DIFFUSION OF GASES

by

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BSTRACT

The effective diffusion coefficient of the binary gas pair, hydrogen and nitrogen, has been measured for diffusion through several types of porous solids.

Electrical conductivities through the pore spaces of the same solids were also measured with a view towards testing the analogy between ordinary diffusion and electrical conductivity. The results obtained show some discrepancies (up to 25%) from exact equivalence, especially in porous solids with a mean hydraulic diameter of less than 1 micron.

The diffusion apparatus was also used to determine the temperature dependence of the ordinarys diffusion coefficient in the range 20 - 300°C. The results obtained show close agreement with the Hirschfelder, Bird and Spotz theoretical equation for non-polar gas pairs.

The data were also compared with other values reported for this system and good agreement was found.

It is therefore concluded that the flow apparatus used is satisfactory for the investigation of the temperature dependence of the binary diffusion coefficient.

Calibration of the apparatus at one temperature will yield satisfactory absolute values for binary diffusion coefficients at other temperatures.

(i)

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a	Constant
A ^r	Cross-sectional area of sample
А, В,	Molecular species
Bo	Viscous-flow Permeability
c, C,	Constant
c _A , c _B ,	Concentrations
đ	Diameter
D _{AB} , D _{BA} ,	Diffusion coefficient.
De	Effective diffusion coefficient
Do	Diffusion coefficient, hydrogen, nitrogen.
Do / De	Diffusion ratio
I	Current density
k	Boltzmann constant
k ^t , K,	Constant
K t	Kozeny Constant
Ко	Specific electrical conductance.
L	Length of sample
m	Hydraulic radius
M_{i}, M_{A}, M_{B}	Molecular weights
N _i , N _A , N _B	Number of moles
p, pA, pB	Partial pressures
Р	Total pressure
Pc	Capillary pressure
, P *	Permeability
r, r _A , r _B	Molecular diameter

X

r _{AB}	Collision diameter
r _o	Reciprocal specific conductivity
R	Resistance of saturated sample
Rc	Capillary Radius
R _o	Resistance of sample volume of electrolyte
R/R _o	Electrical resistivity ratio
R [¢]	Gas constant
S	Area per unit bulk volume
So	Specific Surface Area
T	Absolute temperature
u	Velocity of gas flow
V	Potential
Λ,	Volume of gas diffused /sec.
Vf	Rate of flow
v _A , v _B	Molar volumes
₩ (') ^(')	Collision integral
X	Index of temperature (Andrussow Equation)
Z	Length of diffusion path
E	Maximum energy of attraction
θ	Porosity
η	Viscosity
σ	Interflacial Surface tension
ø	Angle of Contact

.

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DIFFUSION OF GASES

INTRODUCTION AND THEORY

A. Diffusion in Porous Solids

Many examples of chemical reactions which take place within porous solids can be found in the broad fields of heterogeneous catalysis and combustion. For these processes, it is frequently necessary to have a knowledge of the flux of diffusing molecules to and from the boundaries of the porous solid, and within the solid itself.

Four main types of gas transport are possible in porous solids:

Knudsen diffusion Bulk, or ordinary diffusion Surface diffusion Poiseuille or forced flow

Knudsen diffusion occurs whenever the mean free path between intermolecular collisions is large compared to the pore diameter. This means that a molecule after having had a collision with a pore wall, will fly to another wall before having a collision with a second molecule. In general, Knudsen diffusion occurs in pores about 400 Å or less in diameter for most common gases at one atmosphere pressure. The mean free path in this case is about 1000Å.

The second type of diffusion possible in pores is ordinary "bulk" diffusion. Molecules strike one another much more frequently than they strike the pore wall in this case. At 1 atmosphere pressure, the bulk value of the diffusion coefficient holds in fairly large pores; 5000 Å in diameter or larger. A transition state between Knudsen and bulk diffusion occurs in pores from 400 Å to 5,000 Å.

Forced flow through a porous solid occurs when a total pressure difference exists across the faces of the solid. Whenever the mean free path is large compared to the pore diameter, the forced flow will be Knudsen flow which is indistinguishable from Knudsen diffusion. However, when the mean free path is small compared to the pore diameter, Poiseuille (stream-line) flow will occur. The rate of flow is given by Poiseuille's law,

$$V_f = \frac{\pi d^4}{128 \eta} \cdot \frac{\Delta P}{L} \qquad (1)$$

where Vf = rate of flow d = diameter η = viscosity of gas $\frac{\Delta \rho}{L}$ = pressure drop per unit length of porous solid. For solids with pore diameters in the region of 5,000 Å, this

· 2

type of forced flow is highly inefficient because of the d⁴ term in Poiseuille's law (relative to the rate of diffusion)

Finally, surface diffusion can occur. This is a two-dimensional diffusion along the pore wall as opposed to ordinary three-dimensional diffusion in the pore void space. The molecules may be pictured as 'hopping' from one adsorption site to the next. However, it is generally true that this mechanism contributes little to the total transport at temperatures above the critical temperature of the gas in question.

