure variant. Once a pressure dependence is established, then Equation (48) must be used to calculate an effective diffusion coefficient. The coefficients are given in Tables 7 and 8.

C. Determination of the experimental effectiveness factor for the molecular diffusion coefficient

Equation (45) presents the expression for the rate of diffusion for any species in a binary counter-diffusing system in any region of flow. It may be noted that, with the exception of the correction term or effectiveness factor for the molecular diffusion coefficient ($\frac{\epsilon}{q_d}$), all of the other values are determined experimentally from the material balance.

As stated in Section V, Theory, Equation (11) can be used to calculate only diffusion coefficients in the Knudsen region of flow. The only problem which arises, therefore, is how to establish with reasonably certainty that Knudsen flow prevails. This is easily done by measuring diffusion
rates over a wide range of total pressures, using Equation (11) to calculate all coefficients, and note when the coefficient begins to be affected by the pressure change. In true Knudsen flow the coefficient is not pressure dependent. In the present work this technique was employed and the Knudsen coefficient effective for the particular porous solid studied is determined independently from any other determination.

With the Knudsen coefficient established, Equation (45) can be used to calculate the molecular diffusion coefficient effectiveness factor directly from the higher pressure experimental measurements. It may be noted that this solution must be a trial-and-error one since the quantity, $\frac{\mathcal{E}}{q_D}$, to be determined appears in both the linear and the log terms.

The porosity of the solid can be determined from the pore volume data and the actual solid volume, so with this value of $\mathcal{E}$ known, the tortuosity, $q_D$, can be determined. These values are shown in Table 9.

D. Transition diffusion coefficients

As stated earlier, the application of Equation (11) to Knudsen diffusion does not account for the fact that the resistance for diffusion of a gas in a binary mixture must include the momentum transferred between counter-diffusing gas molecules of different species. Therefore in the region
where the mean free path of the gas molecules approaches the pore diameter, or becomes less than the diameter of the pore through which diffusion is to take place, Equation (48) must be used. It can be noted that all of the values needed for substitution into this equation have been determined from the experimental data. A direct calculation of $D_N$ can then be made, and the results are indicated in Tables 7 and 8.

E. Determination of the tortuosity factor, $q_K$, for Knudsen diffusion

Equation (60) establishes the method for determining an effective length corrective factor, or tortuosity, for Knudsen flow. In order to calculate this value, the pore-size distribution spectrum for the solid must be known. The model assumed is one in which all of the pores are regular cylinders which have a tortuosity which is some common multiple of the length of the actual experimental solid. The only data needed for this calculation is:

1) An established Knudsen diffusion mechanism and one measured flux value at a known pressure,
2) the concentration gradient for this transfer,
3) the total pore volume of the solid,
4) the length of the actual experimental solid, and
5) the volume distribution spectrum, that is, the fraction of the total volume which exists at any given pore radius, $\bar{r}$.
It should be stressed that the pore-size distribution analysis of the porous solid which precedes Equation (60) applies only to mass transfer by diffusion in the Knudsen range. It is in only this type of flow that the integration of Equation (11) strictly applies and it is only in Knudsen flow that the diffusion coefficient is known to be a function of the mean pore radius, $\bar{r}$.

The pore volume distribution is given in Tables 10, 11, and 12. The macro-pore data is obtained from the California Research Corporation and is given in Table 10. These determinations are made by the usual mercury penetration techniques. The micro-pore data is obtained by nitrogen adsorption analysis from the Gulf Research and Development Company. The results from their automatic unit are given in Table 11 for Sample 1 and in Table 12 for Sample 2.

Original pore volume data on the powders before compression to the cylindrical solids is obtained from the American Cyanamid Company, and this data is also given in Tables 11 and 12.

It is usually assumed that the nitrogen adsorption method determines the micro-pore structure, and all of the pores which lie in range of diameters larger than about 300 Å constitute the macro-pore region. This division also applies to the present work.
F. Description of items tabulated

Table 1—Flowmeter (capillary) calibration data

  a) Volumetric measurements are indicated for gas flowing through the capillaries of known dimensions. A calculated mass flow rate assuming laminar flow through the capillaries at known pressure drops is compared to the actual flow volumes.

  b) The calibration data for flowmeters, P-5, for both nitrogen and helium gas, P-6 for nitrogen and P-7 for helium are presented.

Table 2—Sample properties

  The properties of both Sample 1 and Sample 2 are presented. In this table, \( L \) is the actual length of the pellet; \( D \) is the actual diameter of the pellet; \( D_e \) is the effective surface diameter available for diffusion since part of the surface is covered by the glass tubes in the mounting process; \( A_R \) is the ratio of the effective surface area of the solid to the cross-sectional area of the capillary through which the flow measurements are made; \( q_D \) is the molecular tortuosity; \( W \) is the weight of the pellet in grams; \( q_K \) is the Knudsen tortuosity; \( S_g \) is the total surface area per gram of solid as measured by the American Cyanamid Company; \( V_g \) is the total pore volume in cubic centimeters per gram of solid as measured by the usual water-filling of the solid techniques; \( V_t \) is the actual
volume of the pellet including both the solid volume and the pore volume; \( V_p \) is the volume of the original uncompressed powder, and is the reciprocal of the bulk density of the powder; \( \rho_s \) is the density of the solid alumina as calculated knowing the total volume of the solid and the total pore volume.

Table 3—Experimental nitrogen data, Sample 1 and Sample 2

This table presents the raw experimental data for both samples and includes all of the properties of the system measured when an experimental determination is made, including the output voltage from the T/C cells.

Table 4—Experimental helium data, Sample 1 and Sample 2

This table presents the experimental data for helium as measured at the same time as was the nitrogen data in Table 3. Counter-diffusion measurements are made for each pressure level, and an experimental run consists of measuring both the nitrogen and helium flux rates at the same time.

Table 5—Diffusion rates of Sample 1

A presentation of the actual fluxes for sample one as a function of pressure is made in this table. The flux rates are calculated from the material balance relationships established in Equations (83) and (84). The ratio of the helium flux to the nitrogen flux, \( R_{AB} \), as well as the concentration gradient is presented here. This table also
presents the calculated molecular diffusion coefficients for the binary system.

Table 6--Diffusion rates of Sample 2

This table presents the same data for Sample 2 as did Table 5 for Sample 1.

Table 7--Comparison of diffusion coefficients, Sample 1

The experimentally measured diffusion coefficients for the first sample are presented in this table. A comparison is given of the diffusion coefficients as calculated from Equation (11) with those calculated from Equation (39) which considers the effect of the counter-diffusing gas. All calculations according to Equation (11) were originally made to determine the point at which the coefficient became a function of the system pressure. This establishes the indicated Knudsen diffusion coefficient. When the effective molecular and Knudsen coefficients are established, Wheeler's Equation (4) is used to calculate the effective coefficients as given in the last two columns of this table.

Table 8--Comparison of diffusion coefficients, Sample 2

This table presents the same data for Sample 2 as did Table 7 for Sample 1.
Table 9—Calculation of $\frac{E}{q_D}$ from Equation (45), Sample 1 and Sample 2

The calculated value of the effectiveness factor for molecular diffusion is presented here. Each value is calculated from actual experimental data for each of the counter-diffusing gases. The calculated value includes the experimentally measured fluxes and flux ratios, as well as the concentration gradient established. The effective Knudsen coefficients from Tables 7 and 8 are used in the calculations. An average value for $\frac{E}{q_D}$ is given for the six determinations for each solid. This value is used in the statistical analysis as the true value for the molecular diffusion effectiveness factor. The calculations are made at the three higher pressure levels.

Table 10—Mercury penetration pore-volume data

This table presents the raw data as recorded by the California Research Corporation for both samples. Their total pore volume determinations are also listed as $(V_g)_1$ and $(V_g)_2$. The assumed surface tension and contact angle for mercury and the alumina solid is given.

Table 11—Pore volume distribution, Sample 1

Presented in this table is the total pore volume as measured by the American Cyanamid Company, Gulf Research and Development Company, California Research Corporation and by the present study. The Gulf Research and Development Company
raw data is presented in columns 3 and 6, and the distribution data as used in the calculations for the Knudsen tortuosity, $q_K$, are presented in columns 1, 2, 4, and 5.

Table 12—Pore volume distribution, Sample 2

This table presents the same data for Sample 2 as did Table 11 for Sample 1. Since there was an overlap in the pore volume data as obtained from California Research Corporation and Gulf Research and Development Company, the percentage of the total pore volume which exists in the three pore radius ranges, $0.124 - 81.1$ microns, $0.124$ microns - $275$ angstroms, and $0 - 275$ angstroms is calculated as shown in Section IX, Part E.
<table>
<thead>
<tr>
<th>Sample</th>
<th>L</th>
<th>D</th>
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<tr>
<td>Sample 1</td>
<td>1.66091 cm</td>
<td>2.6474 cm</td>
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<tr>
<td></td>
<td>D_e (less glass coverage) = 7.1477 x 10^3</td>
<td>2.1904 cm</td>
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<tr>
<td></td>
<td>A_R = 7.1477 x 10^3</td>
<td>q_D = 6.3004</td>
</tr>
<tr>
<td></td>
<td>W = 5.7792 gm</td>
<td>q_K = 2.268</td>
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<tr>
<td></td>
<td>S_g = 199 m^2/gm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>V_t = 1.582 cc/gm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>p_s = 2.755 gm/cc</td>
<td></td>
</tr>
<tr>
<td>Sample 2</td>
<td>1.2440 cm</td>
<td>2.6645 cm</td>
</tr>
<tr>
<td></td>
<td>D_e (less glass coverage) = 7.2575 x 10^3</td>
<td>2.2071 cm</td>
</tr>
<tr>
<td></td>
<td>A_R = 7.2575 x 10^3</td>
<td>q_D = 7.847</td>
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<td></td>
<td>W = 8.4481 gm</td>
<td>q_K = 3.02</td>
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<tr>
<td></td>
<td>S_g = 202 m^2/gm</td>
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</tr>
<tr>
<td></td>
<td>V_t = 0.8212 cc/gm</td>
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</tr>
<tr>
<td></td>
<td>p_s = 3.138 gm/cc</td>
<td></td>
</tr>
</tbody>
</table>
Greenberg and Weber (15), Hutchinson et al. (19), Schiedegger (32), Wang (37), Wilson et al. (45) and many others engaged in petroleum production research.

In the usual catalytic reactor, small particles are placed in a bed through which the reacting gases are passed. In this case the pressure drop across any one particle is negligible and the molecular movement into the particles is due to a partial pressure gradient at a field total pressure. This diffusion movement is a function of the size of the pores into which the gases pass, or is a function of the distribution of the pore size within the particle.

Of the two cases of gas flow within porous solids mentioned, the second will be studied by this work. The first flow phenomenon, namely, that which exists due to a total pressure gradient across the particle has great application in the field of petroleum recovery research. In secondary oil-well recovery, a total pressure gradient is induced by any of several techniques (underground combustion, water injection, etc.) and as a result, liquids and gases flow through the porous rocks and out into the recovery area. It is our purpose in this study, however, to examine only that flow which is induced by a concentration or partial-pressure gradient which is typical of the heterogeneous catalytic research area.

It is known that most catalyst particles have an internal surface area which is considerably greater than the
### TABLE 3.--Experimental nitrogen data

<table>
<thead>
<tr>
<th>Run</th>
<th>Flow cm Hg</th>
<th>T °C</th>
<th>P,s mm</th>
<th>P,R cm</th>
<th>a ma</th>
<th>emf mv</th>
<th>conc. % He</th>
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</thead>
<tbody>
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<td>24.7</td>
<td>0.464</td>
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<td>130</td>
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<td>7.770</td>
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<td>0.900</td>
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<tr>
<td>3</td>
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<td>3.23</td>
<td>3.429</td>
<td>130</td>
<td>+7.280</td>
<td>11.270</td>
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<tr>
<td>4</td>
<td>10.788</td>
<td>23.4</td>
<td>8.14</td>
<td>4.079</td>
<td>140</td>
<td>-5.975</td>
<td>11.63</td>
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<td>15.545</td>
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<td>130</td>
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<td>25.0</td>
<td>101.74</td>
<td>10.389</td>
<td>130</td>
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</table>

Sample 2

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<th>T °C</th>
<th>P,s mm</th>
<th>P,R cm</th>
<th>a ma</th>
<th>emf mv</th>
<th>conc. % He</th>
</tr>
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<tbody>
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<td>10.03</td>
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<td>-9.440</td>
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<td>23.8</td>
<td>3.26</td>
<td>4.183</td>
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<td>Run</td>
<td>Flow (cm Hg)</td>
<td>T (°C)</td>
<td>P, s (mm abs)</td>
<td>P, R (cm abs)</td>
<td>a (ma)</td>
<td>emf (mv)</td>
<td>conc (% N₂)</td>
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<td>140</td>
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<td>23.4</td>
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<td>15.409</td>
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<td>+12.240</td>
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<table>
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<tr>
<td>7</td>
</tr>
<tr>
<td>8</td>
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TABLE 5.—Diffusion rates of sample 1

<table>
<thead>
<tr>
<th>P, s mm Hg</th>
<th>N_A^c gm-mole cm^2-sec</th>
<th>N_B^c gm-mole cm^2-sec</th>
<th>X_A</th>
<th>X_B</th>
<th>R_AB NB/NA °C</th>
<th>T cm^2/sec</th>
<th>( \Omega_{AB} )</th>
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<tr>
<td>0.458</td>
<td>1.343 \times 10^{-5}</td>
<td>3.256 \times 10^{-5}</td>
<td>0.02550</td>
<td>0.06475</td>
<td>2.42</td>
<td>24.7</td>
<td>1159.3</td>
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<td>0.900</td>
<td>2.516 \times 10^{-5}</td>
<td>5.386 \times 10^{-5}</td>
<td>0.03625</td>
<td>0.06875</td>
<td>2.14</td>
<td>24.8</td>
<td>590.27</td>
</tr>
<tr>
<td>3.23</td>
<td>9.323 \times 10^{-5}</td>
<td>2.093 \times 10^{-4}</td>
<td>0.05275</td>
<td>0.11270</td>
<td>2.24</td>
<td>24.5</td>
<td>164.22</td>
</tr>
<tr>
<td>8.19</td>
<td>2.187 \times 10^{-3}</td>
<td>5.498 \times 10^{-3}</td>
<td>0.0555</td>
<td>0.1163</td>
<td>2.51</td>
<td>23.4</td>
<td>64.408</td>
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<td>5.296 \times 10^{-3}</td>
<td>1.1547x10^{-2}</td>
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<td>0.2471</td>
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<td>26.1</td>
<td>0.89262</td>
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<td>151.16</td>
<td>1.7355x10^{-3}</td>
<td>4.7245x10^{-2}</td>
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<td>29.55</td>
<td>7.232 \times 10^{-4}</td>
<td>1.537 \times 10^{-3}</td>
<td>0.113</td>
<td>0.162</td>
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<td>26.2</td>
<td>18.104</td>
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<tr>
<td>101.76</td>
<td>1.613 \times 10^{-3}</td>
<td>3.148 \times 10^{-3}</td>
<td>0.1381</td>
<td>0.2135</td>
<td>1.95</td>
<td>25.1</td>
<td>5.2284</td>
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Avg. 2.286
TABLE 6. --Diffusion rates of sample 2

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<tr>
<th>P, s mm Hg</th>
<th>N_A^C gm-mole/cm²-sec</th>
<th>N_B^C gm-mole/cm²-sec</th>
<th>X_A</th>
<th>X_B</th>
<th>XAB</th>
<th>RAB NB/NA</th>
<th>T °C</th>
<th>DAB cm²/sec</th>
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<tr>
<td>0.500</td>
<td>4.372 x10⁻⁵</td>
<td>11.00 x10⁻⁵</td>
<td>.0407</td>
<td>.0888</td>
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<td>25.9</td>
<td>1068.6</td>
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<tr>
<td>1.506</td>
<td>8.568 x10⁻⁵</td>
<td>2.6205x10⁻⁴</td>
<td>.0358</td>
<td>.1003</td>
<td>3.06</td>
<td>24.8</td>
<td>352.75</td>
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<tr>
<td>8.000</td>
<td>4.6528x10⁻⁴</td>
<td>1.2325x10⁻³</td>
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<td>.2646</td>
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<td>30.72</td>
<td>1.0984x10⁻³</td>
<td>3.0605x10⁻³</td>
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<td>.3416</td>
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<td>5.674 x10⁻²</td>
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<td>.2925</td>
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<td>.2312</td>
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<tr>
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<td>1.2206x10⁻²</td>
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<tr>
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<td>.5640x10⁻³</td>
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<td>.1370</td>
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<td>23.8</td>
<td>162.64</td>
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<td>Avg.</td>
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<table>
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<th>$D_{KA}^e$</th>
<th>$D_{KB}^e$</th>
<th>$D_{WA}^e$</th>
<th>$D_{WB}^e$</th>
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<tbody>
<tr>
<td>mm Hg</td>
<td>Equation (47)</td>
<td>cm$^2$/sec</td>
<td>Equation (48)</td>
<td>Equation (4)</td>
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<td>.3371</td>
<td>.1390</td>
<td>.3371</td>
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<td>.1995</td>
<td>.07378</td>
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<td>.3109</td>
<td>.1463</td>
<td>.3109</td>
</tr>
<tr>
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<td>.1059</td>
<td>.2066</td>
<td>.1079</td>
<td>.2317</td>
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$D_{KA}^e = .1385$ cm$^2$/sec

$D_{KB}^e = .3320$ cm$^2$/sec
TABLE 8.—Comparison of diffusion coefficients, Sample 2

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<tr>
<th>P, s mm Hg</th>
<th>$D_{KA}^e$</th>
<th>$D_{KB}^e$</th>
<th>$D_{NA}$</th>
<th>$D_{NB}$</th>
<th>$D_{WA}^e$</th>
<th>$D_{WB}^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>abs cm²/sec</td>
<td>cm²/sec</td>
<td>cm²/sec</td>
<td>cm²/sec</td>
<td>cm²/sec</td>
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</tr>
<tr>
<td>0.500</td>
<td>0.3209</td>
<td>0.8074</td>
<td>0.3209</td>
<td>0.8074</td>
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<td>--</td>
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<tr>
<td>1.506</td>
<td>0.2103</td>
<td>0.6433</td>
<td>0.2103</td>
<td>0.6433</td>
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<tr>
<td>8.00</td>
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<td>0.8789</td>
<td>0.3318</td>
<td>0.8789</td>
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<td>--</td>
</tr>
<tr>
<td>30.72</td>
<td>0.2571</td>
<td>0.7164</td>
<td>0.2571</td>
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<tr>
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<td>0.06034</td>
<td>0.1619</td>
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<td>0.3208</td>
<td>0.7109</td>
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<td>0.7109</td>
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</tbody>
</table>

$D_{KA}^e = 0.3067 \text{ cm}^2/\text{sec}$

$D_{KB}^e = 0.7650 \text{ cm}^2/\text{sec}$
TABLE 9.--Values of $\varepsilon/\eta_D$ from equation (45)

<table>
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<tr>
<th>$P, s$ (\text{mm Hg})</th>
<th>((\varepsilon/\eta_D)_{N_2})</th>
<th>((\varepsilon/\eta_D)_{He})</th>
<th>(R_{AB_{NB/NA}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>599.05</td>
<td>0.1735</td>
<td>0.1610</td>
<td>2.18</td>
</tr>
<tr>
<td>151.16</td>
<td>0.0775</td>
<td>0.0810</td>
<td>2.72</td>
</tr>
<tr>
<td>101.76</td>
<td>0.1335</td>
<td>0.1075</td>
<td>1.95</td>
</tr>
</tbody>
</table>

Avg $\varepsilon/\eta_D = 0.1223$

| Sample 2                |                  |                  |                  |
| 600.12                  | 0.0892           | 0.0865           | 2.86             |
| 299.69                  | 0.0676           | 0.0780           | 2.37             |
| 100.63                  | 0.0685           | 0.0780           | 2.62             |

Avg $\varepsilon/\eta_D = 0.0780$
### TABLE 10.—Mercury penetration pore-volume data

Measurements performed by the California Research Corp.

<table>
<thead>
<tr>
<th>Pressure, psia</th>
<th>Diameter, microns</th>
<th>Sample 1</th>
<th>Sample 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.13</td>
<td>194.7</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>1.79</td>
<td>129.4</td>
<td>0.012</td>
<td>0.104</td>
</tr>
<tr>
<td>2.40</td>
<td>91.7</td>
<td>0.037</td>
<td>0.132</td>
</tr>
<tr>
<td>3.60</td>
<td>61.1</td>
<td>0.070</td>
<td>0.212</td>
</tr>
<tr>
<td>5.50</td>
<td>40.0</td>
<td>0.103</td>
<td>0.288</td>
</tr>
<tr>
<td>8.20</td>
<td>26.8</td>
<td>0.136</td>
<td>0.382</td>
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<tr>
<td>12.40</td>
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<td>0.211</td>
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<tr>
<td>18.50</td>
<td>11.89</td>
<td>0.277</td>
<td>0.642</td>
</tr>
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<td>28</td>
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<td>0.783</td>
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<tr>
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<td>0.565</td>
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<tr>
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<td>3.44</td>
<td>1.021</td>
<td>11.07</td>
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<td>17.28</td>
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<td>150</td>
<td>1.467</td>
<td>4.90</td>
<td>20.7</td>
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<tr>
<td>230</td>
<td>0.957</td>
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</tr>
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<td>350</td>
<td>0.629</td>
<td>8.37</td>
<td>25.5</td>
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<td>520</td>
<td>0.423</td>
<td>9.88</td>
<td>27.2</td>
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<td>0.275</td>
<td>15.75</td>
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</tr>
<tr>
<td>1015</td>
<td>0.217</td>
<td>20.25</td>
<td>29.5</td>
</tr>
</tbody>
</table>

\[
\bar{d} = \frac{4 \gamma \cos \phi}{P}
\]

\(\gamma = \text{surface tension} = 404 \text{ dynes/cm}\)

\(\phi = \text{contact angle} = 160^\circ\)

\(P = \text{pressure}\)

\((V_g)_1 = 1.228 \text{ cc/gm}\)

\((V_g)_2 = 0.5024 \text{ cc/gm}\)
TABLE 11.— Pore volume distribution - Sample 1

\[ V_g \text{ (powder)} = 1.04 \text{ cc/gm} - \text{American Cyanamid Co.} \]
\[ V_g \text{ (pellet)} = 0.74 \text{ cc/gm} - \text{Gulf Research & Development Co.} \]
\[ V_g \text{ (pellet)} = 1.219 \text{ cc/gm} - \text{California Research Corp. & J. P. Henry, Jr.} \]

<table>
<thead>
<tr>
<th>Mercury</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F )</td>
<td>( X_{VR}^% )</td>
</tr>
<tr>
<td>( \mu )</td>
<td></td>
</tr>
<tr>
<td>81.1</td>
<td>.012</td>
</tr>
<tr>
<td>55.3</td>
<td>.025</td>
</tr>
<tr>
<td>38.2</td>
<td>.033</td>
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<tr>
<td>25.3</td>
<td>.033</td>
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<tr>
<td>16.7</td>
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</tr>
<tr>
<td>11.1</td>
<td>.074</td>
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<tr>
<td>7.41</td>
<td>.066</td>
</tr>
<tr>
<td>4.94</td>
<td>.090</td>
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<tr>
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<td>.196</td>
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<tr>
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<td>.453</td>
</tr>
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<tr>
<td>.397</td>
<td>1.81</td>
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<tr>
<td>.264</td>
<td>1.50</td>
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<tr>
<td>.175</td>
<td>5.83</td>
</tr>
<tr>
<td>.124</td>
<td>4.47</td>
</tr>
<tr>
<td>20.12%</td>
<td>10-7</td>
</tr>
</tbody>
</table>

\*Nitrogen Adsorption = Gulf Research & Development Co.

\**(X_{VR})_C = X_{VR} \cdot \frac{60.70}{100} = .6070 \cdot X_{VR}\text{ based upon micro-pore fraction of } V_{TP} \text{ (see Section IX, p.166).}**
TABLE 12.—Pore volume distribution - Sample 2

<table>
<thead>
<tr>
<th>Mercury</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{r}{\mu} )</td>
<td>( X_{vr} % )</td>
</tr>
<tr>
<td>81.1</td>
<td>.104</td>
</tr>
<tr>
<td>55.3</td>
<td>.028</td>
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<tr>
<td>38.2</td>
<td>.080</td>
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<td>16.7</td>
<td>.094</td>
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<tr>
<td>11.1</td>
<td>.103</td>
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<tr>
<td>7.41</td>
<td>.157</td>
</tr>
<tr>
<td>4.94</td>
<td>.141</td>
</tr>
<tr>
<td>3.28</td>
<td>.288</td>
</tr>
<tr>
<td>2.17</td>
<td>9.999</td>
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<td>1.43</td>
<td>6.21</td>
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<td>1.937</td>
<td>3.42</td>
</tr>
<tr>
<td>0.607</td>
<td>2.6</td>
</tr>
<tr>
<td>0.397</td>
<td>2.2</td>
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<tr>
<td>0.264</td>
<td>1.7</td>
</tr>
<tr>
<td>0.175</td>
<td>1.6</td>
</tr>
<tr>
<td>0.124</td>
<td>0.7</td>
</tr>
<tr>
<td>29.500%</td>
<td>10-7</td>
</tr>
</tbody>
</table>

*Nitrogen adsorption - Gulf Research & Development Co.

**(\( X_{vr} \)) = 0.2685 \cdot X_{vr} \) based upon micro-pore fraction of \( V_{tp} \) (see Section IX, p. 169).
exposed external area. However, since diffusion to this area is much more difficult than to the external area, it is necessary that the mechanism of diffusion into the pores of the particles be understood as fully as possible.

In porous media, four types of diffusion are known to exist. The type of diffusion present in any given system depends upon the gases involved, the size of the pore through which the internal surface area is available to the reacting gases, the temperature of the system, and the pressure of the system.

A. Molecular diffusion

The first type of diffusion, molecular diffusion, depends only on the gases involved, the temperature, and the pressure of the system and is independent of the pore size as long as the mean free path of the reacting gases is considerably smaller than the diameter of the pores through which they flow. The ideal case in which all of the molecules of a gas travel a length equal to the mean free path of the molecule before collision would show that as long as the diameter of the pores into which the gases diffuse is greater than this value, molecular diffusion would be the movement mechanism.

It is of some value therefore to look at the real meaning of the mean free path of a gas molecule. Burrows (46) states that the mean free path is usually defined as the
IX. CALCULATION OF DATA

A. Sample calculation of Knudsen diffusion coefficients from equation (11)—low pressures

1. Experimental Data:

Run Number 1
Sample Number 1
Sample Properties: L = 1.66091 cm
AR = Area Pellet
Area Capillary
= 7.1477 x 10^3

a) Nitrogen System: T = 24.7°C
Flow Differential, P-6 = 61.119 - 57.316 = 3.803 cm Hg
Absolute Pressure, P-10 = 0.464 mm Hg
Current to T-1 = 130 milliamperes
Emf = +23.910 millivolts
Reference Pressure, P-3 = 48.819 - 48.063 = 0.756 cm Hg abs.
Concentration (from T-1 calibration) = 6.475% Helium

b) Helium System: T = 24.7°C
Flow Differential, P-7 = 51.280 - 47.281 = 3.999 cm Hg
Absolute Pressure, P-10 = 0.452 mm Hg
Current to T-2 = 130 ma.
Emf = +29.565 mv.
Reference Pressure, P-3 = 48.819 - 48.063 = 0.756 cm Hg abs.
Concentration (from T-2 calibration) = 2.550% Nitrogen

2. Calculation of Diffusion Coefficients

a) Nitrogen bulk flow, P-6:

\[ G^M = \text{theoretical molar flow rate, Equation (70)} \]
\[ = \frac{(h_1^2 - h_0^2)}{57.1211 \times T \times \mu} \quad \text{gm mole/cm}^2\text{-sec.} \]
\[ G^M = \frac{(3.803 + 0.045)^2 - 0.045^2}{57.1211 \times 297.9 \times 1.840} \]
\[ = \frac{3.849^2 - 0.046^2}{57.1211 \times 297.9 \times 1.840} \]
\[ = 4.7310 \times 10^{-4} \text{ gm mole/cm}^2\text{-sec} \]

Since the nitrogen capillary is exactly 5.00 cm long, no correction need be made for length.

From calibration curve for P-6, Figure 11, slope = 0.9730

Therefore:

\[ G^M_x = \text{nitrogen experimental molar flow rate} \]
\[ = \frac{4.7310 \times 10^{-4}}{0.9780} = 4.8374 \times 10^{-4} \text{ gm mole/cm}^2\text{-sec.} \]

b) Helium bulk flow, P-7:

\[ G^M = \text{theoretical flow rate corrected for the deviation of the length of P-7 from} \]
\[ = 4.8192 \times 10^{-4} \text{ gm mole/cm}^2\text{-sec} \]

\[ G^M(L_0) = \text{theoretical flow rate corrected for the deviation of the length of P-7 from} \]
\[ 5.00 \text{ cm} \]
\[ = 4.8192 \times 10^{-4} \times \frac{5.00}{4.6311} \]
\[ = 5.2031 \times 10^{-4} \text{ gm mole/cm}^2\text{-sec.} \]

Slope of calibration curve, Figure 10 = 0.9533
Therefore:
\[ G_x^M \text{ (helium)} = \frac{5.2031 \times 10^{-4}}{0.9533} = 5.4580 \times 10^{-4} \]
= gm mole/cm²-sec.

c) Calculation of \( N_A^C \) and \( N_B^C \) from Equations (83) and (84), Section VIII, Experimental Data -

\[ R_A = \text{nitrogen bulk flow} = 4.8374 \times 10^{-4} \]
= gm mole/cm²-sec

\[ R_B = \text{helium bulk flow} = 5.4580 \times 10^{-4} \]
= gm mole/cm²-sec

\[ X_A = \text{nitrogen mole fraction} = 0.0255 \]
\[ X_B = \text{helium mole fraction} = 0.06475 \]
\[ T = 273.2 + 24.7 = 297.9^\circ K \]
\[ P = \text{Average absolute pressure} = \frac{0.464 + 0.452}{2} \]
= 0.458 mm Hg absolute

\[ C_A = \frac{X_A}{1 - X_A} = 0.02617 \]
\[ C_B = \frac{X_B}{1 - X_B} = 0.06923 \]

\[ C_A \cdot C_B = 0.001812 \]

\[ N_A^C = \frac{C_A (R_B - C_B R_A)}{1 - C_A C_B} \]
= \[ 0.02617 \left( 5.4580 \times 10^{-4} - 0.06923 \times 4.8374 \times 10^{-4} \right) \]
\[ \frac{1}{1 - 0.001812} \]
= \[ 1.343 \times 10^{-5} \text{ gm mole/cm²-sec based upon the capillary cross-sectional area} \]

\[ N_B^C = \frac{C_B (R_A - C_A R_B)}{1 - C_A C_B} \]
= \[ 0.06923 \left( 4.8374 \times 10^{-4} - 0.02617 \times 5.4580 \times 10^{-4} \right) \]
\[ \frac{1}{1 - 0.001812} \]
= 3.256 x 10^{-5} \text{ gm mole/cm}^2\text{-sec} \text{ based upon the}
\text{capillary cross-sectional area}

d) Calculation of the Knudsen diffusion coefficients, Equation (87), Section VIII, Experimental Data,
\[ D_{KB}^e = \frac{N_B^e \times R \times T \times L}{P \times A_R \times \Delta X_B} = \text{cm}^2/\text{sec} \]
\[ D_{KB}^e = \frac{0.3256 \times 10^{-4} \times 6.233 \times 10^3 \times 297.9 \times 1.66091}{0.0458 \times (0.97450 - 0.06475) \times 7.1477 \times 10^3} \]
\[ D_{KB}^e = 0.3371 \text{ cm}^2/\text{sec} \]

\[ D_{KA}^e = D_{KB}^e \times \frac{N_A^e}{N_B^e} = 0.3371 \times \frac{0.1343}{0.3256} \]
\[ D_{KA}^e = 0.1390 \text{ cm}^2/\text{sec} \]

B. Calculation of the molecular diffusion coefficient effectiveness Factor, \( \varepsilon/q_D \), from equation (45), Section V, Theory

\[ N_B = \frac{P}{R L T} (\frac{\varepsilon D_{AB}}{q_D}) (\frac{1}{1 - R_{BA}}) \ln \frac{\varepsilon D_{AB}}{q_D D_{KB}^e} + 1 - X_{BL} (1 - R_{BA}) \]

Run Number 5

\[ N_B^e = 0.5674 \times 10^{-2} \text{ gm mole/cm}^2\text{-sec} \]
\[ P = 100.63 \text{ mm Hg absolute} \]
\[ T = 273.2 + 24.8 = 299.0^\circ \text{K} \]
\[ L = 1.2440 \text{ cm} \]
\[ R = 6.2313 \times 10^3 \text{ cm}^3\text{-cm Hg/mole-}^\circ \text{K} \]
\[ R_{BA} = 0.3819 \text{ since } N_A^e = .2167 \times 10^{-2} \text{ gm mole/cm}^2\text{-sec} \]
\[ X_{BL} = 0.2925 \]
\(X_{BO} = 0.8362 = (1 - X_{AL})\)

\(D_{KB}^e = 0.7650 \text{ cm}^2/\text{sec}\)

\(A_R = 7.2575 \times 10^3\) for sample 2

\(N_B = N_B^c/A_R = 7.8181 \times 10^{-7} \text{ g mole/cm}^2\text{-sec}\)

\(D_{AB}\) is calculated from Treybal (59)

\[D_{AB} = 9.292 \times 10^{-4} \cdot T^{3/2} \frac{(\frac{1}{M_A} + \frac{1}{M_B})}{(P)(r_{AB})^2 \cdot [f(kT/\varepsilon_{AB})]}\]

where \(r_{AB} = 3.1905\)

\(M_A = 28.02\)

\(M_B = 4.002\)

\(f(kT/\varepsilon_{AB}) = 0.359\)

\[D_{AB} = 5.2792 \text{ cm}^2/\text{sec}\]

Substitution of the above listed data into Equation (45) allows a trial-and-error solution to be found for \(\frac{\varepsilon}{q_D}\).

Three assumed values for \(\frac{\varepsilon}{q_D}\) established that,

\(\frac{\varepsilon}{q_D} = 0.0780\) for Sample 2.

C. Calculation of the transition diffusion coefficient at higher pressures from equation (48), Section V, Theory

\[D_N = \frac{\varepsilon \cdot D_{AB}}{q_D^e} \cdot \ln \left(\frac{X_{BO} - X_{BL}}{(1-R_{BA})}\right)\]

\[\frac{\varepsilon \cdot D_{AB}}{q_D^e} + 1 - X_{AL}(1 - R_{BA})\]

Sample Number 2 Run Number 5
\[ \epsilon_0 / q_D = 0.0780 \]
\[ \mathcal{D}_{AB} = 5.2792 \text{ cm}^2/\text{sec}. \]
\[ X_{BO} = 0.8362 \]
\[ X_{BL} = 0.2925 \]
\[ R_{BA} = 0.3819 \]
\[ \mathcal{D}^e_{KB} = 0.7650 \text{ cm}^2/\text{sec} \]

Therefore
\[ D_N = 0.3484 \text{ cm}^2/\text{sec} \text{ from Equation (48)} \]

D. Calculation of Wheeler coefficient for transition region, equation (4)

\[ \mathcal{D}^e_{W1} = \mathcal{D}^e_{AB} \left[ 1 - \exp\left( \frac{\mathcal{D}^e_{K1}}{\mathcal{D}^e_{AB}} \right) \right] \]

Sample Number 1  Run Number 8

\[ P = 101.76 \text{ mm Hg absolute} \]
\[ \mathcal{D}_{AB} = 5.2284 \text{ cm}^2/\text{sec} \]
\[ \mathcal{D}^e_{KA} = 0.1385 \text{ cm}^2/\text{sec} \]
\[ \epsilon_0 / q_D = 0.1223 \]
\[ \mathcal{D}^e_{AB} = \frac{\epsilon_0}{q_D} \mathcal{D}_{AB} = 0.6394 \text{ cm}^2/\text{sec} \]

\[ \mathcal{D}^e_{WA} = 0.6394 \left[ 1 - \exp\left( -0.1385/0.6394 \right) \right] \]
\[ = 0.1205 \text{ cm}^2/\text{sec} \]
E. Calculation of the effective tortuosity, \( q_K \), for Knudsen flow (effective macro-pore tortuosity)

Sample 1 \( T = 25^\circ C \)

\[
V_{TP} = 1.219 \times 5.7792 = 7.0448 \text{ cm}^3
\]

\[
D_{KA} = 9.7 \times 10^3 \frac{\bar{r}}{\sqrt{T/M}} = 9.7 \times 10^3 \frac{\bar{r}}{\sqrt{298.2}}
\]

\[
= 31.6433 \times 10^3 \text{ cm}^2/\text{sec}
\]

\[
D_{KB} = 83.7323 \times 10^3 \text{ cm}^2/\text{sec}
\]

\[
N_A^t = \frac{V_{TP} \Delta c_A}{q_K^2 L^2} \sum_{\bar{r}} x_{v_r} \cdot D_{KA} = \frac{7.0448 \times 31.6433 \times 10^3 \Delta c}{q_K^2 x 1.660912}
\]

\[
\sum_{\bar{r}} x_{v_r} \cdot \bar{r} = \text{ gm mol/sec}
\]

\[
\Delta c = \frac{P}{RT} \Delta X \quad \text{Run 1} \quad P = 0.456 \text{ mm}
\]

\[
R = 6.2313 \times 10^3
\]

\[
T = 298.2^\circ K
\]

\[
X_{Ao} = .93525
\]

\[
X_{AL} = .02550
\]

\[
\Delta c = \frac{.0458 (.93525 -.02550)}{6.2313 \times 298.2}
\]

\[
= 2.2424 \times 10^{-8} \text{ gm mole/cm}^3
\]

\[
\therefore N_A^t = \frac{181.202 \times 10^{-5}}{q_K^2} \sum_{\bar{r}} x_{v_r} \cdot \bar{r} = \text{ gm mole/sec (N}_2\text{)}
\]

\[
N_B^t = \frac{479.279 \times 10^{-5}}{q_K^2} \sum_{\bar{r}} x_{v_r} \cdot \bar{r} = \text{ gm mole/sec (He)}
\]
From mercury penetration data—Table 10

\[
\begin{array}{cccc}
\bar{r} & (X_{VR})_{CRC} & \frac{X_{VR}}{\mu} & \bar{r} \cdot \frac{X_{VR}}{\mu} \\
81.1 & .012 & .012 & 16.6819 \\
55.3 & .025 & .025 & 1.3825 \\
38.2 & .033 & .033 & 1.2606 \\
25.3 & .033 & .033 & .8349 \\
16.7 & .033 & .033 & .5511 \\
11.1 & .075 & .074 & .8214 \\
7.41 & .066 & .066 & .4891 \\
4.94 & .091 & .090 & .4446 \\
3.28 & .197 & .196 & .6429 \\
2.17 & .456 & .453 & .9830 \\
1.43 & 2.049 & 2.034 & 2.9086 \\
.937 & 1.83 & 1.82 & 1.7053 \\
.607 & 1.65 & 1.64 & .9955 \\
.397 & 1.82 & 1.81 & .7186 \\
.264 & 1.51 & 1.50 & .3960 \\
.175 & 5.87 & 5.83 & 1.0203 \\
.124 & 4.50 & 4.46 & .5543 \\
81.1 & 20.25 \% & 20.12 \% & 16.6819 \\
\end{array}
\]

\[
\sum \bar{r} \cdot \frac{X_{VR}}{\mu} = 16.6819 \times 10^{-6} \text{ (cm units)}
\]

Since from the nitrogen adsorption data, \( V_g = .74 \text{ cc/gm} \)

\% volume in the pure range, \( 0-300 \bar{r} = \frac{.74 \times 100}{1.219} \)

\% = 60.70 \% (micropore range)
From nitrogen adsorption data—Table 11

<table>
<thead>
<tr>
<th>r₀ [Å]</th>
<th>Xvr</th>
<th>r₀ · Xvr</th>
</tr>
</thead>
<tbody>
<tr>
<td>275</td>
<td>1.46</td>
<td>401.50</td>
</tr>
<tr>
<td>225</td>
<td>3.64</td>
<td>819.00</td>
</tr>
<tr>
<td>175</td>
<td>7.10</td>
<td>1242.5</td>
</tr>
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<td>125</td>
<td>10.81</td>
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<td>95</td>
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<td>2.06</td>
<td>87.55</td>
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<td>70.50</td>
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<td>1.76</td>
<td>48.40</td>
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<tr>
<td>22.5</td>
<td>1.15</td>
<td>25.88</td>
</tr>
</tbody>
</table>

\[
300 \sum_{0}^{a} = .6231 \times 10^{-6} \text{ (cm units)}
\]

Volume fraction of porosity between pore sizes

275 Å - 1240 Å = 100.00 - 20.12 - 60.71

\[V_{TP} (275 \text{ Å} - 1240 \text{ Å}) = 19.17\%
\]

Since in Knudsen flow, \(N_A \sim \bar{r}^3\)

a cubic average of the radius is used.

\[
\bar{r} = \left( \frac{r_2^3 + r_1^3}{2} \right)^{1/3} = \left( \frac{.124^3 + .028^3}{2} \right)^{1/3} = .988 \bar{\mu}
\]
therefore \[ \sum_{275}^{1240} \bar{F} X_{V} = 0.988 \times 1.917 = 1.8950 \times 10^{-6} \text{(cm units)} \]

\[ \sum_{0}^{275} \bar{F} X_{V} = 16.6819 \times 10^{-6} \times 1.8950 \times 10^{-6} \times 0.6231 \times 10^{-6} \times 19.2000 \times 10^{-6} \text{(cm units)} \]

From Run 1

\[ N_A^c = 1.343 \times 10^{-5} \text{ gm mole/cm}^2 \text{-sec} \]
\[ N_B^c = 3.256 \times 10^{-5} \text{ gm mole/cm}^2 \text{-sec} \]
\[ A_c = 5.2685 \times 10^{-4} \text{ cm}^2 \]

\[ N_A^t = 7.0756 \times 10^{-9} \text{ gm mole/sec} \]
\[ N_B^t = 17.1542 \times 10^{-9} \text{ gm mole/sec} \]

\[ (qK)_A^2 = \frac{181.202 \times 10^{-5} \times 19.2000 \times 10^{-6}}{7.0756 \times 10^{-9}} = 4.917 \]

\[ (qK)_A = 2.218 \]

\[ (qK)_B^2 = \frac{479.279 \times 10^{-5} \times 19.2000 \times 10^{-6}}{17.1542 \times 10^{-9}} = 5.364 \]

\[ (qK)_B = 2.318 \]

\[ q_K = \frac{2.218 + 2.318}{2} = 2.268 \]

Sample 2 - The calculations for sample two are performed in exactly the same manner, however, due to some distribution measurement overlap, the method for determining the volume fraction in the three regions, \( 81.1 \mu \sim .124 \mu \), \( .124 \mu \sim 275 \AA \), \( 275 \AA \sim 0 \AA \), is as follows:

\[ V_{TP} = 0.5025 \text{ cm}^2/\text{gm} \]

\[ (V_{TP})_{81.1 \mu \sim .124 \mu} = 29.5\% \text{ - California Research Corporation} \]

\[ (V_{TP})_{275 \AA \sim 0 \AA} = 60.705\% \text{ Sample 1} \]
average distance traveled by a single molecule between successive collisions. Denoting the mean free path of a molecule by \( \lambda \) (cm) and if \( \bar{c} \) (cm/sec) is its mean speed, then \( \bar{c}/\lambda \) gives the number of collisions per second made by the molecule. It should be noted that the speed of a single molecule averaged over a long period of time is equal to the average speed of a large number of molecules of the same kind at a single instant under the same prevailing conditions.