For a porous solid, an effective diffusion coefficient, made up of contributions from the above mechanisms, is obtained. The effective diffusion coefficient is smaller in value than the bulk diffusion coefficient for three main reasons: (a) only a fraction of the porous solid is open structure, the remaining fraction $(1 - \theta)$ being solid matter. (b) due to the deviousness of the pore structure, the gas molecules must travel a further distance through the solid than its geometric length.

(c) it has recently been shown ⁽¹⁾ that periodic variations in pore cross-sectional area can substantially reduce the rate of diffusive gas transport through porous media.

Wheeler ⁽²⁾ has presented some empirical formulae which permit calculation of the effective diffusion coefficient from a knowledge of the average pore diameter, the porosity and the gas system employed. They are, however, based on simplified models of the pore structure and allow only qualitative

deductions regarding the effects of diffusional transport on chemical reaction rates.

With respect to experimental techniques for measuring diffusion rates within porous solids, two principal methods have been reported.

(1) The sides of a cylindrical pellet are sealed off and the two flat faces are contacted with two different gases. The rate of steady state diffusion through the pellet is determined by analysis of the gas streams for "contamination" by the other component.

(2) The second method depends on first filling the pore structure with one component and then measuring its rate of efflux into a second component. In this study, the first of these two methods is employed.

To study the effects of bulk diffusion alone, it should be possible to select a porous solid, a gas pair, and a set of conditions of temperature and pressure, so that all mechanisms except bulk diffusion do not contribute significantly to mass transport.

From the range of commercially available porous solids, one with a suitable average pore size and narrow pore size distribution, can be selected. Similarly, a suitable gas pair can be chosen so that in conjunction with the porous solid, operation under constant total pressure conditions and over fairly wide ranges of temperature and pressure will give a diffusion process which is almost entirely due to ordinary or bulk diffusion.

A diffusion ratio can be defined:

Diffusion Ratio =
$$\frac{Do}{De}$$
 - - - - - - - (2)

where, Do = value of the bulk diffusion coefficient at a given temperature and pressure.

> De = value of the effective diffusion coefficient for the particular porous solid at the same conditions

of temperature and pressure (obtained experimentally) The diffusion ratio is a property of the solid and is independent of the gas pair used in the diffusion measurements provided bulk diffusion only takes place. A number of porous solids were obtained whose properties would fulfill the requirements that ensure bulk diffusion only occurs. (Table I.) A gas pair, hydrogen-nitrogen, was employed in diffusion ratio measurements on the above solids. In particular, with the Selas solids, using the hydrogen-nitrogen gas pair, bulk diffusion measurements should be possible at pressures up to 100 atmospheres and temperatures up to any achievable value.

Values of the diffusion ratio, for porous solids at 1 atmosphere pressure and room temperature can range from 2.50 -100.0 depending on the type of solid tested. It is important to note that the value of the diffusion ratio can differ widely for a nearly-unconsolidated solid and a consolidated solid having the same porosity value. There is no present correlation of the diffusion ratios with other properties of a porous solid, such as the porosity, the viscous-flow permeability, or the specific surface area.

Therefore it would be extremely useful to discover some easily measurable property of a porous solid with which the diffusion ratio could be correlated.

B. Properties of Porous Solids

Some of the properties of a porous solid have already been mentioned. It is however necessary to distinguish between the two main classes of properties a porous solid can have:

Direct properties

Derived properties

Direct properties are the true properties of the porous solid and are independent of the method of measurement. Derived properties are those whose magnitude may depend on the method and defining theory of the experimental measurement. Some of the more important direct properties are:

> Bulk density True density Porosity or fractional Void volume Physical dimensions, etc.

and some of the more important derived properties are:

Viscous-flow permeability Specific surface area Average pore size Pore size distribution Electrical Resistivity Ratio Diffusion Ratio, etc.

1. Porosity

The pore volume can be determined from a knowledge of the difference in weight between a dry sample and a sample saturated with a liquid of known density. The porosity, or the fractional void volume, is the ratio of the pore volume to the bulk volume, calculated from the physical dimensions of the sample.

2. Viscous-flow Permeability

The specific permeability constant, Bo, is defined by Darcy's Law:

$$-u = \frac{B_o}{\gamma} \cdot \frac{\partial P}{\partial L} \quad (1)$$

where u = velocity of gas flow.

By regarding a porous solid as being equivalent to a bundle of parallel capillaries, a Poiseuille law expression can be derived for the total pressure drop,

$$\Delta P = \frac{32 \cdot u L \eta}{d^2} \qquad (2)$$

From these two equations together with a number of simplifying assumptions, and the definition of specific surface as

So =
$$\frac{5}{1-\theta}$$
 - - - (3)
where S is the surface area per unit bulk volume
and θ is the poposity

it is possible to derive the Kozeny equation

$$B_{o} = \frac{1}{K' S^{2}} \frac{\Theta^{3}}{(1-\Theta)^{2}} - (4)$$

Carman (3) gives a value of K' = 5. However, for better accuracy $C_{K'}$ should be determined experimentally. By determining Bo and Θ experimentally it is possible to calculate a specific surface area, as defined by this equation. By use of another derivation, it is also possible to define an average pore size for the porous solid on the basis of the same assumptions as those used in deriving Kozeny's equation.

3. Pore Size Distribution

A more accurate means of determining the average pore size and the specific surface area is afforded by a knowledge of the pore size distribution. This can be determined by using the mercury porosimeter method of Ritter and Drake.⁽⁴⁾

From the pore size distribution chart, the average pore size can be determined by taking the pore size that lies under the peak of the curve. This has been shown to be statistically correct for the type of curves obtained by this method.⁽⁴⁾

The specific surface area can also be calculated by means of a summation of the surface areas of a unit of pores and a knowledge of the pore volume, assuming pores of cylindrical shape.

4. Specific Surface Area

The most accurate means of determining the specific

surface area experimentally is the Brunauer-Emmett-Teller ⁽³⁾ method. This method locates the point on the nitrogen adsorption curve where all the surface is covered with a layer of adsorbed gas, one molecule thick. The B-E-T method locates this point by extending the Langmuir Isotherm to apply to multilayer adsorption. Unfortunately, only one sample was tested by this method. This result is given in Table \ddagger together with the result from mercury penetration for the particular sample tested.

5. Electrical Resistivity Ratio

Consider a pore space filled with an electrically conducting liquid. Assuming the solid is a non-conductor, the conductivity of a unit volume of the liquid-filled porous sample will be less than the specific conductivity of the liquid.

The electrical resistivity ratio is then defined as the ratio of the apparent specific conductivity of the solid to the specific conductivity of the liquid.

In general for a porous sample, of length L, and cross-sectional area A^{l} ,

 $\frac{R}{R_{o}} = \frac{R}{T_{o} \perp A'} - (1)$ where $\frac{R}{R_{o}} =$ electrical resistivity ratio R = resistance of the saturated sample $\bar{R}_{o} =$ reciprocal specific conductivity of the saturating liquid.

From a logical standpoint, the property most analogous to the diffusion ratio would seem to be the electrical resistivity ratio. Much data on this ratio can be found in the literature. As it is easier to measure than the diffusion ratio, such an analogy could usefully be employed to predict effective diffusivities for porous solids.

From a theoretical standpoint, the differential equations for the two processes of diffusion and electrical conductivity are also seen to be mathematically identical:

> $NA = - Do grad C_A$ (2) I = - Ko grad V (3)

Where N_A - number of moles of A passing through through unit cross-sectional area per unit time

> Do - diffusion coefficient CA - concentration of species A I - current density Ko - specific electrical conductivity V - potential

For a more detailed account of the properties of porous solids, the work of Carman (3) should be consulted.

C. Diffusion of Gases

1. Binary Diffusion Coefficient

In a mixture of two gaseous components A and B, the rate of transfer of A will not only be determined by the rate

of diffusion of A but also by the behaviour of B. The molar rate of transfer of A, per unit area, due to molecular motion is given by Fick's Law,

$$N_{A} = -D_{AB} \cdot \frac{\partial C_{A}}{\partial z} \qquad (1)$$

where N_A = molar rate of diffusion per unit area, A, D_{AB} = the diffusion constant of A in B C_A = the molar concentration of A Z = the distance in the direction of diffusion.