Calculations can therefore be based upon statistical methods since this is permissible when dealing with large numbers of molecules. Avagadro's work shows that large numbers of molecules are involved even at very low pressures.

It is extremely important that the significance of the mean free path of a molecule and its relationship to the probable number of collisions in a group of molecules not be misrepresented. Not all of the molecules in a given group travel a distance equal to their mean free path without collision. There is, of course, no certainty that an individual molecule will travel any distance without a collision, but by using the elements of probability we can see that when the molecules travel a distance equal to their mean free path, that is, when \( r \) (distance) equals \( \lambda \) (mean free path), 37 per cent of the molecules travel this distance without an impact and 63 per cent of the molecules collide.
American Cyanamid measurements show that, based upon the micro-pore volume of the powder,

\[
\text{Sample 2 - micro-pore volume} = \frac{(V_{TP})^2_{0-275\text{Å}}}{(V_{TP})_{0-275\text{Å}}} = 0.46 = 0.4423
\]

Therefore \( (V_{TP})^2_{0-275\text{Å}} = 0.4423 \times 60.705 = 26.85\% \)

By difference

\[
(V_{TP})_{0.124\text{μ}} - 275\text{Å} = 100.00 - 26.85 - 29.50 = 43.65\%
\]

Therefore, for Sample 2

\[
(V_{TP})_{0-275\text{Å}} = 26.85\%
(V_{TP})_{275\text{Å} - 0.124\text{μ}} = 43.65\%
(V_{TP})_{0.124\text{μ} - 31.1\text{μ}} = 29.50\%
\]

\[
100.00\%
\]
X. RESULTS AND DISCUSSION

A. Nature and structure of the porous solids studied

The solids studied in this work are those prepared by the compression of aluminum oxide powders into cylindrical pellets as described in Part 9 of Section VI. The tooled alumina solid was prepared as described in Part 10 of Section VI, but when it was submitted for pore-size distribution measurements it was found to have the major part of its porosity in pores having a mean pore radius greater than 70,000 Å. The flow or diffusion through this solid was so great that the analytical techniques generally employed in this study were not accurate. It can be noted that the diffusion through this solid was almost entirely of the molecular type, and further study of the solid would not aid in the present work.

The ordered-plug and the Wood's metal plug were not used because they are known to have an average pore size of about 250 microns, and again, the pore diameter is so large that primarily molecular diffusion would occur. Since it is important to this work that the Knudsen flow range be covered, the compressed solids were then utilized, and they show a range covering the desired diffusion mechanisms.
The two samples will be referred to as Sample 1 and Sample 2, since they were studied experimentally in that order. The properties of these solids are listed in Table 1. The total pore volume of the two samples was measured by determining the weight increase of a pre-weighed sample after its pore structure was saturated with water. The difference in the initial weight and the final weight gives the amount of water in the pore structure, and thus the total pore volume can be measured directly. Knowing the total pore volume and the volume of the compressed powder pellet, the density of the solid itself can be calculated. A calculation of this type established solid densities of 2.755 and 3.138 gm/cc for Sample 1 and Sample 2, respectively, and these are within the range of densities usually reported for aluminum-oxide, 2.42-3.99. It is therefore reasonable to assume that the total pore volume measurement technique is accurate.

It is interesting to note that Sample 1 has a nitrogen surface area of 199 square meters per gram and a total volume of 1.219 cubic centimeters per gram. Using the original Wheeler concept and Equation (2) it can be shown that the mean pore radius for this solid should be about 122.5 Å. Sample 2 has a nitrogen surface area of 202 square meters per gram and a total pore volume of 0.5025 cubic centimeters per gram. Equation (2) predicts a mean pore radius for this solid as 49.8 Å. In examining the above
data one would expect the Knudsen coefficient for Sample 1 to be greater than that for Sample 2, since the Knudsen coefficient, $D_K$, is very nearly directly proportional to the mean pore radius. The experimental results in Figures 23 and 24, show, however, that the Knudsen diffusion coefficients for Sample 2 are larger than those for Sample 1. The picture therefore is not one as explained by Equation (2), and an indication appears that the distribution of the pores must be such that the larger pores appear in Sample 2 than those of Sample 1, a fact which is not indicated by taking the mean pore radius directly from total surface area and pore volume measurements. The mercury-penetration distribution measurements indicated that Sample 2 does have pores in the macro-pore range which are larger than those of Sample 1. Sample 2 shows a macro-pore peak at a pore diameter of about 5.24 microns while Sample 1 has a macro-pore peak at about 3.44 microns and another peak at about 0.423 microns. This simple fact seems to bear out the conclusions that the macro-pores are those primarily available for diffusion.

The fact that the macro-pores seem to be responsible principally for the diffusion phenomenon shows the need for further study into the problem of diffusion into porous media. It is known that the majority of the surface available for catalytic reaction lies in the micro-pore structure, and these micro-pore regions are "fed" by the macro through
Figure 23.—Diffusion coefficients--Sample 1.
Figure 24.—Diffusion coefficients—Sample 2.
pores. The resistance to chemical reaction must therefore occur in the micro-pore regions, but the transport to the surface occurs primarily in the macro-pore regions.

A look at the construction of the studied porous solids will help understand the structure of the solids. The powder which contains the micro-pore network is compressed into a cylindrical pellet. The powder particles are so compacted that they entertain such cohesive forces as needed to keep the pellet from breaking apart. Between each of the compressed powder particles there is a region of space which is known as the macro-pore structure. The macro-pore structure therefore is primarily that network of large pores which lies between all of the compressed powders.

Since the macro-pore network is established by the compressing operation, unless the smaller particles actually fracture upon compression, it would seem reasonable to assume that the macro-pores do not have very many dead-end pore spaces. A dead-end pore might arise from two phenomena, the first of which is the fact that if the small particles fracture, the powder could build up a barrier across one of the macro-pores or several of the macro-pores. This does not seem too likely at the compression pressures studied in this work. The second possible reason for dead-end pores is that several of the particles could contribute a mutual touching phenomenon whereby they all meet, physically, at
one point in the solid thus establishing a solid barrier to flow.

A microscopic analysis as shown in Figure 25 of the two solids studied shows that the actual structure of the powder which was compressed to form Sample 1 is spherical. The individual powder particles are regular spheres of the sizes indicated by their screen analysis. This would rule out the possibility of the touching particles blocking the flow paths since the spheres would present only point contact areas rather than surface contact areas.

Microscopic analysis of Sample 2 shows that this solid has a much more irregular structure than Sample 1. The particles seem to be more nearly irregular ellipsoid shapes, with a considerably rougher surface than Sample 1. The possibility for macro-pore blockage is greater in Sample 2 than in Sample 1, but the shapes of the second sample's original powder is not irregular enough to imagine a surface to surface contact, but rather would again indicate point contacts.

It is therefore assumed by this work that the mercury penetration method for determining the macro-pore size distribution is an effective one, and the mercury flows into all of the channels of the given pore radius, including the dead-end pores. The later assumption is reasonable, since the displacement of the air in the dead-end pores could be easily performed by the flowing mercury in that the mercury
Sample 1

Sample 2

Figure 25.—Photomicrograph of alumina powders.
actually penetrating the macro-pore could force the air out through the micro-pore structure in any area thus completely filling all of the macro-pore volume, including both through channels and dead-end pores.

The nitrogen adsorption and desorption techniques for pore-size distribution are known to be effective over all of the volume of the solid, including through pores and dead-end pore volumes.

A problem arises in the strict interpretation of the experimental data due to the method of solid mounting. It can be seen in Section VI, that part of the actual solid surface available for diffusion is covered by the glass mounting spacers. This leads to the problem as to just what area one should use to base the flux values on since they are usually expressed as gram moles per square centimeter per second. For the present study, the cross-sectional area that is actually exposed is used in the calculations, that is, the total cross sectional area of the solid minus the glass coverage. It is known, however, that the glass-covered area will have some effect upon the actual fluxes measured, and that the actual effective area is larger than the exposed cross-section. Even though this would present an error in the actual value of the calculated fluxes, this deviation from the true cross-sectional area would be consistent through the entire study, and would not affect the results significantly. It would perhaps change the actual
A general relationship between the ratio $r/\lambda$ and the probability that a molecule will collide when traveling the distance, $r$, is shown in Figure 1. It is noticed that if $r$ is finite then the mean free path must approach infinity if intermolecular collisions are to be avoided altogether.

From Figure 1 it may be concluded that molecular diffusion usually takes place above a value where the pore diameter is about five times the mean free path of the diffusing molecule. At atmospheric pressure, this would necessitate a porous solid having pores of an extremely large diameter, an unreal occurrence in actual reactors.

B. Knudsen diffusion

Knudsen diffusion, or diffusion of the second type occurs when the mean free path of a gas is larger than the diameter of the pore through which diffusion takes place. In this case the resistance to flow is due to a gas-pore wall collision rather than intermolecular collisions. Based upon the statistical definition of the mean free path, however, for the actual case purely Knudsen diffusion takes place when the mean free path is about ten times greater than the pore diameter (see Figure 1). Since most catalyst particles have a mean pore diameter smaller than 200 Å, one would suspect that most diffusion at atmospheric pressure in porous catalysts would be of this type. It should be noted that Knudsen diffusion is independent of any counter diffusing
experimental values slightly, but would not affect the conclusions in any way. This problem can be eliminated by using other mounting techniques, but for the present study, these techniques were not available.

Considering Sample 1, it is known that the total cross-sectional area of the solid is 5.505 square centimeters. The cross-sectional area of the solid less the amount of surface covered by the glass is 3.769 square centimeters. The calculations are based upon this latter area. The arithmetic mean cross-sectional area of the two areas is 4.637 square centimeters, while the mean calculated considering an area expansion and contraction through the solid based upon an assumed geometric conic structure with the base of the cone equal to the actual cross-sectional area of the solid is 4.603 square centimeters. This latter area assumes that the area for diffusion expands uniformly from the glass-covered cross-sectional area at the surface of the solid to the true cross-sectional area of the solid at the mid-point of the solid. Twice the volume of this cone section divided by the length of the solid equals the average area. An integrated average area considering the change in flux with a change in area shows that an area value of 4.350 square centimeters should be used. This calculation is also based upon a uniform area expansion from the glass covered area at the surface to the true solid cross-section at the midpoint.
B. Conditions necessary to establish diffusion equation over range of all diffusion mechanisms

The most important relationship that has been developed for all of the diffusion range is Equation (45). A simplification of this equation in terms of an effective diffusion coefficient is given as Equation (48). It can be noted that if three constants can be determined, then for any established concentration gradient, the mass flux can be calculated. The three constants are:

1) the Knudsen diffusion coefficient, \( D_{KA}^e \).
2) the flux ratio, \( R_{AB} \), and
3) the molecular diffusion coefficient effectiveness factor, \( \mathcal{E}/q_D \).

In Equation (45), the actual length of any porous solid, \( L \), can be measured and \( P \) and \( T \) are the pressure and temperature of the diffusing system. The molecular diffusion coefficient \( D_{AB} \) can be calculated from any of the conventional methods, i.e., Treybal (59). Using the known gas constant, \( R \), with these three constants, the mass flux, \( N_A \), can be predicted if the concentration gradient, \( X_{AO} - X_{AL} \), is known.

The present work establishes that if two diffusion measurements can be performed, then the three constants can be determined with reasonable accuracy. The conditions are that mass flux values are measured at two established system pressures. One measurement of two counter-diffusing gases is
taken at near atmospheric pressure and the other at a pressure of 5 mm Hg absolute or lower.

The three constants are determined as follows:

1) Knudsen Coefficient

The Knudsen coefficient, $D_{KN}^e$, is known to be a function of only the molecular species diffusing and not the pressure or the presence of a counter-diffusing gas. The nature of this type of diffusion is such that if a calculated coefficient can be shown to be pressure independent, then the flow is known to be of the Knudsen type. Figure 23 for Sample 1 shows that an effective coefficient for the solid studied is independent of pressure over the range of pressures from 0.5 mm Hg absolute to about 10 mm Hg absolute. All of the original experimental data were calculated using an integrated form of Equation (11) which is in effect Equation (47). When the effect of pressure is noted on the experimentally determined diffusion coefficient as calculated from Equation (47) the effect of the counter-diffusing gas must be accounted for and Equation (11) would no longer strictly apply. When the established curve showed a deviation from the 45° line of pressure independence in Figure 23, then Equation (48) was used to calculate an effective diffusion coefficient. Since the counter-diffusing gas flux is measured at any pressure value the nitrogen and the helium Knudsen coefficient are measured simultaneously, as shown in
Figure 23. For any experimental determination a material balance necessitates the measurement of both fluxes. The values for the effective Knudsen coefficient for Sample 1 are, for nitrogen at room temperature (25°C), 0.1385 cm²/sec, and for helium at room temperature, 0.3320 cm²/sec. This value was taken from the 45° line at any established pressure value. It should be noted that if one accurate experimental diffusion coefficient were measured in the Knudsen range, then the value of the first constant, $D^e_{\text{KA}}$ or $D^e_{\text{KB}}$ for Equation (45) would be determined. From Figure 23 one can observe that with care of measurements, one experimental determination would establish both of the binary system's Knudsen diffusion coefficients.

It should be stressed that this coefficient as calculated from Equation (11) includes the properties of the solid $\mathcal{E}_K/q_K$, namely the porosity divided by the length multiple to take care of the tortuosity of the path through the solid in Knudsen flow. The true Knudsen coefficient for the solid would be calculated by dividing this effective coefficient by the quantity, $\mathcal{E}_K/q_K$. The Knudsen tortuosity, $q_K$, differs from the molecular tortuosity, $q_D$, as shown later in this Section.

Figure 24 gives the effect of pressure on the diffusion coefficients of Sample 2. It may be noted that the pressure independent range for this solid is from 0.5 mm Hg
absolute to about 8-10 mm Hg absolute. It may also be noted that one measurement of the flux rates through the solid made at 0.5 mm Hg absolute would establish the effective Knudsen coefficients for both gases in the sample. The values for the effective Knudsen diffusion coefficient for Sample 2 are, 0.3067 cm²/sec for nitrogen and 0.7650 cm²/sec for helium.

In conclusion therefore, by making one careful experimental determination at a pressure of near 1.0 mm Hg absolute, the effective Knudsen diffusion coefficients for counter-diffusing gases could be established for most commercial catalyst particles.

It should be stressed that if the Wheeler radius as defined in Equation (2) were used as the true mean pore radius, both gases would appear to be in Knudsen flow over the entire range of pressure since the mean free path of both gases is larger than this average radius at atmospheric pressure. It can be seen from Figures 23 and 24 that Knudsen flow is not established until the ratio, \( \overline{r}/\lambda \), is between .01 and .001 of the Wheeler radius instead of the usually assumed value of unity in porous solids. This is due to the fact that the larger pores contribute the most to the total flux through the pellet, a fact not accounted for in the total surface area and pore volume measurements.

The experimentally determined diffusion coefficients are tabulated in Tables 7 and 8.
2) Flux ratio, $R_{AB}$

The flux ratio, $R_{AB}$, is the ratio of the actual mass flux of species B diffusing to the mass flux of species A that is counter-diffusing. It may be noted from Tables 5 and 6 for Sample 1 and Sample 2, respectively, the flux ratio is essentially pressure independent. Although there is considerable experimental deviation of this measured value over the pressure range studied, there is no trend indicated to show that this value is pressure dependent. It should also be noted, that if the diffusing species obeyed strict momentum transfer relationships, or if Knudsen diffusion for a binary system strictly adhered to the established principles for ideal flow of one gas, then the mass flux ratio should vary inversely proportional to the square roots of the molecular weights of the counter-diffusing gases at constant and equal temperature. It may be noted that for both samples, the average flux ratio was lower than that expected for the adherence to the inverse square root of the molecular weight relationship. The square root of the molecular weight of nitrogen to helium is 2.645, while the average flux ratio for helium to nitrogen for Sample 1 is 2.286 and for Sample 2 is 2.635. It may be noted that Sample 2 more nearly corresponds to the ideal relationship, but the variation of the flux ratio from the average value for individual measurements does not establish the 2.635 value absolutely. If any trend may be noted it appears that the
flux ratio is not inversely proportional to the square root of the molecular weights of the binary mixture, but that it is somehow influenced by the size of the macro-pore structure, thus accounting for the larger average of the ratio in Sample 2 than in Sample 1. The importance of the present work is that it establishes the fact that the flux ratio is not pressure dependent, so if the ratio is established at any system pressure, then this value may be used over the entire pressure range. Since this value differs from the square root relationship discussed earlier, it must be determined for each particular solid.

It may be noted that the flux ratio is established in the determination of the Knudsen diffusion coefficients since \( N_A \) and \( N_B \) are measured at low pressures. This value may be used for \( R_{AB} \), but since one other experimental determination must be made at a higher pressure to establish the effective molecular diffusion coefficient for the solid, another value for \( R_{AB} \) will be measured. The average of these two values would then be used, and with \( R_{AB} \) and the Knudsen coefficients established, one can proceed directly to calculate the effective molecular diffusion coefficient from experimental data.

Note that if Sample 1 had been determined from two measurements, one at 0.5 mm mercury absolute and one at 600 mm mercury absolute, the flux ratio average would have been 2.30 as compared to the over-all average of 2.286, while for Sample 2, the experimental average for the lowest and highest
determinations would have been 2.690 as compared with 2.635 for the entire series of experimental determinations.

The reasons for the deviation of the experimentally determined flux ratio from the square root relationship has not been established. This deviation has been noted by several researchers, however, principally Rothfeld (56) and Robertson and Smith (52) recently. Rothfeld proposes that this deviation from ideality may arise when helium is one of the components of the binary mixture, but since all of the described works, including the present one use helium, this suggestions cannot be verified. The flux ratio for the Rothfeld data is greater than the square root relationship, while the present work and the Robertson and Smith data show a flux ratio that is lower than the square root relationship. Further work will have to be performed to illustrate or show why this deviation is found to exist. Rothfeld proposed that surface transport might be the reason for the deviation, but then established that it is not. The present work shows that surface flow would probably not account for this deviation since, if surface flow were significant, the flux ratio would probably be pressure dependent, a fact which is not indicated by data presented in Table 5 and Table 6.

3) Molecular diffusion coefficient effectiveness factor, $E \eta_D$

The effective molecular diffusion coefficient, $E \eta_D$ $D_{AB}$, is known to be a function of the properties of the
solid, as was the Knudsen coefficient. The importance of
the calculation of the constant $\varepsilon/q_D$ lies in the fact that
this is the value that expresses the effect of the solid on
the diffusion coefficients as calculated from molecular
theory. The value $\varepsilon$ is the area correction factor since it
is the porosity of the solid, and $q_D$ is the length correc-
tion factor since it is an expression of the actual diffusion
length of the molecules throughout the tortuous path of the
solid.

The constant, $\varepsilon/q_D$, is the correction of the molecular
diffusion coefficient for the effect of the porous solid
properties on this coefficient. It is therefore assumed that
the constant is a multiple of the molecular diffusion
coefficient. Knowing the molecular coefficient from the
usual methods for predicting the binary molecular diffusion
coefficients as in Treybal (59), the constant can be evalu-
at ed from Equation (45).

The object of the present study is to determine with
what accuracy $N_A$ or $N_B$ can be predicted with the experimental
determination of the constant, $\varepsilon/q_D$, from one high pressure
measurement. Actually three pressure levels were studied for
each solid, and a value of the constant was determined for
each gas. The established values of the constant for each
solid are listed in Table 9.

Note that in the calculation of the constant, $\varepsilon/q_D$, for each run, actual experimental values of the mass flux,
flux ratio and concentration gradient are used. An average value of the Knudsen diffusion coefficient is taken from the earlier low pressure studies. Since the flux ratio was found to vary due to experimental error, the use of the higher pressure and low pressure average value for $R_{AB}$ would probably give a more correct value for the constant.

Sample 1 showed experimental variation in the determination of the molecular diffusion effectiveness factor, while Sample 2 showed a more consistent determination. This was due primarily to experimental technique, and since the technique was much better established in the second sample study, it is reasonable to assume that the deviation for one study could be more accurately calculated from the deviation of this solid rather than the consideration of both of the samples. It should be noted that the order of experimental determinations was such that seven of the determined values were established for Sample 1, then the eight values for Sample 2, and to show data consistency, Sample 1 was remounted in the apparatus and a determination was made at a pressure of 8.2 mm mercury absolute. Note that this latter value falls very near the expected curve as drawn through the previous data, and this fact indicates that once the technique is established, accurate values can be determined. It also shows that the data is consistent even after the removal and remounting of the solid. This latter determination proves that one experimental determination
STADY-STATE COUNTERT-DIFFUSION
OF GASES IN POROUS SOLIDS

DISSERATION
Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By
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* * * * *

The Ohio State University
1963

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Figure 1.—Probability of collision.
could be accurate in determining the Knudsen or molecular coefficient once the technique of data-gathering is well established.

The difficulty in gathering absolutely accurate data arises in the determination of the concentration gradients. The thermal conductivity cells are extremely pressure sensitive, and the fluctuation in pressure by even the slightest amount, causes an error in the determination. Since the concentration is not only used in the gradient determination, but also in the material balance for the calculation of the mass flux rates, a slight error in the concentrations would cause considerable error in the actual calculation of the effectiveness constant. Techniques were gradually developed for the most efficient and accurate methods for concentration measurements and this is the principal reason why Sample 2 should present more representative data for the limits of experimental accuracy in this work.

Once the experimental data has been gathered at any particular pressure, a trial-and-error solution of Equation (45) will enable the value of the constant, $\mathcal{E}/q_D$, to be established. The experimental values, and the over-all average are reported in Table 9. As was mentioned earlier, it can be seen that Sample 2 gave a more consistent value for the constant over the pressure range than did Sample 1, but this is due primarily to the better established technique in the measurements of the properties of Sample 2.
A statistical analysis was made of the experimental determinations of the constant, $\varepsilon/q_D$. Using the relationship for the analysis of variance,

$$\sqrt{\frac{\sum \Delta N_A^2 + \Delta N_B^2}{n-1}}$$

(88)

where $\Delta$ is the statistical deviation between the experimental determination and the calculated value of the mass flux, $\Delta N_A$ is the difference between the calculated and experimental value of the nitrogen flux, $\Delta N_B$ is the difference between the calculated and experimental value of the helium mass flux, and $n$ is the number of determinations made.

Assuming that the experimental values were those expected, the variance analysis shows that one can assume an absolute accuracy in flux value of $\pm 1.5852 \times 10^{-7}$ gm mole/cm$^2$-sec. for any calculated flux using an average $\varepsilon/q_D$ from one measurement. This value is calculated from the entire population of both sample's experimental data, and consists of 36 actual statistical samples. The calculation is made as follows:

1) the average value of $\varepsilon/q_D$ is determined for any one pressure level experimental run and this value is the average $\varepsilon/q_D$ calculated from the nitrogen and helium experimental data

2) the difference between a calculated $N_A$ and $N_B$ using this average and the experimentally measured value for $N_A$ of $N_B$ is determined for all of the three
pressure levels (the same calculation is used for each of the two samples)
3) the average is determined at another pressure level and the difference between the calculated \( N_A \) and \( N_B \) and the experimentally determined values is again tabulated for the entire pressure range
4) the method is repeated until the average \( \mathcal{E}/q_D \) value of each pressure run was used, and the difference between the experimentally measured \( N_A \) or \( N_B \) and the calculated \( N_A \) or \( N_B \) based upon the average \( \mathcal{E}/q_D \) is noted for both samples for the three pressure levels.

If the preceding values were used as the statistically correct one in the total population of 36 samples, an error of about 9 per cent would be the most accurate that could be expected for any given determination at the higher pressure while an absolute error of 70 per cent could be expected at lower pressures. Since this calculation assumes that the experimental value for all pressure levels for both samples was the absolute one, the analysis is not realistic.

A second analysis was made using the average \( \mathcal{E}/q_D \) for all of the determinations for each sample as the accurate one for that sample. The difference between a \( N_A \) or \( N_B \) as calculated using this value and the experimentally determined \( N_A \) or \( N_B \) was noted. Using a population consisting of the
data of both Sample 1 and Sample 2, an absolute accuracy that can be expected by making only one run at a higher pressure is about 6 per cent at the higher pressure levels and 50 per cent at the lower pressure levels. This is based upon the value of $\pm 1.0176 \times 10^{-7}$ gm mole/cm$^2$-sec as the range of absolute accuracy. The average calculated flux is compared to the measured flux in Figure 26 for both samples. This figure shows that the data is consistent and reasonably accurate. The deviation for the second analysis is less than the first analysis as can be expected because an average $E/q_D$ for the six values is used instead of two.

The third analysis was made considering the experimental data gathered in the study of Sample 2. Since the average value of the constant, $E/q_D$, deviated only about 8 per cent from the actual experimental values, and the technique for experimental measurements was better developed for this study, this analysis should be considered as a more representative value for counter-diffusion measurement techniques as described in the present work. Considering only Sample 2, the statistical analysis showed that if only one high pressure measurement were made, the range of accuracy that can be expected from this one measurement of the mass fluxes is $\pm 0.6705 \times 10^{-7}$ gm mole/cm$^2$-sec. This would give a percentage error in a flux calculation of 4.8 percent for the high pressure helium measurements for the best data and an error of 21.5 per cent for the low pressure nitrogen
Figure 26.—Average—experimental flux.
measurement. It should be noted that since the mass flux rates of helium are much larger than those of nitrogen, the error would principally appear in the nitrogen measurements. This error is based upon an analysis of the deviation of the calculated $N_A$ and $N_B$ values of individual determinations of the $E/q_D$ constant from the best $N_A$ and $N_B$ values calculated from the average $E/q_D$ for the entire series of experiments. In all, this study involved a population of 18 samples.

From Table 9 and from the third statistical analysis it can be concluded that the value of the effectiveness constant, $E/q_D$ from one measurement can be determined with good precision from Equation (45). The fluctuation of the experimental values with pressure appears to be one due to experimental error rather than any trend to show a pressure dependence. Since the effectiveness constant should be a function of the solid properties, this is to be expected. It may also be concluded that with properly developed experimental techniques, the error in calculation of $E/q_D$ from one higher pressure measurement can be reduced considerably, as is shown by the reduction of error from the study of Sample 1 to Sample 2.

C. Knudsen flow and Knudsen tortuosity

Since it is known that in molecular flow, at constant temperature and pressure, the diffusion coefficient is a
function of the properties of the gas system only, then for molecular flow, all of the pores would contribute directly to the total flux through a solid proportional to their number and cross-sectional area. It would therefore appear that the tortuosity for molecular flow, \( \gamma_D \), would be an average tortuosity based upon the proportional flow through all of the pores whether they be micro-pores or macro-pores. It is true that the micro-pores would carry less than the larger pores, but the amount actually carried by the pore system in molecular flow is directly proportional to the area, therefore to the square of the pore radius.

In Knudsen flow, however, it is known that the diffusion coefficient is proportional to the radius of the pore through which diffusion is taking place. Therefore, the total flux through the solid in purely Knudsen flow would be proportional to the diffusion coefficient multiplied by the area, or would be proportional to the cube of the radius, \( r^3 \). In Knudsen flow therefore, it would appear that the macro-pores contribute much more to the total flow than do the micro-pores.

In the present work, a systematic analysis of the pore-size distribution and its effect on Knudsen flow is made. Assuming that the porous solid is made up of a series of parallel pores, cylindrical in shape and having a length equal to some multiple of the solid length, \( qKL \), Equation (60)
can be used to establish the value of the Knudsen tortuosity factor, $q_K$. Using the distribution data as reported in Tables 10, 11, and 12, the value for $q_K$ for Sample 1 is 2.268 and for Sample 2 is 3.02.

A summary of the percentages of the calculated amounts of nitrogen or helium flowing through the solid in the various pore ranges considered are:

1) Sample 1, pore range 81.1-124 microns 86.88%
   pore range 1240-275 angstroms 9.87%
   pore range 275-0 angstroms 3.25%

2) Sample 2, pore range 81.1-124 microns 57.09%
   pore range 1240-275 angstroms 42.80%
   pore range 275-0 angstroms 0.11%

The volume distribution through the various pore ranges is:

1) Sample 1, pore range 81.1-124 microns 20.12%
   pore range 1240-275 angstroms 19.18%
   pore range 275-0 angstroms 60.70%

2) Sample 2, pore range 81.1-124 microns 29.50%
   pore range 1240-275 angstroms 43.65%
   pore range 275-0 angstroms 26.85%

It can therefore be concluded that even though the macro-pores contribute only a small amount to the total pore volume of the solid, their contribution to Knudsen diffusion is considerable. In fact, for Sample 1, the macro-pores,
81.1-124 microns carry most of the flux. Since the resistance to flow of the macro-pores is so much smaller than the resistance of the micro-pores, the value of the constant, $q_K$, for the macro-pores is much smaller than the molecular tortuosity, $q_D$, i.e.,

Sample 1: $q_D = 6.304$
$q_K = 2.268$

Sample 2: $q_K = 7.847$
$q_K = 3.02$

It should be stressed that the Knudsen tortuosity, $q_K$, is not strictly a length multiple, or is not truly representative of the devious route for diffusion through the solids. It would only be a true representation of the length parameter if the porous solid's structure corresponded to the parallel cylindrical pore model assumed. The value of $q_K$ therefore includes:

1) the variation of diameter of the cylinder throughout the solid, that is, the structure may actually be one of pores which enlarge and constrict throughout the length of the solid,

2) the deviations from cylindrical shapes,

3) errors due to model's failure to consider pore interconnections, and

4) dead-end pore's contributions to the volume but not to the steady-state flux, and
5) deviations due to pore branching structures.

If it is assumed that the micro-pores and the macro-pores are parallel resistances to flow, and that the molecular diffusion tortuosity, \( q_D \), represents the total contribution of the entire pore network to flow, then the effect of the micro-pores can be calculated as an effective tortuosity for the micro-pore region, \( q_M \). The calculation can only be made, however, if it is assumed that the value for the Knudsen tortuosity, \( q_K \), represents the macro-pores contribution to the over-all transfer, a reasonable assumption considering the percentage volume-percentage flux carried by the pores described earlier in this section.

The parallel flux relationship can be expressed as:

\[
\frac{\mathcal{E}}{q_D} = \frac{\mathcal{E}_M}{q_M} + \frac{\mathcal{E}_K}{q_K}
\]  

(89)

where \( \mathcal{E} \) is the total porosity of the solid and \( q_D \) is the molecular (total) tortuosity; \( \mathcal{E}_M \) is the porosity of the micro-pore region and \( q_M \) is the micro-pore tortuosity; and \( \mathcal{E}_K \) is the porosity of the macro-pore region and \( q_K \) is the macro-pore (Knudsen) tortuosity.

The above statement, Equation (89), is equivalent to stating that the total resistance to flow is equal to the sum of the parallel resistances of the micro-pores and the macro-pores.
gases and is not a function of pressure as long as the mean free path is sufficiently greater than the pore diameter. Therefore, diffusion in the Knudsen region is the same process whether the flow be induced by a total pressure gradient or a partial pressure gradient since resistance to flow is due to molecule-wall collisions and not those of an intermolecular type.

Knudsen's original work performed in 1909, as described by Wheeler (39), shows that molecular diffusion in small capillaries is hindered because at each collision with the wall there is a very brief period of adsorption when the molecule loses some of its momentum to the solid surface. The molecule then leaves the surface upon which it had been adsorbed at an angle different from its original path direction. This random travel accounts for the high diffusional resistance of small pores in catalysts. Knudsen, applying the principles of the kinetic theory of gases, showed that an expression for the diffusivity for gas species per unit cross-sectional area of pore is given as:

$$D_{ki} = \frac{2}{3} \bar{r} \bar{v} = 9.7 \times 10^3 \bar{r} \sqrt{\frac{T}{M_i}}$$

where $\bar{r}$ is the pore radius in centimeters, $\bar{v}$ is the average velocity of the molecule, $T$ is the temperature expressed in degrees Kelvin and $M_i$ is the molecular weight of the diffusing gas of species $i$. 
A synthetic division will be assumed to separate the micro-pore region from the macro-pore region. All of the pores that are measured by the mercury penetration measurements, that is, the larger pores of the solid, are assumed to constitute the macro-pore region. Those pores below this size are assumed to constitute the micro-pore region. A more common division might be made on the basis of the nitrogen adsorption measurements covering the micro-pore region, and anything larger than about 300 angstroms constituting the macro-pore region, but experimental error and the experimental pore-size distribution determination overlap of Sample 2, will not allow the calculation to be made.

With the assumption established that the macro-pore region exists in the pore range of from 81.1 - .124 microns radius, and the micro-pore range from 1240 - 0 angstroms radius, calculation of the value for the effective micro-pore tortuosity shows that for Sample 1, $q_M = 11.42$ and for Sample 2, $q_M = 23.71$. This realistically shows that the resistance of the micro-pores is considerably greater than that of the macro-pores.

Since the total pore volume of Sample 1 is larger than that of Sample 2 and both samples have nearly the same total surface area, Equation (2) would predict that Sample 1 has a larger Knudsen diffusion coefficient than Sample 2 because this coefficient is directly proportional to the average
pore radius. This is not the case as observed experimentally since the measured Knudsen diffusion coefficient for Sample 2 is larger than Sample 1. Since Sample 2 has a distribution which shows that the majority of the pores are of the macro-pore nature, it would be concluded that Sample 2 would have a larger diffusion coefficient than Sample 1. Therefore, one should not use the Wheeler model as a criterion in establishing the diffusion mechanism since it might lead to serious error, i.e.,

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \bar{r}, \text{Å} )</th>
<th>( D_e^{KA}, \text{cm}^2/\text{sec} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>122.5</td>
<td>0.1385</td>
</tr>
<tr>
<td>2</td>
<td>49.8</td>
<td>0.3067</td>
</tr>
</tbody>
</table>
XI. CONCLUSIONS

1. The results of this study show that the Rothfeld equation, Equation (45), can be used to satisfactorily determine the molar flux rates for diffusion in porous solids at constant pressure over the entire range of pressure, 0.5 mm Hg absolute to near-atmospheric pressure. This pressure range encompasses two of the three mechanisms for diffusion in porous solids, namely Knudsen and transition flow. It is of significant value that this conclusion can be verified since the porous solids studied are typical of any of the commercial catalyst carriers that are presently employed in heterogeneous catalysis research and development. The mechanisms studied, then, are the same mechanisms that will generally be encountered in commercial catalysts.

In order to determine the Rothfeld equation for any given porous solid, two experimental measurements must be made. These data are needed to establish the properties of the solid that affect the diffusion mechanisms.

The data needed for the determination of Equation (45) for any solid are:

1) The effective Knudsen diffusion coefficient, \( D_{ki}^e \), a constant which can be measured by making one low
pressure experimental determination of the fluxes by the techniques developed in this thesis.

2) The molecular diffusion coefficient factor, $\varepsilon/D$, a constant which shows the effect of the porous solid on the molecular diffusion coefficient. This constant is determined by measuring the diffusion fluxes at near-atmospheric pressure.

3) The flux ratio, $R_{AB}$, a pressure independent constant which is established twice, once at low pressure when measuring the effective Knudsen diffusion coefficient, and once at higher pressure when establishing the molecular diffusion coefficient factor, $\varepsilon/q_D$. An average of these two values gives an accurate value for $R_{AB}$, the flux ratio.

Once these three constants are determined, the flux can be determined at any pressure level if the concentration gradient for diffusion is established. Many authors have used assumed expressions for the region of diffusion from Knudsen flow to molecular diffusion, but the present work shows that the rigorous expression developed by Rothfeld (58) and Scott and Dullien (33) can be used with a minimum of experimental data.

2. The macro-pore structure of the solids studied can be assumed to carry at least 70 per cent of the flow through a porous solid with the smaller pores contributing significantly to the surface area, but contributing little to the
actual flux. Since the macro-pore volume is only about 20-30 per cent of the total pore volume, it is important that the macro-pore structure be as large as possible when particles of large surface area are compressed. These macro-pores therefore act as "feeder pores" to the network of micro-pores which contribute the most surface area for chemical reaction.

The length multiple for diffusion, the tortuosity, is about 5-10 times as large for the micro-pores as for the macro-pores. This establishes without much doubt that the bulk of the resistance to diffusion lies in the micro-pores.

3. The Wheeler model does not suitably provide a basis for the calculation of Knudsen coefficients. In fact, using the Wheeler model exclusively for prediction of diffusion rates or coefficients leads to serious error. It is extremely important that the pore-size distribution be considered rather than the total solid properties of pore volume and surface area since the macro-pores contribute much more to the diffusion rates, and their effect and size can only be established from the distribution data.

4. The flux ratio, or the ratio of the mass flux of B to the mass flux of A in a binary counter-diffusing system is independent of pressure and is different from the theoretical value established by simple momentum transfer considerations. Reasons for this deviation from the theoretical value can only be established by further research in the area.
XII. RECOMMENDATIONS

The following recommendations are made for further work in the area of diffusion in porous solids based upon the present study, and the information available in the literature.

A. Further experimental work

1) With the presently designed system it is impossible to study true molecular diffusion in the porous solids. To find the limits of the transition region it would be desirable to construct an experimental apparatus so that higher pressures could be achieved, and finally enable true binary molecular coefficients to be evaluated for porous solids.

2) The present experimental set-up determines concentrations of the effluent streams by means of thermal conductivity cells. This is the greatest possible source of experimental inaccuracies. It is therefore suggested that some other method for determining low pressure concentrations be used, i.e., mass spectrographic analysis.

3) Since the molar species flux ratio differs from the theoretically expected one, a study of another inert gas with nitrogen should be made to see if the deviation is due in some way to the physical properties of helium. Rothfeld
(58) also observed a nitrogen-helium deviation from ideality, and makes the same suggestion.

4) It is known that the macro-pores contribute the most to the diffusion mechanism, a study might be made of various powder mixtures in order to establish a maximum macro-porosity for the largest possible total surface area of the catalyst. The effect of a mixture of various size powder particles upon the value for the over-all tortuosity, $q_D$, might be studied, as well as this effect upon the micro-pore tortuosity, $q_M$, and the macro-pore tortuosity, $q_K$.

5) The effect of the actual particle shape (roughness) might be observed with respect to its relationship to the effective diffusion coefficients. Wheeler suggests that the diffusion coefficient for Knudsen flow is directly proportional to the particle roughness.

6) A better method for mounting the sample in the system should be found to eliminate the problem of the expanding area through the solid.

7) The application of the effect of the structure of a porous solid on gas separation phenomena might be examined in more detail both theoretically and experimentally.

8) It can be shown that the study of forced flow through a porous solid, i.e., Poiselle flow due to an established pressure drop, can be used to determine even more accurately the effect of the macro-pore structure on mass transport. This is because the flux is approximately
proportional to the fourth power of the diameter, and studies of this nature would determine a better value of $q_K$.

9) Unsteady-state or frequency response techniques can be used to determine the effect of the dead-end pores upon diffusion through the porous solids. A study should be made as to what effect the solid has on unsteady-state diffusion coefficients.

B. Theoretical model studies

1) Since the constants determined in this study all include the deviation of the porous solid from an ideal homogeneous structure, it would be desirable to study known geometric systems in order to eliminate some of the variables. The ordered plug as described earlier in this work could be used for molecular studies if the system were redesigned for higher pressure applications.

2) Porous Vycor glass, having a single node, uniform pore-size distribution, as opposed to the binodal distribution of commercial catalyst particles, could be studied to evaluate the various constants for a more accurately designed solid.

3) Studies should be made with cylindrical tubes in parallel of various sizes to determine Equation (45) exactly, and to establish the value of $q_K$.

4) A model could be proposed to take into account the fact that the pores of the solid actually interconnect. This should have some direct relationship to the value of $q_K$. 
5) The effectiveness factor, $E/q_D$, and the theory of the various tortuosities should be extended to include situations which might arise in which concentration gradients, temperature gradients and pressure gradients exist simultaneously in the pellet. This means that simultaneous momentum, mass and heat transfer studies should be made and the effect of surface transport on diffusion should be studied.
NOMENCLATURE

a = T/C cell current, milliamperes
A = Nitrogen species subscript
Ac = Capillary cross-sectional area, cm²
Ar = Area of pore of radius r, cm²
AR = Area ratio = D²_e/D²_cap
AT = Total open cross-sectional area, cm²
B = Helium species subscript
c = Total concentration, gm mole/cc
\bar{c} = Mean molecular speed, cm/sec
c_i = Concentration of species i, gm mole/cc = X_i \cdot c
C_i = X_i / (1 - X_i)
d = Diameter of tube, Equation (66), cm
\bar{d} = Mean pore diameter, cm
D = Actual pellet diameter, cm
DB = Wheeler bulk diffusion coefficient, Equation (4), cm²/sec
Dc = Wheeler over-all diffusion coefficient for catalyst particle, cm²/sec
D_cap = Diameter of capillary tube, cm
de = Effective diameter for actual surface available for diffusion, cm
Do = Bulk diffusion coefficient at 0°C and 1 atm. pressure, cm²/sec
The problem of using a correct value for $\bar{r}$ in the above equation has been studied by many authors. Wheeler (39), assuming smooth-walled cylindrical pores suggests that the average pore radius be given by:

$$\bar{r} = 2V_g / S_g$$  \hspace{1cm} (2)

since

$$\frac{V_g}{S_g} = n_r \pi \bar{r}^2 L / 2\pi n_r \bar{r} L$$  \hspace{1cm} (3)

where $n_r$ is the total number of pores in the solid having an average pore radius, $\bar{r}$, and $L$ is the length of the pore path or the length of the solid. The pore volume, $V_g$, per gram of catalyst particle may be found by filling the pores with water and determining the change in weight of the particle due to the water. This change in weight divided by the density of water gives the total pore volume. The surface area per gram, $S_g$, is computed from the BET adsorption curve of the particular catalyst.

Much of the recent work done in studying Knudsen diffusion has been complicated by the inability to accurately establish or compute a mean pore radius, $\bar{r}$. Several authors lump the deviation of the radius from assumed cylindrical pores together with other unmeasured values such as the variation of the length of the pore into a value called the tortuosity or some similar term. Among these are Bockhoven and Hoogschagen (3), Evans et al. (11), Henry et al. (17),
\[ D_W = \text{Wheeler over-all diffusion coefficient, Equation (4), cm}^2/\text{sec} \]
\[ D_{AB} = \text{Effective binary over-all diffusion coefficient, Equation (22), cm}^2/\text{sec} \]
\[ D_{AB} = \text{Binary molecular diffusion coefficient, cm}^2/\text{sec} \]
\[ D_{KI} = \text{Knudsen diffusion coefficient for species i, cm}^2/\text{sec} \]
\[ D_{Ni} = \text{Effective over-all diffusion coefficient for species i, Equation (47), cm}^2/\text{sec} \]
\[ D^e_{AB} = \text{Effective binary bulk diffusion coefficient, cm}^2/\text{sec} \]
\[ \left( \frac{E}{q_D} \right) D_{AB} \]
\[ D^e_K = \text{Effective Knudsen diffusion coefficient, cm}^2/\text{sec} \]
\[ D^e_W = \text{Effective Wheeler over-all diffusion coefficient, cm}^2/\text{sec} \]
\[ f = \text{Friction factor, Equation (65)} \]
\[ F_A = R_A - N_A^C \]
\[ F_B = R_B - N_B^C \]
\[ g = \text{Mass flow rate, gm/sec} \]
\[ \bar{g} = \text{Acceleration of gravity, cm/sec}^2 \]
\[ G = \text{Mass flux, gm/cm}^2\text{-sec} \]
\[ G^M = \text{Molar flux, gm mole/cm}^2\text{-sec} = G/M \]
\[ Q_x = \text{Experimental mass flux, Equation (64), gm/cm}^2\text{-sec} \]
\[ Q_t = \text{Theoretical mass flux, Equation (70), gm/cm}^2\text{-sec} \]
\[ Q^c_t = \text{Length corrected theoretical mass flux, gm/cm}^2\text{-sec} \]
\[ h = \text{Height of mercury column, cm} \]
\[ \overrightarrow{J_A} = \text{Molar flux of species A relative to the molar average velocity, gm mole/cm}^2\text{-sec} \]
\[ K_{OA} = \text{Knudsen flow permeability constant for species A, cm} \]
$L = \text{Actual pellet length, cm}$

$L_p = \text{Length of effective through-pore, Knudsen flow, cm}$

$M_i = \text{Molecular weight of species } i$

$M_{ij} = \text{Momentum transferred between molecules of species } i \text{ and } j \text{ due to collision, gm-cm/sec}$

$M_{iw} = \text{Momentum transferred between molecule of species } i \text{ and pore wall, gm-cm/sec}$

$n = \text{Number of statistical samples}$

$n_p = \text{Number of pores per unit surface area of pellet, cm}^{-2}$

$n_r = \text{Number of pores of radius, } \bar{r}$

$N_i = \text{molar flux of species } i \text{ in } z \text{ direction, gm mole/cm}^2\text{-sec}$

$N_A = \text{Molar flux of species } A \text{ with respect to stationary coordinates, gm mole/cm}^2\text{/sec}$

$N_i^a = \text{Total molar flux calculated from experimental data and average } (\mathcal{E}/q_p), \text{ gm moles/sec}$

$N_i^c = \text{Total experimental flux of species } i \text{ based upon capillary cross-sectional area, } A_c, \text{ gm mole/cm}^2\text{/sec}$

$N_i^r = \text{Molar flux of species } i \text{ through cylinders of radius } \bar{r}, \text{ gm mole/sec}$

$N_i^t = \text{Total molar flux of species } i \text{ through cylindrical model, gm mole/sec}$

$N_i^x = \text{Total experimental flux of species } i \text{ through solid, gm mole/sec}$

$N_{Kn_i} = \text{Knudsen number of species } i, (\mathcal{E}/q_D) D_{ij}/D_{Kn_i}$

$N_{Re} = \text{Reynold's number } = dG/\mu$

$P = \text{Absolute pressure, cm Hg}$

$P_R = \text{Experimental reference pressure, cm Hg}$

$P_S = \text{Experimental sample pressure, cm Hg}$

$q_D = \text{Bulk diffusion tortuosity factor}$
\( q_K \) = Knudsen diffusion tortuosity factor (macro-pore)

\( q_M \) = Micro-pore tortuosity factor

\( r \) = Distance of molecular travel, cm

\( \bar{r} \) = Mean pore radius, cm

\( R \) = Universal gas constant, cc - cm/gm mole-°K

\( R_A \) = Nitrogen feed to diffusion cell, gm mole/cm\(^2\)-sec

\( R_B \) = Helium feed to diffusion cell, gm mole/cm\(^2\)-sec

\( R_{AB} \) = Flux ratio = \( N_B / N_A \)

\( S_g \) = Total surface area, cm\(^2\)/gm

\( T \) = Temperature, °K

\( \bar{v} \) = Average molecular velocity, cm/sec

\( \Delta \) = Deviation, Equation (88)

\( \bar{v}^* \) = Average molar velocity, cm/sec

\( \bar{v}_i \) = Drift velocity of species \( i \), cm/sec

\( V \) = Gas volume, cc

\( \bar{V} \) = Gas volume per unit mass, cc/gm

\( V_g \) = Total pore volume, cc/gm

\( V_p \) = Volume of uncompressed powder, cc/gm

\( V_r \) = Pore volume of cylinders having a radius \( \bar{r} \), cc

\( V_t \) = Actual pellet volume, cc = \((\pi D^2/4)L\)

\( V_{TP} \) = Total pore volume of sample, cc

\( w \) = Work, gm-cm\(^2\)/sec\(^2\)-gm

\( W \) = Pellet weight, gm

\( X_i \) = Mole fraction of species \( i \)

\( X_{VR} \) = Volume fraction of pores of radius \( \bar{r} \)
\( z \) = Thickness, cm

\( \alpha \) = Angle between surface plane and axis of 45° pore, Wheeler

\( \gamma \) = Surface tension, dynes/cm

\( \Delta \) = Gradient

\( \varepsilon \) = Total porosity of solid

\( \varepsilon_k \) = Macro-porosity of solid

\( \varepsilon_m \) = Micro-porosity of solid

\( \varepsilon / \varepsilon_D \) = Effectiveness factor for the molecular diffusion coefficient

\( \varrho \) = Void fraction (Wheeler) = porosity,

\( \lambda \) = Mean free path, cm

\( \mu \) = Viscosity, poise, gm/cm.-sec

\( \bar{\mu} \) = Radius dimension, micron

\( \pi \) = 3.14159.....

\( \rho \) = Density, gm/cc

\( \rho_s \) = Alumina solid density, gm/cc

\( \phi \) = Mercury contact angle, degrees
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I, John Patrick Henry, Jr. was born in Burley, Idaho, December 24, 1935. I received my secondary education in the public schools of Nampa, Idaho, and my undergraduate training at Gonzaga University in Spokane, Washington which granted me a Bachelor of Science degree with a major in chemical engineering in 1957. As a senior at Gonzaga University, I was appointed a laboratory instructor for the Department of Chemistry. I received the Master of Science degree in Chemical Engineering from Northwestern University in 1959. While completing this work I was awarded a University Teaching Assistantship for the academic year, 1957-8. I was appointed University Fellow at Northwestern University in 1958. While working toward the Doctor of Philosophy degree at The Ohio State University, I was teaching assistant for the Department of Chemical Engineering for the academic year, 1959-60. I was appointed to the Eastman Kodak Fellowship for the academic year, 1960-1.
Hutchison et al. (19), Kraus et al. (24), Mittington (27), Scott and Dullien (33), Villet and Wilhelm (36), Wicke and Vollmer (43), Wilson et al. (45), Weisz (38), Wicke and Brotz (41), and Wicke and Kallenbach (42). These authors used either the tortuosity factor itself or a mean pore radius as defined by Equation (2).

Some work has been done trying to use the pore-size distribution function in determining diffusion coefficients, but this study is still in its initial stages of development. Among those working in this area are Barrett et al. (1), Mingle and Smith (26), and Robertson and Smith (52). As this area is extremely important, it is to be expected that others will enter the field using the distribution approach. The present work considers this analytic technique in explaining measured diffusion data.

C. Transition diffusion

The third type of diffusion or diffusion in the transition region has been known to exist for some time but little work has been done in this area. This is the diffusion phenomenon that lies in the range of pore sizes where Knudsen and molecular diffusion interact, or where the mean free path of the molecule approaches the diameter of the pores through which diffusion is to take place. Pollard and Present (29) have examined this region and have given a complex expression for self-diffusion in the transition
region. Scott and Dullien (33) have examined this region to some extent, and an initial theory is proposed assuming that the resistance to flow is due to molecular-wall collisions and intermolecular collisions of gases of different species, but the experimental data are based upon an average pore radius and this establishes such a broad range of possible diffusion coefficients that the theory cannot be strictly compared to their data even though agreement is shown to be very good. Rothfeld (58) examines the same region that Scott and Dullien discuss, and arrives at the same general equation for the transition region. His work is discussed in detail in Chapter V. In other words, little is known of this region because the difference between Knudsen and molecular flow has been disguised by inaccuracies used in determining porous solid physical characteristics.

D. Layer flow

The fourth type of flow in a porous solid is that whereby diffusion takes place in an adsorbed layer of molecules over the surface of the catalyst particle. A little work has been done in this area by Carman (4), Jones (20) (21) and Rutz (31). It is not the scope of the present work to examine this type of diffusion.
III. LITERATURE REVIEW

A. Introduction

Diffusion phenomena in porous solids as an area for research effort has been defined for years. It has, however, only recently become an area to which any extensive work has been devoted. Perhaps Knudsen (23) established or at least encouraged the problem when in 1909 he began to study the effect of small capillaries on the flow of gases. He found that the size of the opening through which the gases can flow greatly effects the diffusion mechanism, and it was at this time that Knudsen flow was first defined. He noticed that as the size of the capillary grew smaller eventually the resistance of a gas to flow was not due to intermolecular collisions but was rather due to molecular-wall bombardments. Using the analytic techniques of the kinetic theory of gases he arrived at an expression for a diffusion coefficient when the mean free path of a gas is larger than the diameter of the opening through which diffusion is to take place. The Knudsen diffusion coefficient, Equation (1), depends only on the size of the opening through which gases are diffusing, the temperature of the gas and the molecular weight of the diffusing gas. He also noted that the diffusion of one gas is not affected by any other moving species as long as all
are in this Knudsen region. Once established, Knudsen flow is independent of pressure.

Ordinary molecular diffusion of gases and gas mixtures has been studied by many researchers and will be discussed later. In this case, flow resistance is due to intermolecular collisions and therefore the presence of one or several gasses has a decided effect on the diffusion processes. Molecular diffusion is a function of pressure and it occurs when the mean free path of a gas is considerably smaller than the pores through which diffusion is taking place. Molecular diffusion usually occurs in the larger pores of most catalytic solids at atmospheric pressure while Knudsen diffusion may be occurring in the micro-pores of the same solid.

There is no defined break between Knudsen and molecular diffusion for several reasons. First, no porous solid has a uniform pore diameter and, therefore, the same flow phenomenon need not be occurring in all of the pores. Secondly, the mean free path concept is a statistical one, and in a transition region intermolecular as well as molecular-wall collisions will be important as resistance terms.

B. Experimental studies (steady state)

Bockhoven and Hoogschagen (3) use a very general method to determine the diffusion coefficient of oxygen through a porous plug. The oxygen is absorbed upon heated
copper and the amount of diffusion is calculated by weight difference in the copper. An effective diffusion coefficient is calculated for several solids and they found it to be 4 to 12 per cent of the free gas diffusion coefficient and they therefore assumed Knudsen diffusion as the flow mechanism. Their effective diffusion coefficient includes all possible errors, and it is based on an average pore diameter.

Hedley (16) studies the molecular flow of gases through various types of porous solids. He also incorporates mean pore size and lengths into his diffusion calculations.

Henry et al. (17) and Henry (50) measure counter diffusion rates in a porous solid and calculate effective diffusion coefficients based upon a mean pore size, and they present a model to show the possible structure of one pore. Effective diffusion coefficients calculated from this interconnected pore model give one possible explanation for the high resistance to flow in the experiments that they conducted. The diffusion mechanism is not well established in their work even though the average pore size would place the diffusion mechanism in the Knudsen range.

Hoogschagen (18) measures labyrinth factors or tortuosity factors which show that the length of the diffusion path in a porous solid is greater than the length of the solid itself based upon resistance calculations for the
solid's actual length. He uses the same technique as before with Bockhoven (3). He also calculates a "diffusability" which is the ratio of the actual effective diffusivity to a theoretical diffusivity. His work is based on a mean pore size.

Hutchison et al. (19) study the flow of gases through a fine-pore graphite and they correlate their results with an equation for simultaneous viscous and slip flow of a gas in the porous solid. Their object is to use their experimental values to determine the mean-pore size, surface area and tortuosity factor of the solid.

Rhodes and Amick (30) use average values in their determination of binary gaseous diffusivities in porous materials. They study principally molecular diffusion. Rutz (31) in his study of the diffusion of hydrocarbon gases and vapors through microporous media gives a good analysis of adsorbed layer flow. His work is based upon average solid properties.

Van Bavel (35) studies gaseous diffusion and porosity in porous media using average properties of the solid. Weisz (38) measures flow through porous solids and its relation to internal reaction velocities. He uses average solid properties and therefore the flow mechanisms are not well established. His work is a classic, though, in that the experimental techniques used are those most widely employed
today. The technique used in this present work is based upon the original work of Weisz.

Wicke and Brotz (41) measure flow rates through zinc oxide tablets using the same technique as Weisz and they compute laybrinth factors for the solids based upon mean solid properties. Wicke and Kallenbach (42) experimentally determine laybrinth factors also as do Wicke and Vollmer (43).

Wilson et al. (45) discuss thoroughly the three flow ranges, Knudsen, molecular and transition. Using the concept of slip flow where there is an apparent decrease in the viscosity coefficient ascribed to a slipping of the gas at the walls, they conclude that the transition and slip regions are the same despite different postulated mechanisms. This usually occurs at low pressures. By means of a slip coefficient they derive a general expression for flow through a porous plate. Using three stainless steel porous plugs, they vary the pressure to change the mean free path of a gas, and from their measurements they calculate an effective pore radius. They induce flow by establishing a pressure gradient across the plates, and conclude that molecular or viscous flow exists if the ratio of the mean free path to the pore diameter is less than 0.025 and free molecular flow exists if this ratio is greater than 1.6.
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C. Theoretical studies (steady state)

Beek (2) studies the measurements of gaseous diffusion through porous materials analytically and concludes that diffusion coefficients may be measured only if both counter-diffusing fluxes are known. He studies diffusion in the molecular range only and performs no experimental work.

De Marcus (7) studies the problem of Knudsen flow and suggests a solution to the integral equations by using probability kernels. His work is not applicable to the present study. Deryagin and Bakanov (8) propose a theory of the flow of a gas in a porous material in the near-Knudsen region but provide little experimental evidence for their theory.

Evans et al. (11) propose a model for gaseous diffusion in porous media at uniform pressure by assuming that the solid is a collection of dust particles which is treated formally as large molecules forming one component of a multicomponent mixture. For instance, a binary diffusing gas through a porous medium is formally considered a ternary mixture with the dust component restricted to remain stationary in space. This analysis is known as the "dusty gas problem."

Jones (20) discusses an equation to describe flow of an adsorbed layer over the surface of a capillary and presents a detailed analysis, but his work is not directly
applicable to the present study. In another work, Jones (21) discusses surface flow through pores of molecular dimensions.

Kaganar (22) studies the diffusion of three mixtures of helium through porous partitions with pore sizes of a few tenths of a micron. The effect of the pressure before and after the partitions, of the mean pressure, and of the fraction of the gas having passed the partition on the separation coefficient is studied and determined. He gives some data on the deviation of his coefficient as measured from the theoretically determined coefficient.

Peterson (28) proposes a theoretical study of molecular flow by considering a model which differs from the conventional smooth-walled cylindrical model. His work is concerned with the quantitative effect of periodic pore constructions on the effective diffusivity. His assumed pore model was one in which the constrictions occur at the vertex of a hyperbola of revolution. He conducts no experimental work. Michaels (25) discusses the same problem as Peterson but proposes a much simpler model to arrive at the same conclusions. Henry (50) discusses the same model as Michaels in conjunction with his work as described earlier.

Mittington (27) proposes a method for deriving a characteristic which determines the flow in porous systems. This characteristic combines both area and path-length factors used by earlier authors. For a gas, he found that
diffuse flow is proportional to the \( 4/3 \) power of the gas-filled porosity and this function is derived from consideration of the planar distribution of spherical pores and the interaction of two adjacent planes.

Pollard and Present (29) develop a complex expression for self-diffusion of a gas in the transition zone. Rothfeld and Watson (51) and Rothfeld (56) present an analysis of diffusion in the transition zone and present an equation for predicting this diffusion coefficient. Their experimental work is based upon mean pore sizes and they do not study the complete transition zone. They conclude that in stead counterdiffusion of two gases in porous media, the flux ratio is independent of total pressure and different from the theoretically expected one over the entire range from Knudsen to bulk diffusion. Scott and Dullien (33) give a good treatment of the transition zone, but their data do not cover the entire three mechanism range, and they use mean pore properties to calculate their diffusion coefficients. The last two articles are the best presentations of this problem to date and the present study includes an extension of this work.

Thiele (34) follows Knudsen's original work by applying it to gaseous reactions in porous materials. Although Thiele's work is primarily theoretical and restricted by severe conditions, it is a primary contribution to an
understanding of the problem of diffusion mechanisms as a controlling factor in heterogeneous catalysis.

D. Transient studies of diffusion phenomena in porous solids

Several workers have devoted considerable effort to determining the effect of dead-end pore volume in a porous catalyst upon catalyst effectiveness. Goodnight et al. (14) study and measure molecular flow in porous sandstone and derive a series of equations which, when solved on a computer, agree with their experimental data. A system of equations is derived that describes pressure transients during non-steady state flow of a fluid through a linear porous medium which contains known dead-end pore volume. They conclude that dead-end pore volume (defined as volume which contains the flowing or diffusing species but through which there is no flux during steady-state fluid flow or diffusion) may alter transient fluid flow or diffusion behavior.

Dye and Dalla Valle (10) correlate diffusion coefficients as a function of porosity using compressed powdered potassium perchlorate plugs. They compare their data to the Buckingham equation as used in soil mechanics treatments. They found that diffusivity is independent of medium thickness by a series of unsteady-state measurements. They solve a differential equation for unsteady-state diffusion and use it
for comparison with their data. They are primarily concerned with molecular flow.

Currie (6) presents a study of gaseous diffusion in porous media using non-steady state techniques with dry granular solids but is not concerned with variation in flow mechanisms. Kraus et al. (24) make two studies: (1) to see if the surface area (by flow measurements) agrees with the BET adsorption method and (2) to explain discrepancies by taking into account the dead pore volume as a flow resistance. They use powders of various sizes and find that transient flow areas obtained with helium are from 12-19 per cent higher than the nitrogen flow or adsorbed areas. A possible explanation might be the smaller size of the helium atom which can penetrate into extremely minute crevices and channels inaccessible to the nitrogen.

Villet and Wilhelm (36) make two studies, one employing steady-state techniques and the other involving transient diffusion in the Knudsen region. They conclude that the accumulation within a porous pellet (dead end volume) is negligible and they show that the Knudsen diffusion coefficient is independent of pressure as it should be. They state that gases do not diffuse inversely proportional to their molecular weight but do not discuss this issue extensively. Their conclusion seems to disagree with previous studies, but since their work is restricted to the Knudsen region, comparison is difficult.
E. Structure of porous materials

A major problem encountered in diffusion studies in porous media arises due to the inability of researchers to measure the physical properties of the solid accurately. Fatt (12) studies the pore structure of sintered glass from diffusion and resistance measurements. Dubinin (9) discusses branched porous structures with reference to his work on the structure of active carbon adsorbents.

Wang (37) studies diffusion as a function of "effective thickness for diffusion" in various substances such as porcelain, stainless steel, carbon, graphite, alumina scale, and glass powder packing. He devises an experimental procedure for estimating the gas film thickness, average pore length and porosity of these solids. His pore structure studies involve only molecular diffusion techniques. Wiggs (44) studies the relationship between gas permeability and the pore structure of solids, but is not concerned with diffusion mechanisms as such.

F. Pore size distribution

An area of study at present, and one which may provide a major break-through in the understanding of the problem of diffusion in porous solids is the analysis of surface area available for diffusion as a function of the pore size distribution within the solid. Several techniques are well known for measuring the pore-size distribution within a solid,
the principal one consisting of an analysis of the resistance to the flow of mercury in the solid at various pressures. The smaller pores require considerably more pressure for mercury to flow through them than do the larger ones.

Barrett et al. (1) have devised methods for measuring the pore size distribution of a porous solid. Mingle and Smith (26) present a new expression for the thickness of the adsorbed layer of nitrogen on a porous catalyst, and by using their expression, adsorption isotherms can be developed for determining analytical pore-size distribution functions of any type.

Robertson and Smith (52) have presented a model of possible pore size distribution in a catalyst particle and use this model for comparison with their experimental data. They are concerned with a binodal pore size distribution and they assume that the Knudsen diffusion mechanism is occurring in the micro-pores but that the transport through the macro-pores was large enough to render the micro-pore transport insignificant. They conclude that effective diffusivities determined from the data for the macro-region are about 60 per cent of those computed from the equation proposed by Wheeler for the range between Knudsen and bulk transport.

G. Pressure distribution in porous solids

Several authors have been concerned with pressure distribution which occurs when gases are flowing through
porous solids. Field and Watts (13) measure the distribution of pressure for gas flow through some solids. Greenberg and Weber (15) study the flow of gases through porous sintered metals with high pressure gradients but they are involved principally with molecular flow.

Evans et al. (48) consider forced flow diffusion and give some experimental comparison to their theoretical analysis but they do not cover the entire three mechanism range.

The importance of the three preceding studies lies primarily in the consideration of molecular flow since Knudsen flow, once established, is independent of pressure. The transition and molecular flow regions are pressure dependent.

H. General work

Carman (4) has examined the diffusion and flow of gases and vapors through micro-pores and has presented a study of surface flow as well as slip flow and molecular flow. Carman (5) has also presented a complete study of the flow of gases through porous media, but with particular application to the petroleum industry and therefore the problem of three well-established flow mechanisms is not encountered. Scheidegger (32) has prepared a text on the physics of flow through porous media and it shows that there
is little experimental work performed on establishing the three flow regimes.

Wheeler (39)(40) presents an analysis of the problems involved in heterogeneous catalysis introduced by the use of porous solids and gives a good review of the techniques employed in determining solid properties. The mean pore radius concept of Wheeler, as given in Equation (2), is one used extensively in experimental calculations. Klinkenberg (47) discusses the analogy between diffusion and electrical conductivity measurements in porous rocks. He finds excellent agreement between the two. Collins (49) recently has prepared a text on the flow of fluids through porous materials which is a good summary of the work completed to date.

Scott and Dullien (54) use Knudsen's data and the kinetic theory to explain the transition from molecular to Knudsen flow in capillaries. The authors discuss the significance of the actual meaning of the term, mean-free path, and discuss the minimum which occurs in the flow rate versus pressure curve for the same capillaries. They briefly discuss porous solids, but this study is particularly significant in that they use Knudsen's original work for flow in small tubes.
I. Application of diffusion principles in porous media

In a recent study Harper (53) discusses the transport properties of gases in porous media at reduced pressures with reference to freeze-drying. A theory is outlined which considers the effect of pressure on permeability and thermal conductivity of gases in porous solids in the slip-flow and free-molecule flow regions. Results show that the usual operating pressure range of freeze-dryers (0.1 - 1.0 mm of mercury absolute) corresponds to the transition region between slip-flow and free-molecule flow.

J. Survey conclusions

Analysis of the literature shows that the study of the occurrence of the three flow mechanisms in a porous solid has only been rarely undertaken, and in all cases, a pore-size distribution was reduced to a mean value for computation. Much of the value of the studies may be lost by such an assumption, and it is with this in mind that the present study is undertaken.
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IV. STATEMENT OF THE PROBLEM

The object of this investigation is to determine the effect of the properties of a porous solid upon the mass flux for diffusion through the solid.

A nitrogen-helium counter-diffusing system will be studied, and an attempt to evaluate the constants of the rigorous equation proposed by Rothfeld (58) and Scott and Dullien (54) will be made.

The present study will include the measurement of Knudsen diffusion coefficients for the solid, and an assumed model will be correlated with experimental results.

The pore-size distribution of the sample will be measured, and the effect of this distribution upon the mass flux through the solid will be studied. An attempt will be made to quantitatively establish the relative contribution to diffusion of the macro-pores and the micro-pores of the porous solid.

A study of the transition from Knudsen to molecular flow will be undertaken with emphasis upon the change from Knudsen to transition flow.

An experimental technique will be developed for accurately establishing an equation for the entire range of diffusion mechanisms, that is, from Knudsen flow through transition diffusion to molecular diffusion.
V. THEORY

The problem of the evaluation of an effective counter-diffusion coefficient has been met by many researchers, as described in Section III, Literature Review. Many of these workers have proposed synthetic models for the actual structure of the solid, but these models are limited strictly to those solids which have the model structure. They are valuable in giving an empirical picture of the diffusion phenomena, but their applicability is extremely restricted.

Two outstanding theories have been proposed, the first of which is an empirical relationship based upon an understanding of the physical picture of the change from Knudsen flow through the transition region to Molecular diffusion and is proposed by Wheeler (39). The second is one proposed by Rothfeld (56), and substantiates a slightly different approach given earlier by Scott and Dullien (33). Each of these studies will be considered in this section of the present work.

A complete discussion of the Knudsen flow phenomenon and its application to porous solids is given in the third part of this study. It is original to this work but will refer to a recent publication on the structure of porous solids as given by Robertson and Smith (52).
A. Wheeler's Model—An empirical approach

The theory for the prediction of diffusion coefficients through the three diffusion processes in porous solids begins with an empirical equation of Wheeler (39). In his study of reaction rates and selectivity in catalytic reactions he intuitively proposes that

\[ D_W = D_B \left( 1 - e^{-D_{KI}/D_B} \right) \]  \hspace{1cm} (4)

where \( D_W \) is the diffusion coefficient in pores of any size and \( D_B \) and \( D_{KI} \) are the "bulk" or molecular diffusion coefficient and Knudsen diffusion coefficient for species \( i \) respectively.

The physical explanation of Equation (4) as given by Wheeler is that elementary kinetic theory gives for the bulk diffusion coefficient in a mixture of molecules of similar mass and molecular diameter, the formula

\[ D_B = \frac{1}{3} \bar{v} \lambda \]  \hspace{1cm} (5)

where \( \lambda \) is the mean free path and \( \bar{v} \) is the average velocity. Since the Knudsen coefficient can be expressed as

\[ D_{KI} = \frac{2}{3} \bar{r} \bar{v} \bar{v} \]  \hspace{1cm} (6)

where \( \bar{r} \) is the pore radius in centimeters and \( \bar{v} \) is the same as in Equation (5), the ratio \( D_{KI}/D_B \) is exactly the ratio of pore diameter (2\( \bar{r} \)) to the mean free path, \( \lambda \). When
this ratio is large the exponential term in Equation (4) is zero and we have bulk diffusion, $D_w = D_B$. When this ratio is small (0.2 or less), expansion of the exponential in a power series gives $D_w = D_K$, so that Equation (4) automatically seems to give the correct type of diffusion in any region and a smooth transition between the two major types at any pore size or pressure.

Wheeler then presents an analysis for conversion of this single pore equation to computation of the diffusion coefficient $D_c$ within an actual catalyst granule as follows:

In computing the diffusion coefficient $D_c$ within an actual catalyst granule, its value should be the diffusion coefficient for a single pore times the number, $n_p$, of pores per unit surface of pellet.

To obtain the number of pores per unit external surface, one must look at the surface structure. The external surface of a catalyst pellet (as well as any imaginary internal surface) is made up of a fraction, $\theta$, of voids which are pore mouths, plus a fraction, $(1-\theta)$, of solid catalyst. It can be shown that this fraction, $\theta$, must be equal to the porosity or volume fraction of voids in the whole pellet. Thus the total number of pore mouths must be equal to the total area of pore mouths divided by the area per pore mouth. If pores ran exactly at right angles to the surface, the area per mouth would be $\pi r^2$ where $\bar{r}$ is the average pore radius and the total number of pore mouths per
square centimeter external surface would be $\theta/\pi \bar{r}^2$. It is a very specialized assumption, however, to assume that randomly directed pores run at right angles to a given surface. Instead, Wheeler assumes that on the average, the pores run at about a $45^\circ$ angle, since some pores run at almost right angles but others will run almost parallel to the surface. Hence, the area of intersection of an average pore with the surface will be $\sqrt{2}$ larger or $(\sqrt{2} \pi \bar{r}^2)$ since a cylinder of radius $\bar{r}$ intersects a plane in an ellipse of area $\pi \bar{r}^2 \sin \alpha$ where $\alpha$ is the angle between the plane and the axis of the cylinder ($45^\circ$, in this case). Adding this up, he finds that the number of pore mouths per unit external surface of catalyst pellet is approximately $\theta/\sqrt{2} \pi \bar{r}^2$, where $\bar{r}$ is the average pore radius. He further notes that by the "direction of a pore" he means the direction of the "streamlines" along which molecules flow through the pore structure.

Therefore the diffusion coefficient for an actual catalyst pellet will be $D_w$ times $\theta/\sqrt{2} \pi \bar{r}^2$ times a factor $1/\sqrt{2}$ since pores on the average run at about $45^\circ$ to a given surface. That is, only a factor $1/\sqrt{2}$ of the concentration gradient normal to the surface is operative in the direction of the pore axis, or alternatively, molecules must travel $\sqrt{2}$ farther than the straight-line normal to a surface due
to deviousness of the pore structure. Putting this all together;

\[ D_c = \frac{1}{2} \theta D_w \]  

(7)

where \( D_c \) is the over-all diffusion coefficient within a porous catalyst pellet, \( \theta \) is the porosity and \( D_w \) is the diffusion coefficient for a single catalyst pore given by Equation (4). Equation (7) shows that the diffusion coefficient in a porous pellet is smaller than that for the pores that make up the pellet due to two factors; (a) only a fraction, \( \theta \), of the pellet is open structure, the remainder \((1 - \theta)\) being solid, and (b) a factor of approximately \(1/2\) arises due to the deviousness of the pore structure, since the factor \( \sqrt{2} \) is used twice: once in the number of pores per unit area and again because each pore runs at an angle of about \(45^\circ\) to a given surface.

Thus Equations (4) and (7) present a complete theory of the diffusion coefficient in porous catalysts. The principal arguments to this theory are both concerned with the "average" or "mean pore radius" concept. This value is an extremely arbitrary one and therefore this theory is limited to solids having a uniform pore structure which is definitely not a typical situation. Most porous solids have a wide spectrum of pore sizes and Knudsen diffusion may be occurring in some while "molecular" or "bulk" diffusion occurs in others, with possibly transition flow occurring in the
majority of pores. The flow or diffusion picture is therefore considerably more complex than Wheeler's simplified model. The $\sqrt{2}$ factor is extremely arbitrary and is subject to serious question. However, for an initial picture, this theory proves to be empirically of considerable value.

It is interesting to note that the only experimental data necessary for this theory are surface areas and pore volumes of the samples in order to compute the average pore radius and porosity. The molecular diffusion coefficient can be found in the literature and corrected to experimental conditions by the approximate relationship

$$D_\theta = D_o \left( \frac{T}{273} \right)^{1.75} \left( \frac{1}{P} \right)$$

(8)

where $D_\theta$ is the bulk diffusion coefficient at $0^\circ$ Centigrade and 1 atmosphere pressure as obtained from the International Critical Tables or from any of a number of empirical relationships such as that of Gilliland. The Knudsen coefficient can be calculated from the experimental data and Equation (1).

Since Equation (4) was formulated without considering the direction of the pores, if the effective coefficients $D_{AB}^e$ and $D_{KA}^e$ for the particular solid could be obtained, a more reasonable effective coefficient $D_{WA}^e$ may be found. The present study will use this approach in an evaluation of Equation (4).
B. General theory for gaseous counter-diffusion

1) Mechanisms of Gaseous Diffusion

a) Knudsen diffusion: The Knudsen diffusion coefficient, $D_{KA}$, for a particular gas is shown by Carman (5) to be

$$D_{KA}^e = \frac{4}{3} K_{OA} \overline{c}_A$$

(9)

where $K_{OA}$ is the Knudsen flow permeability constant, which has a dimension of length (cm) and is a function of the physical properties of the porous solid, and $\overline{c}_A$ is the equilibrium mean molecular speed. Kinetic theory shows that an expression for $\overline{c}_A$ may be given as:

$$\overline{c}_A = \sqrt{8RT/\pi M_A}$$

(10)

where R is the universal gas constant, T is the temperature of the system in degrees Kelvin, $\pi$ is the usual constant equal to 3.14159..., and $M_A$ is the molecular weight of the particular gas in question. Knudsen's original work shows that $K_{OA}$ is proportional to the characteristic pore diameter.

From Equation (9), it is noticed that the Knudsen diffusion coefficient is independent of the total pressure and the flux of any particular component of a gas system (at constant temperature) is inversely proportional to the square root of its molecular weight.
The flux for a gas, $A$, in Knudsen diffusion in a porous solid at constant pressure, $P$, and temperature, $T$, can be expressed as

$$\overrightarrow{N}_A = - D_{KA} c \nabla x_A$$  \hspace{1cm} (11)

where $\overrightarrow{N}_A$ is the molar flux of species $A$ with respect to stationary coordinates, based on the total cross sectional area of the solid.

In Equation (11), $c$ is the total molar concentration, which, for ideal gases, can be expressed as $P/RT$, where $P$ is the total pressure. The mole fraction gradient over which the diffusion flux takes place is expressed as $\nabla x_A$.

It should be noted that by the very nature of the Knudsen diffusion process, the molar flux, $\overrightarrow{N}_A$, is independent of any counter-diffusing gas. The reason for this statement is that Knudsen diffusion is a function of only the momentum transfer between the molecules of the diffusing species and the walls of the solid and not to intermolecular collisions whether they be between species of the same type or species of a different type. It should be noticed that Knudsen diffusion only occurs when the mean free path of the diffusing gas is larger than the diameter of the pores through which diffusion takes place.

b) Bulk Diffusion: In defining the bulk diffusion coefficient, care must be taken in using the proper flux.
From molecular theory,

$$\mathbf{j}_A^* = - D_{AB} \mathbf{c} \nabla x_A$$

(12)

Where $D_{AB}$ is the bulk diffusion coefficient for a binary system A-B, $\mathbf{c}$ is the total molar concentration, $x_A$ is the mole fraction of species A and $\mathbf{j}_A^*$ is the molar flux of species A relative to the molar average velocity based upon the total cross sectional area. Since the flux can be written for species B as,

$$\mathbf{j}_B^* = - D_{BA} \mathbf{c} \nabla x_B = - \mathbf{j}_A^*$$

(13)

and

$$x_A + x_B = 1$$

(14)

it is apparent that $D_{AB} = D_{BA}$. It should be noted here that $\mathbf{j}_A^*$ is a local flux with respect to the molar average velocity while $N_A^*$, the measured flux, is taken with respect to fixed coordinates. Although the law of mass conservation requires that $N_A^*$ be uniform at steady state, this restriction does not apply to $\mathbf{j}_A^*$. 

Bird, Stewart, and Lightfoot (57) give the relation between the fluxes as

$$N_A^* = \mathbf{j}_A^* + C_A \mathbf{v}^*$$

(15)

where $\mathbf{v}^*$ is the molar average velocity, expressed as
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\[ \vec{V} = X_A \vec{V}_A + X_B \vec{V}_B \]  

(16)

where \( \vec{V}_A \) is the drift velocity of species A, and \( \vec{V}_B \) is the drift velocity of species B.

Substitution yields

\[ \vec{N}_A = \vec{f}_A + C_A (X_A \vec{V}_A + X_B \vec{V}_B) \]  

(17)

if \( c_A = x_A \cdot c \), then

\[ \vec{N}_A = \vec{f}_A + X_A (C_XA \vec{V}_A + C_XB \vec{V}_B) \]  

(18)

where

\[ \vec{N}_A = C_A \vec{V}_A \]  

(19)

Therefore

\[ \vec{N}_A = \vec{f}_A + X_A (\vec{N}_A + \vec{N}_B) \]  

(20)

It should be noted that for counter-diffusing gas systems the sign of \( \vec{N}_B \) should be negative. If equimolar counter-diffusion exists, if \( \vec{N}_A = -\vec{N}_B \), the Equation (20) reduces to Fick's first law,

\[ \vec{N}_A = -C \nabla X_A \]  

(21)

Experimentally this has never been observed.
c) Over-all Diffusion: Molecular, Transition and Knudsen

An effective diffusion coefficient for all ranges is defined as

\[ \vec{J}^*_A = -C \frac{\partial C}{\partial X_A} \]  

(22)

and a diffusion tortuosity is defined for bulk diffusion, as,

\[ \left( \vec{J}^*_A \right)_{\text{bulk}} = -(\varepsilon/q) D_{AB} C \nabla X_A \]  

(23)

where \( \varepsilon \) is the porosity of the solid and \( q \) is a tortuosity defined specifically with respect to bulk diffusion. With a new Knudsen coefficient defined by

\[ \left( \vec{J}^*_A \right)_K = -D^K_{AB} C \nabla X_A \]  

(24)

it is noticed that

\[ D^K_{AB} = D^K_{BA} \]  

(25)

It should be noted that this Knudsen coefficient is a theoretically defined one. It does not exist if the original premise for Knudsen diffusion, that intermolecular collisions contribute essentially nothing to the momentum transfer process when compared with molecule-wall collisions, is true. However, mathematically, this definition is necessary to the following development.
A relationship between $D^K_{AB}$ and $D^e_{KA}$ can be established as follows:

$$
\left(\frac{D^K_{AB}}{D^e_{KA}}\right)_a = \frac{N_A}{N} \left[1 - X_A \left(1 + \frac{N_B}{N_A}\right)\right]
$$

(26)

$$
-D^K_{AB} = -D^e_{KA} \left[1 - X_A \left(1 + \frac{N_B}{N_A}\right)\right]
$$

(27)

$$
D^K_{AB} = D^e_{KA} \left[1 - X_A \left(1 + \frac{N_B}{N_A}\right)\right]
$$

(28)

It is noted that $D^K_{AB}$ is a function of the mole fraction of each component where $D^e_{KA}$ is not.

Rothfeld (58) develops a relationship between the effective diffusion coefficient as defined in Equation (22), the bulk diffusion coefficient of Equation (23), and the defined Knudsen coefficient in Equation (24) by making a momentum balance of the system as follows:

Consider a one dimensional, isothermal porous medium at steady-state conditions containing a multicomponent gas mixture. The system is at uniform total pressure.

Assume:  

a) Shear stresses are negligible or no radial momentum transfer exists,

b) the gases are ideal and obey Dalton's law of partial pressure,
c) Concentrations and drift velocities are functions of the axial coordinate only and there are no transverse drift velocities, and d) the squares of the drift velocities are much less than the mean square thermal velocities. Drift velocity is defined as the arithmetic mean velocity of the species A or B, and the mean square thermal velocity is the arithmetic mean of the molecular speed. For diffusion processes, the drift velocity is about 1 cm/sec while the mean molecular speed is in the order of $10^5$ cm/sec. By making assumption (d), Rothfeld (58) shows that in a multi-component gas of non-uniform composition with a mass average velocity $\overrightarrow{V}$, not far from equilibrium, the partial pressure of any species is the flux of the normal component of momentum relative to $\overrightarrow{V}$, carried by that species across a plane moving with velocity $\overrightarrow{V}$, regardless of the orientation of the plane. The total pressure is the sum of the partial pressures.

A balance of z-momentum on the molecules of species i in a differential slice of the porous medium parallel to the faces and perpendicular to the z-axis is made. The slice has unit cross-sectional area and thickness dz. It is known that the flux of z momentum carried by species i across a filed plane normal to the z-axis is $P_i$. The flux of z-momentum transferred to the walls and the z-momentum
transferred to molecules of other species is:

$$-\varepsilon \frac{dP_i^w}{dz} = M_{iw} + \sum M_{ij}^*$$  \hspace{1cm} (29)$$

It is now assumed that:

\begin{align*}
e) M_{iw} &= M_i^\infty \quad \text{for all Knudsen numbers and} \\
f) M_{ij} &= M_{ij}^* \quad \text{for all Knudsen numbers, } N_{Kn}.
\end{align*}

Then

$$-\varepsilon \frac{dP_i^w}{dz} = M_{iw}^\infty + \sum M_{ij}^*$$  \hspace{1cm} (30)$$

To evaluate $M_{ij}^*$, the Stefan-Maxwell equations (57) are used.

$$M_{ij}^* = \frac{Q_D X_i X_j (\vec{V}_i - \vec{V}_j)}{D_{ij}}$$  \hspace{1cm} (31)$$

from the theory of multi-component bulk diffusion modified for porous media at $N_{Kn} = 0$.

The momentum transferred to the walls at infinite Knudsen number is known from the theory of Knudsen flow (5) as

$$M_{iw}^\infty = \frac{3F N_i RT}{4 Ko_i C_i}$$  \hspace{1cm} (32)$$

where

$$D_{ki}^e = \left(4/3\right) Ko_i C_i$$  \hspace{1cm} (33)$$
Substitution of Equations (31) and (32) into (33) yields,

\[-\frac{\varepsilon d P_i}{d z} = \frac{\varepsilon N_i R T}{D_{ki}} + \sum g_0 P X_i X_j \frac{(V_i - V_j)}{D_{ij}}\]  

(34)

Assuming ideal gases, \( P = c \cdot R \cdot T \),

\[-\frac{d C_i}{d z} = \frac{N_i}{D_{ki}} + \frac{g_0}{\varepsilon} \sum \frac{(C_i X_j V_i - C_j X_i V_j)}{D_{ij}}\]  

(35)

If \( N_1 = c_1 V_1 \)

\[-\frac{d C_i}{d z} = \frac{N_i}{D_{ki}} + \frac{g_0}{\varepsilon} \sum \frac{N_i X_j - X_i N_j}{D_{ij}}\]  

(37)

then for a binary system,

\[-c \frac{d X_A}{d z} = \frac{N_A}{D_{kA}} + \frac{g_0}{\varepsilon} \frac{(X_A N_A - N_A X_A)}{D_{AB}}\]  

(38)

From Equations (20), (22) and (28) and (38), it can be shown that

\[\frac{1}{D_{AB}} = \frac{1}{D_{kA}} + \frac{g_0}{\varepsilon D_{AB}}\]  

(39)

Substituting (28) into (39) and rearranging

\[D_{AB} = \frac{(\varepsilon/g_0) D_{AB} [1 - X_A (1 - R_{AB})]}{N_{knA} + [1 - X_A (1 - R_{AB})]}\]  

(40)
where \( R_{AB} \) is the flux ratio, \( N_B/N_A \).

In steady counter-diffusion \( N_A \) is measured and from a combination of Equations (20) and (22),

\[
N_A = -\frac{D_{AB}C \nabla X_A}{[1-X_A(1-R_{AB})]}
\]  \( \text{(41)} \)

By substituting (40) into (41),

\[
N_A = -\left(\frac{E \rho_0}{\rho_D E_D}ight)\frac{D_{AB}C}{N_{KnA} + 1 - X_A(1-R_{AB})} \frac{dX_A}{dZ}
\]  \( \text{(42)} \)

Integration of Equation (42) gives

\[
\left(\frac{N_{KnA} L}{C}\right)\left(\frac{\rho_D}{E_D D_{AB}}\right)(1-R_{AB}) = \ln \left[\frac{N_{KnA} + 1 - X_{AL}(1-R_{AB})}{N_{KnA} + 1 - X_{AO}(1-R_{AB})}\right]
\]  \( \text{(43)} \)

Equation (43) is the principal equation for a study of the counter-diffusion of gases at constant total pressure. It should be noted that if the Knudsen coefficient can be determined experimentally, and the ratio, \( R_{AB} \), established, measurement of the inlet and outlet concentration, \( X_{AO} \) and \( X_{AL} \), at one measured value for \( N_A \) will enable the calculation of the constant \( q_D/E \). This should be true at any pressure.

Since the Knudsen number, \( N_{KnA} \), can be expressed as

\[
N_{KnA} = \frac{E D_{AB}}{\rho_0 D_{KnA}}
\]  \( \text{(44)} \)
and since the gases obey the ideal gas law, Equation (43) can be simplified to

\[
N_A = \left( \frac{P}{kT} \right) \left( \frac{3 D_{ab}}{g_D} \right) \left( \frac{1}{1 - R_{ab}} \right) \ln \left[ \frac{\frac{3 D_{ab}}{g_D}}{\frac{3 D_{a0}}{g_D} + 1 - X_{al} \left( 1 - R_{ab} \right)} \right] \tag{45}
\]

It should be noted that Scott and Dullien (33) arrive at exactly the same equation by considering an over-all momentum balance.

Rothfeld does not use Equation (45) to evaluate the Knudsen diffusion coefficient and the molecular diffusion coefficient effectiveness factor, \( q_D \), since he had no way of determining either of these quantities experimentally and independently. He therefore assumes an approximate expression,

\[
\frac{C D_{kh}^e}{N_A L} = 1 + \frac{1}{N_{kn}} \left( \frac{R_{ab} - 1}{\ln R_{ab}} \right) \tag{46}
\]

which is an intuitive development. He states that this equation agrees with Equation (45) within a few per cent, but the use of the exact Equation (45) is much more desirable in the evaluation of the constants. The present work uses Equation (45) only.

It should be noted that Equation (45) reduces to the equation for molecular diffusion at high pressures, and the series expansion of the logarithm term reduces the equation to the Knudsen equation at low pressures.
To calculate an effective diffusion coefficient for steady-state diffusion measurements, Scott and Dullien (33) propose using an integrated form of Equation (11)

\[
N_A = \frac{C D_{NA} (X_{A0} - X_{A})}{L} \tag{47}
\]

where \( D_{NA} \) is the effective diffusion coefficient for species \( A \) throughout all of the flow ranges. Eliminating \( N_A \) between Equation (45) and Equation (47), an expression for the effective diffusion coefficient, \( D_{NA} \) can be shown to be

\[
D_{NA} = \frac{\varepsilon}{\varepsilon_0} \frac{D_{AB}}{(X_{A0} - X_{A}) (1 - R_{AB})} \ln \left[ \frac{\frac{\varepsilon D_{AB}}{\varepsilon_0 D_{NA} + 1 - X_{A}} (1 - R_{AB})}{\frac{\varepsilon D_{AB}}{\varepsilon_0 D_{NA} + 1 - X_{A0}} (1 - R_{AB})} \right] \tag{48}
\]

It should be noted that Equation (45) reduces to the expression for ordinary diffusion in one limit (at higher pressures) and to the expression for Knudsen diffusion in the other limit. For ordinary diffusion at constant pressure at steady-state, the integrated Maxwell equation for porous solids is

\[
N_A = \frac{\varepsilon}{\varepsilon_0} \frac{D_{AB} \rho}{RTL (1 - R_{AB})} \ln \left[ \frac{1 - X_{A}}{1 - X_{A0} (1 - R_{AB})} \right] \tag{49}
\]

At low pressures, the Knudsen equation is

\[
N_A = \frac{D_{KAP}}{RTL} (X_{A0} - X_{A}) \tag{50}
\]
For ordinary diffusion the Knudsen diffusion coefficient, $D_{e}^{K}$, is much larger than the molecular coefficient, $D_{e}$, and the ratio $D_{e}^{K}/D_{e}$ is small. Equation (45) and Equation (49) therefore become identical. For Knudsen diffusion, however, the Knudsen coefficient is much smaller than the molecular coefficient, and the ratio $D_{e}^{K}/D_{e}$ becomes very large and the logarithm term of Equation (45) approaches unity and can therefore be replaced by the first term of the series expansion of the logarithm, and Equation (45) and Equation (50) become identical.

It may be noted that in the present study, the effective Knudsen coefficient is measured by means of Equation (50), the molecular coefficient by means of Equation (45) and the effective coefficient for the transition region is calculated from Equation (48).

It should be stressed that if a suitable pressure range is studied for the diffusion phenomenon in a particular solid, the effective Knudsen and molecular diffusion coefficients can be determined independently.

C. General theory for Knudsen diffusion and the effect of the porous solid structure on flow phenomena

As stated in Part B1 of the present section, true Knudsen diffusion or flow is the only flow mechanism that is independent of the total system pressure and is also independent of the effect of a counter-diffusing or co-
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diffusing gas. The only criterion for Knudsen flow is that the mean free path of the gas molecule is larger than the pore structure (diameter) so that the resistance to flow is due to collisions between the wall and the diffusing molecules rather than intermolecular collisions. Wheeler (39) states, "after the collision with the pore wall, a reactant molecule will fly to another wall before having a collision with a second molecule. Intermolecular collisions may thus be neglected and a molecule travels within the pore by a series of "random flights" interrupted by collisions with the pore wall."

Since the effect of counter-diffusing gases can be neglected for Knudsen flow, Equation (11) can be directly applied once it has been determined that Knudsen flow exists. The establishment of Knudsen flow may be noted when the diffusion coefficient as calculated from Equation (50) is constant with a variation in pressure.

Since the original work in this field of gas flow in porous solids was performed by Wheeler (39), his "mean pore radius" concept was generally used in the calculation of the pore size from total surface area and total pore volume data. Equation (2) has been developed assuming that the pore volume and surface area is made up of cylindrical pores of the same radius. This radius was generally used to show whether Knudsen flow was established, that is, if the mean
free path of the gas molecule was larger than this value, Knudsen flow was assumed. The present study, and the work of Robertson and Smith (52), Rothfeld (56), together with those other workers who consider the spectrum of pore sizes known to exist in every porous solid has shown this concept to be not a wholly accurate one. Robertson and Smith (52) and Rothfeld (56), together with those other workers who consider the spectrum of pore sizes known to exist in every porous solid has shown this concept to be not a wholly accurate one. Robertson and Smith (52) and Rothfeld (56) conclude that the macro-pores contribute the major portion of the surface area available for diffusion. This reasonable conclusion leads one to establish that perhaps the macro-pores are the "feeder" pores to the catalyst pellet with the majority of surface area of the solid existing in the micro-pores. The micro-pores are therefore outlets of the macro-pores.

Robertson and Smith (52) choose a model for a catalyst solid whereby the length of the diffusion path for the micro-pores is different from the macro-pores. By an analysis, they conclude that this "length parameter" for the micro-pores and a different "length parameter" for the macro-pores can be determined by flow measurements, while the other necessary quantities can be measured from diffusion measurements. They conclude that in view of their
work, the macro-pores contribute most to the diffusion phenomenon. Their work was entirely conducted in the transition diffusion range. They concluded that because the mean free path of the gases studied was larger than the pore size of their most dense catalyst pellet, the flow was Knudsen. This conclusion is not valid since it has been found experimentally, that Knudsen flow in porous media does not occur until the mean free path is between one hundred to one thousand fold the value of the Wheeler mean pore radius.

Since the only flow regime which shows that all pores contribute proportionally to the diffusion phenomenon is Knudsen flow, if a Knudsen flow regime can be established, an analysis of the effect of the porous solid's structure on the flow can be made as follows:

1) Assume the solid is composed of cylindrical pores of a given cross-sectional area multiplied by the cross-sectional area of a single pore. A summation of all of the areas contributed by pores of a different radius will give the actual total cross sectional area available for flow, as

\[ A_T = \sum_r A_r \eta_r \]  

(51)

2) Assume the length of these cylindrical pores is the length of the solid multiplied by the coverage tortuosity factor for Knudsen flow.

\[ L_p = L q_k \]  

(52)
3) From the pore-size distribution diagram, the total cross-sectional area available for flow at any given radius, \( r \) can be determined from the volume fraction and the length of the solid data. This volume fraction multiplied by the total pore volume will give the volume available at any given radius, \( \bar{r} \).

\[
V_r = X_{vr} \cdot V_T \quad (53)
\]

4) The area available for the volume contribution as discussed in (3), therefore is

\[
A_r = X_{vr} \cdot V_T / q_k L \quad (54)
\]

where \( V_T \) is the total pore volume of the solid, \( X_{vr} \) is the fraction of the volume which has a radius, \( \bar{r} \), \( L \) is the length of the actual solid, and \( q_k \) is the tortuosity factor in Knudsen flow which corrects the pellet's length for the fact that the path is devious through the pellet rather than straight.

5) The Knudsen diffusion coefficient as given by Wheeler (39) for diffusion through cylinders of radius, \( \bar{r} \), is known to be

\[
D_{ki} = 9.7 \times 10^3 \bar{r} \frac{T}{M_i} \quad (55)
\]

6) The total moral transport through the solid for the fraction of pores at any given radius, \( \bar{r} \), is

\[
N^r_i = A_r D_{ki} \Delta C_i / q_k L \quad (56)
\]
where $N_j^r$ is the total transport in moles/second through cylinders of radius, $r$, $A_r$, is the cross sectional area available at any radius, $r$, $D_{K^2}$ is the Knudsen diffusion coefficient at any radius, $r$, $L$ is the length of the actual porous solid, and $\nabla c$ is the concentration gradient over which the diffusion takes place.

7) Substitution of Equation (54) into Equation (56) gives

$$N_j^r = X_{vr} V_{rp} D_{K^2} \Delta C_i / q_k^2 L^2$$

(57)

8) A summation of this total molar transport, Equation (57), over the entire spectrum of pore sizes and each pore size's contribution to the total transport may be expressed as,

$$N_j^t = \sum_r X_{vr} V_{rp} D_{K^2} \Delta C_i / q_k^2 L^2$$

(58)

9) The total molar transport through the solid has been measured experimentally throughout the necessary pressure range to establish the fact that the flow is true Knudsen flow. The measured experimental flux, $N_j^x$, can then be equated to the theoretical flux as calculated from Equation (58)

$$N_j^t = N_j^x$$

(59)
The value for the Knudsen tortuosity factor, $q_K$, can then be found for the particular model assumed as,

$$ q_K = \left[ \frac{V_{tr} \Delta C_i}{N_i^x L^2} \sum_r X_{vr} \cdot D_{ki} \right]^{\frac{1}{2}} $$

with the value for $D_{ki}$ determined from Equation (55).
VI. EQUIPMENT AND EXPERIMENTAL MATERIALS

A. Flow diagram and process description

To measure the amount of helium and nitrogen which diffuse through the experimental porous solids described in this work, the flow system as shown schematically in Figure 2 is used. It may be noticed that nitrogen and helium are so supplied to the system as to keep the pure gases flowing past both sides of the cylindrical porous solid. In this way, a known concentration gradient is established across the solid.

The analysis of the gas streams leaving the porous solid shows that some helium has diffused into the nitrogen stream at S-1 and some nitrogen has diffused into the helium stream at S-2. Since the absolute pressures of S-1 and S-2 are known, the diffusion coefficient is measured as a direct function of the pressure of the system. Since the pressure of the system determines the mean free path of the gases, the flow mechanism can be established if the size of the pores through which diffusion takes place is known.

The solids used in this work have been specially prepared and measured so that the pore size is known within some specified limits. Since the variables of concentration, solid properties (length and pore size), and amount of
Figure 2.—Schematic Flow System.
diffusing gases are known, diffusion coefficients can be calculated, and a study of the effect of pressure on this coefficient will determine the flow regimes which exists through the solid.

A photograph of the flow system is shown in Figure 3.

B. Equipment details

1. Gases and regulating valves

Pure nitrogen and helium are supplied to the system. These gases are stored in large cylinders as purchased from the Matheson Company. Prepurified nitrogen and standard pure helium are used. Standard regulating valves are attached to each tank and these in turn are attached to two vacuum regulator valves. All valves are purchased from the Matheson Company. The vacuum regulator valves are so constructed that they can be set at a delivery pressure between 0-760 millimeters of mercury absolute, and once set they will supply the gas at this pressure. The single stage regulator for the nitrogen cylinder was Regulator No. 1 with a brass check valve and an outlet design No. 580. The vacuum regulator is Regulator No. 49 as supplied to be used with Regulator No. 1. The single stage regulator for the helium cylinder is Regulator No. 1 with a brass check valve and an outlet design No. 590. The vacuum regulator is Regulator No. 49 as supplied to be used with Regulator No. 1.
Figure 3.—Actual flow system.
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XII. RECOMMENDATIONS .................. 204

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All regulator numbers refer to the nomenclature of the Matheson Company.

2. Pumps

Three hi-vacuum pumps are used to establish the desired pressure of the system. All pumps are standard vacuum pumps with a large capacity (33 liters/minute, approximately) and can produce a pressure of 0.1 micron absolute. A five gallon surge tank is connected between the pumps and the system to eliminate pressure surges during an experimental run.

Three separate pump systems are used in this study. They are used continuously and may be designated as:

1) Nitrogen sample removal system which establishes the desired pressure and flow rate in the sample side of the nitrogen T/C cell.

2) Helium sample removal system which establishes the desired pressure and flow rate in the sample side of the helium T/C cell.

3) Helium and nitrogen reference removal system which provides the desired pressure and flow rate in the two reference sides of the T/C cells.

Figure 4 shows a schematic flow diagram of the nitrogen sample pump system, and the same scheme applies to the helium sample system and the reference removal system. A large and a small needle valve are attached to the surge
Figure 4.—Pump system and pressure control.
tank in parallel to enable the operator to bleed air into
the system to raise the pressure to any desired value while
the pumps are operating at full capacity. The surge tanks
are connected directly to the outlet of the thermal con­
ductivity cells.

3. Diffusion cell

The diffusion cell is constructed of glass and is
shown in Figure 5. An actual photograph of the cell is
shown in Figure 6. The cell is so constructed as to enable
a porous solid to be placed between the two sections of flow.
This solid may be removed or replaced at any time. A pre­
vious study by Henry (50) shows that this cell construction
is of proper design so that a stagnant layer of gas does not
build up across the pellet and add an additional resistance
to diffusion.

The cell is mounted in the system so that the porous
solid of any length up to about one and one-fourth inches
may be used. The solid to be used for the diffusional
measurements is placed between two cylindrical glass pieces
that have the same outside diameter as the porous solid.
The glass "spacers" are cut so that they can be attached to
the solid, and the entire piece slipped into the apparatus.
Since the apparatus is constructed so that any length of
solid up to about 3.3 centimeters can be used, these spacers
essentially fill the space between the actual solid length
Figure 5.—Cell detail.
Figure 6.--Actual diffusion cell.
and the 3.3 centimeter space allowed for solid mounting (see Figure 7).

The "spacers" are attached to the porous solid by painting the outside surface of the spacer-solidspacer cylinder with pure beeswax. This not only attaches the spacers to the porous solid but also seals the outside surface of the solid sample so that gases cannot flow around the solid but rather must flow or diffuse through the cross-sectional area that is exposed to the flowing gas streams. Beeswax is used because of its extremely low vapor-pressure, and thus, the entire sample mounting system is inert.

When the "spacers" are firmly attached to the sample and the outside cylindrical surface area of the solid is completely covered with the beeswax, the spacer-solidspacer piece is slipped into the 3.3 centimeter space between the two diffusion cells. The inserted piece is then made more permanent in its mounting by wrapping the glass junction between the sample piece and each side of the diffusion cell with a layer of teflon tape. When the piece is reasonably rigid, the entire outside surface of the junction is painted with beeswax. In this process, it is sometimes desirable to paint the whole junction-spacer-solidspacer-junction surface with hot beeswax in order to make sure that the entire piece is sealed from the atmosphere.
Figure 7.—Preparation of porous solid.
When the wax has cooled for about an hour, the surface is again painted with the hot wax, and if any air holes are noted when the wax is cooled, or if any areas look suspiciously leak-prone, this area can be sealed by heating a glass rod in a burner flame, and by using the hot glass rod to spot melt the wax and reseal it at any desired location. When the sample is checked for atmospheric leaks, a quick seal may be made at any leak point with a hot glass rod.

The solid can be replaced easily by cutting the wax outer layer, or by scraping the outside layer of wax away from the junction. Once the sample is removed another one can be easily inserted in the manner described above.

The teflon tape is a standard dri-seal pipe dope as supplied by Kraloy Chemtrol Company. It is known as Dri-Seal Number 5.

4. Analytic section

To detect the small amount of helium or nitrogen which diffuses through the porous solid, thermal conductivity cells are used. The cells are Gow-Mac temperature controlled thermal conductivity cells, model TR-IIB, and are supplied with a No. 9285 construction geometry. They have hermetic seals for use in vacuum work. One cell is used for each gas system. With reference to Figure 2, T-1 is used to analyze the helium diffusion into the flowing nitrogen
system, and T-2 is for analysis of nitrogen diffusing into the helium flow system. Figure 8 shows the schematic panel and power supply to the cells. The thermal conductivity cells are operated at constant current conditions.

As stated before, two cells are used, one for each gas system. One power supply is used for both cells and a simple five-pole-double-throw switch enables a rapid transfer of power from one cell and system to the other.

Measurement of emf and emf-changes due to diffusion are made using a Leeds and Northrup Portable Precision Potentiometer No. 8662 and an automatic recorder in the cell control system as shown in Figure 8. A Sargent multi-range precision recorder is used to observe the transient behavior of the system and when steady-state is reached, a simple switch is used to change to the potentiometer for actual voltage measurements.

The thermal conductivity cells are kept in an air bath at about 90°F. The heating units of the cells maintain this temperature. The power source to the cells consists of two standard six volt automobile batteries connected in parallel. As current control is necessary for proper accuracy, this arrangement proves to be most satisfactory. Current through the cells is measured with a 0-500 millimeter as indicated in Figure 8.

The nitrogen cell is tested and supplied with a current of about 120 milliamperes while in operation, and the
Figure 8.—Panel and power supply.
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vii
helium cell is operated at a current of about 120 milli-
amperes. These values are arbitrary in that a current is
used so that emf values may be determined easily, and since
relative emf values are used instead of absolute ones, the
actual current supplied need not be any set value. The only
criterion is that it be constant.

A thorough study of the variables which effect the
accuracy of the thermal-conductivity cells is made. It is
found that particularly at low pressures, the output voltage
of the T/C cells depends not only upon the concentration of
the gas mixture passing through them, but also upon the
velocity of the gas flowing through the cells, and the
absolute pressure of the flowing gas. The cells are extremely
sensitive to pressure and velocity, therefore, for each run,
to duplicate the concentration established by the diffusion
processes, a complete calibration of the cells must be made.

To eliminate the velocity variable in the T/C cells,
a small flowmeter or capillary tube is placed in the outlet
sample stream of each of the cells. This capillary has the
same diameter as the other capillaries used throughout the
present study. To keep a reasonably small observable pres-
sure drop, a length of about 2 inches is used. The manom-
eter fluid for these flow meters is vacuum pump oil (Hyvac
Oil supplied by the Central Scientific Company, 93050 No.
3). This oil not only has an extremely low vapor pressure,
but also has a density that is less than water. This enables
an observed pressure drop or a desired pressure drop to be measured very accurately. These manometers are designated P-8 and P-9 in Figure 2. The flow through these meters is controlled by valves V-6 and V-7.

It should be noted that only part of the flowing stream passes through the cell, with the major portion of the stream by-passing the sample side of the cell entirely. This permits a lower velocity to be established in the cell since the Gow-Mac company recommends that a low flow rate be used (50 cc/min).

A typical calibration for any run will show the output voltage of the cells as a function of the absolute pressure of the gas. A plot of these variables as a function of various concentrations of He-N₂ gas mixtures is made at a constant velocity. The absolute value of the velocity need not be known, but it is absolutely essential that it be constant for the calibration and the run.

With the above curve established experimentally, a cross plot can be made for the desired pressure. This plot will show the output voltage as a function of the concentration of the gas mixture. This curve will be determined at constant pressure and constant velocity. From an experimental output voltage then, the concentration may be determined directly at a system pressure that is equal to the calibration pressure.
5. Pressure control and measurement

Since pressure control and measurement is extremely important in this study, precise instruments were acquired. Two GMA-140 Magnevac Vacuum Gauges were purchased from the Consolidated Vacuum Corporation of Rochester, New York. One is calibrated and used for the nitrogen system, and the other is calibrated and used for helium measurements. It is extremely important to note that the standard vacuum gauges do not work for helium gas measurements. A special sensing tube has to be purchased for the helium gauge. The thermal conductivity gauge, GMA-140, covers the pressure range from 1 micron mercury absolute to atmospheric pressure on two scales. A magnetic amplifier provides the basis for a simple circuit which maintains the filament of the sensing tube at a constant temperature of approximately 195°C.

As the pressure in the tube changes, the heat transported from the filament to the tube envelope also changes. The power required to maintain the filament temperature at a constant level is used as a measure of the pressure in the tube.

The Magnevac gauge has a built-in automatic control circuit which operates at the range being used and is independent of the meter. It does not require resetting each time it is activated, but rather acts as a continuous control system. For the present study, pressure control is
achieved by manual setting of the control valves, however, for automatic control, the gauge can be used to activate solenoid valves.

The calibration of the gauges is made by comparing the reading of the gauge to the absolute pressure as determined by a McLeod gauge. The McLeod gauge used in this work was also purchased from the Consolidated Vacuum Corporation and has a triple scale. This enables accurate pressure measurement from 2 microns mercury absolute to 10 millimeters of mercury absolute. For calibration of the gauges at higher pressure, standard absolute mercury manometers are used. The height difference of the absolute manometer is read with an accurate cathetometer.

The Magnevac gauges are checked frequently with the McLeod gauge to keep drifting errors to a minimum.

The absolute manometers are prepared by distilling mercury under vacuum into a 100 centimeter U-tube of pyrex glass. When sufficient mercury has distilled into the U-tube so that about 50 centimeters is noted, one leg of the U-tube is heated carefully until the mercury boils. The vaporizing mercury drives any remaining air out of the tube, and when the process is complete, this leg is sealed. Therefore, nearly total vacuum is achieved in one leg of the U-tube and the other leg is exposed to the system whose pressure is to be noted. These manometers are designated P-3 and P-4 in Figure 2.
Pressure control of the system is achieved by one of two methods. The first method allows the bleeding of nitrogen or helium from the cylinder sources into the system at such a rate as to establish the pressure. This means that for higher pressures a higher flow rate of gas is used. The second method is the one described in the first section of equipment discussion. At a constant nitrogen and helium flow, air can be bled into the vacuum pump surge tanks until the desired higher pressure is achieved as shown in Figure 4. This means that the pumps operating at full capacity are fed with a nitrogen-air or helium-air mixture. Both methods are accurate, but the second one is used in this work.

The advantage of the Magnevac gauges over the McLeod is that the Magnevac gauges are continuously recording gauges. They continuously indicate the system pressure, whereby, if the system pressure is to be noted by the McLeod gauge, it cannot be continuous since the McLeod gauge only works on trapped gas samples, and therefore one sample must be taken and released before another can be measured. The Magnevac gauges are concentration dependent, however, and the McLeod gauge is not.

The McLeod gauge's original calibration as supplied by the Consolidated Vacuum Corporation was checked by determining the total volume of the gauge and the linear volume of the capillaries. The scales were found to be quite accurate.
The Magnevac sensing tubes are mounted into the system so that a check of this gauge's accuracy may be compared to the McLeod gauge at any time.

6. Flow measurement and calibration

Since the flow rates of the gases involved in this study are so low, no commercial rotameters are available. The best method, therefore, for determining nitrogen and helium bulk flow rates is to determine the pressure drop across a piece of precision bore capillary tubing and compare actual flow rates with those theoretically determined assuming that laminar flow exists in the system. Calculations show that laminar flow exists through the entire flow rate range used in this study. Therefore, capillary tubing with an inside diameter of 0.0102 inches plus or minus 0.0003 inches is obtained from Fischer and Porter Company.

Assuming that ideal gases are involved in the flow system, an expression for mass flow rate, \( G \), can be developed as follows:

\[
\rho V = \frac{g}{M} RT
\]

(61)

The units of \( P \) are \( \text{cm Hg absolute} \), \( V \) is cubic centimeters per second, \( T \) is degrees Rankine, \( g \) is grams per second, \( M \) is molecular weight and \( R \) is the universal gas constant in \( \text{cm}^4 \text{per degree Rankine} \).
Since,
\[ G = \frac{9}{A} \] (62)
where \( A \) is the area of flow and \( G \) is in grams per second per square centimeter,

\[ G = \frac{PVM}{RTA} \] (63)

If the area of a capillary whose diameter is 0.0102 inches is combined with the appropriate value of the gas constant, an experimental mass flow rate, \( G_x \), based upon experimental volumetric flow measurements can be shown to be,

\[ G_x = 0.54850 \frac{PVM}{T} \] (64)

Since laminar flow is known to exist throughout the flow rate and pressure ranges, the Hagen-Poiseuille equation can be applied with the friction factor assumed to be,

\[ F = \frac{64}{N_{Re}} \] (65)
where \( N_{Re} \) is the Reynold's number.

The Hagen-Poiseuille law for flow in a pipe may be written

\[ \int \bar{V} dP + \int G^2 \bar{V} dV + \int dZ = -\bar{W} - \frac{1}{2} \int \frac{G^2 \bar{V}^2 f dL}{2d} \] (66)

The units of \( \bar{V} \) is cubic centimeters per gram, \( Z \) is centimeters, \( \bar{W} \) is the work applied in gram-centimeters per
gram, \( \dot{G} \) is grams per second per square centimeter, \( L \) is in centimeters, \( d \) is centimeters, \( P \) is centimeters Hg absolute, and \( f \) is the friction factor \((64/N_{Re})\) for laminar flow.

Since the gases behave ideally at low pressure:

\[
\nabla = \frac{RT}{\rho M}
\]

(67)

and if \( \dot{G} \), mass flow rate, is constant at any given pressure for steady state flow conditions, Equation (66) can be integrated to give

\[
\frac{M}{2RT} \left( \frac{P^2 - P_0^2}{P_0} \right) + \frac{G^2}{\rho_0} \frac{P_0}{P_1} = \frac{32GhM}{d^2}
\]

(68)

since \( \bar{w} = 0 \) and \( \int dz = 0 \).

If \( p = \rho \bar{g}h \) is substituted in Equation (68), where \( p \) is dynes per square centimeter, \( \rho \) is density of mercury in grams per cubic centimeter, \( \bar{g} \) is the acceleration due to gravity in centimeters per second and \( h \) is height in centimeters of mercury (Hg) absolute, an expression for mass flow rate \( \dot{G} \), in terms of the pressure drop across a flowmeter or capillary can be shown to be

\[
h_i^2 - h_0^2 = \frac{4AGhMLRT}{M(d\rho\bar{g})^2} - \frac{2G^2RT}{MP^2\bar{g}^2} \ln \frac{h_0}{h_i}
\]

(69)

where \( \mu \) is viscosity in grams per centimeter per second (poise).

Since the mass flow rates, \( \dot{G} \), are small, the last term may be neglected, and a final equation for flow in
capillary tubing with a diameter of 0.0102 inches and a length of 5.00 inches can be shown to be:

\[ G_t = \frac{(h_i^2 - h_o^2) M}{57.1211 h T \mu} \]  

where \( h \) is centimeters of mercury absolute, \( T \) is degrees Kelvin, and \( \mu \) is in poises times 10000 where \( \mu_{He} = 1.994 \) and \( \mu_{N2} = 1.840 \). According to the kinetic theory of gases, viscosity is independent of pressure, so the above values measured at atmospheric pressure are used as constant valves over the entire pressure range.

Equation (70) can be corrected for any other length of pipe remembering that the pressure drop is directly proportional to the pipe length in a laminar flow. However, for calibration purposes it is assumed that the theoretical length is 5.00 inches and any deviation of experimental from theoretical determinations should be an obvious constant factor. This assumption is made since the nitrogen and helium bulk flow meters are both about 5 inches long.

The calibration of the capillary meters is made by actually measuring the flow rate of the gas through the meters and comparing this flow rate to that determined from the measured pressure drop across the meter. The flow rate of the gas through the meters is measured by observing and timing the displacement of a soap bubble through a calibrated burette. The bubble is essentially an artificially introduced visual barrier into the flow stream and it travels
as a slug of gas through the burette. A schematic illustration of the calibration procedure is shown in Figure 9.

The accuracy of the soap-bubble method is checked against an actual water displacement of the flowing gas, and the comparison of the two determined flow rates is within 1.0 per cent. Since the bubble method is extremely rapid and simple it is used for all flow rate determinations. A wet-test gas meter was shown to be inaccurate for these low flow rates. The $\Delta P_{H_2O}$ was insignificant for all values.

The calibration curves of helium and nitrogen are given in Figures 10 and 11. Data for the calibration curves is given in Table 1. From a measured pressure drop, therefore, an accurate flow volume can be determined. A check of the effect of pressure on the calibration curve showed that this plot is essentially pressure independent for the entire range, 50 microns to atmospheric pressure. Therefore, calibrations are made at atmospheric pressure for convenience.

Flow control through all capillaries in this study is achieved by using extremely sensitive needle valves, V-1, V-2, V-3, V-4, V-5, V-6, and V-7. These valves have a 1/16 inch orifice and require about 32 turns to completely open them from a closed position. The valves were obtained from Consolidated Vacuum Corporation.
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Figure 10.—Calibration of flowmeter P-7.
Figure 11.—Calibration of flowmeter P-6.

NITROGEN FLOWMETER CALIBRATION

L = 5.00"
D = 0.0102"
SLOPE = 0.9780

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TABLE 1.— Flowmeter-capillary calibration data

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7. Diffusion measurements

Since the amount of gas diffusing through the porous solid is about 1-20 per cent of the total gas flow, the measurement of this low flow rate must be performed extremely accurately. The technique used in determining the amount of gas diffusing through the porous solid is as follows:

The system is allowed to reach steady state with pure nitrogen flowing across one face of the solid and pure helium flowing across the other face at constant and equal pressures. When steady-state diffusion is achieved, a constant emf value will be noted on the potentiometer which records the output of the T/C cells with pure nitrogen as the reference gas to the nitrogen cell and pure helium gas as a reference to the helium cell, R-1 and R-2. It should be noted that R-1, R-2, and B-1 and B-2 are expanded glass T's to cut down flow resistance. After recording this emf value, stopcocks 5, 6, 8, 7, 9, and 16 are closed and stopcocks 2, 10, 3, 4, 14, and 15 are opened. This enables the pure flowing gases to by-pass the porous solid through B-2 and B-1 and establishes only pure gases flowing through the T/C cells. The flow rate through B-1 and B-2 will be the same since the flow scheme construction is the same as S-1 and S-2. This flow is metered at P-6 and P-7. A nitrogen-nitrogen and a helium-helium emf is noted on the potentiometer when steady-state is again reached. The difference between this value then and the sample emf value is that emf due to the diffusion
of helium into the nitrogen stream and the diffusion of nitrogen into the helium stream. A known amount of helium can then be bled into the pure nitrogen stream through capillary, P-5, until the same emf value in T-1 is matched, since the flow rate through the capillary is known as a function of the pressure drop across it. A measurement of the actual pressure drop across the capillary, P-5, necessary to establish the sample emf value in T-1 will give the amount of helium gas diffusing through the porous solid. The procedure is then repeated in T/C cell, T-2, with nitrogen being bled into the pure helium stream through P-5.

The capillary tubing used for P-5 is the same precision bore tubing as was used in the bulk flow meter measurements. Capillary P-5 is twice as long as P-6 and P-7, but it is calibrated by the same method as described in Part B. 6. of the section. Since P-5 is used for both nitrogen and helium flow, it is calibrated for both gases, and the calibration curves for this meter are given in Figures 12 and 13. The pressure drop across the capillary can be determined by manometer P-5 and the absolute pressure at the helium side can be determined by either the Magnevac gauge, McLeod gauge, or the absolute manometer. Knowing the absolute pressure on the helium side of the capillary, C-1, and the pressure drop across P-5 the absolute pressure on the nitrogen side of P-5 can be calculated.
Figure 12.—Calibration of flowmeter P-5 (nitrogen).

NITROGEN FLOWMETER
CALIBRATION
L = 9.7847"  
D = 0.0102"  
SLOPE = 0.88041  
7/25/62
Figure 13.—Calibration of flowmeter P-5 (helium).
Control valve V-5 is described in Part B. 6. of this section.

8. Wood's metal plug

One of the easiest porous solids to prepare synthetically and one which has a uniform pore size distribution is prepared by pouring molten Wood's metal through a bed of solid salt particles. Using C. P. grade NaCl, the salt is carefully ground in a mortar and pestle until a considerable amount of the sized solid is retained on a 60-mesh screen (.0097 inch openings), after passing through a 50-mesh screen (0.0116 inch openings). The sized salt particles then have an average diameter (or length unit) of about 273 microns. Seven samples of this sized salt are collected and counted until an average weight of 500 grains of the salt is known to be 0.0183 grams with an average per cent deviation of 3.3 from the mean value.

When the salt crystals have been dried in a dessicator for several days, a bed of about two inches of the dried particles is prepared in the pellet mold, as shown in Figure 14.

Once introduced to the mold, the salt is heated to about 75 degrees Centigrade by applying a voltage through a rheostat to the nichrome wires surrounding the glass walls of the mold. This temperature must be checked carefully several times to insure that a uniformly heated bed is
Figure 14.—Wood's metal—salt mold.