The corresponding rate of diffusion of B is given by:-

$$N_{B} = -D_{BA} \cdot \frac{\partial C_{B}}{\partial z} \qquad (2)$$

If the total pressure, and hence the total molar concentration is everywhere constant,

$$\frac{\partial C_A}{\partial z}$$
, $\frac{\partial C_B}{\partial z}$

must be equal and opposite and therefore A and B tend to diffuse in opposite directions. Let us consider the case of steady-state diffusion which implies the continuous supply and removal of the diffusing material. In the general case the total bulk flow of gas in the Z- direction is $(N_A + N_B)$, the net transfer of component A is the rate of diffusion plus the transfer of A due to bulk flow:-

$$N_{A} = -D_{AB} \cdot \frac{\partial C_{A}}{\partial z} + (N_{A} + N_{B}) \frac{\dot{P}_{A}}{P} \qquad (3)$$

where P is the total pressure.

Substituting $C_A = pA/R^T$ and integrating, results in the following equation, according to Sherwood and Pigford.⁽⁵⁾

$$\frac{D_{AB}P}{R'T_z} ln \frac{1 - (1 + N_B/N_A)P_{Az}/P}{1 - (1 + N_B/N_A)P_{Az}/P} = N_A + N_B - (4)$$

For parallel diffusion, N_A and N_B will have the same signs; for counter diffusion, as in this work; N_A and N_B will have opposite signs. Equation (4) has various applications, but its use depends on knowledge of the relation between N_A and N_B . Hoogschagen ⁽⁶⁾ has shown that for both Knudsen and bulk steady state counter diffusion in a constant total pressure system.

$$N_A \sqrt{M_A} + N_B \sqrt{M_B} = 0$$
 (5)

where M_A - molecular weight of species A.

 M_B - molecular weight of species B. or in general for any number of gases

$$\sum N_i \sqrt{M_i} = 0$$
 (6)

If it is assumed that this relation is true, it is possible to reduce equation (4) to:

$$N_{A} = D_{AB} \frac{P}{R'T} \frac{1}{Z} \frac{\sqrt{M_{B}}}{\sqrt{M_{B}} - M_{A}} ln \frac{(\frac{P_{A}\sqrt{M_{A}} + \frac{P_{B}\sqrt{M_{B}}}{\sqrt{M_{A}} + \frac{P_{B}\sqrt{M_{B}}}{\sqrt{M_{B}}})}{(\frac{P_{A}\sqrt{M_{A}} + \frac{P_{B}\sqrt{M_{B}}}{\sqrt{M_{B}}})_{2}}$$
(7)

where the subscripts 1, 2, refer to the ends of the diffusing path.

2. Use of **P**orous Solids to Measure the Binary Diffusion. Coefficient of Gases

Few experimental data for the variation of the bulk diffusion coefficient with temperature are available. With a suitable apparatus, it should be possible to investigate the variation of the bulk diffusion coefficient with the absolute temperature.

Using a suitable porous solid, a chosen gas pair, and a range oftconditions so that bulk diffusion alone occurs within the pores, it should be possible to investigate the rate of gas diffusion at temperatures above room temperature. Calibration runs would be necessary at room temperature to obtain a calibration factor for a given solid sample which would relate the volume of gas diffused to the known bulk diffusion coefficient at room temperature of the gas pair used.

Accurate determinations of the binary diffusion coefficients are valuable as they can lead to an evaluation of the empirical, semi-theoretical, and theoretical equations that have been proposed to predict this coefficient.

3. Temperature Dependence of the Binary Diffusion Coefficient

A number of theoretical expressions have been published in the literature for the variation of the binary diffusion coefficient with the absolute temperature. The following semiempirical equation was first derived by Maxwell.⁽⁷⁾

$$D_{AB} = \frac{a T^{3/2} \sqrt{1/M_A + 1/M_B}}{T^2_{AB} \cdot P}$$
(1)

where
$$T =$$
 absolute temperature, K
 $T_{AB} =$ collision diameter
 $C =$ numerical constant
This was later modified by Gilliland ⁽⁸⁾ to the

form:-

$$D_{AB} = \frac{a T^{3/2} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{(V_A^{1/3} + V_B^{1/3})^2} P$$
(2)

where V_A , V_B - molar volume at normal boiling point (cc per gram-mole.) of A, B.

Sutherland ⁽⁹⁾ put forward an expression to take the effect of temperature more exactly into account.

$$D_{AB} = \frac{a T^{3/2} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{r_{AB}^2 P (1 + c/T)}$$
(3)

where C is an additional numerical constant. A recent expression, by Andrussow (10) is as follows:

$$D_{AB} = \frac{\alpha T^{x} (1 + \sqrt{M_{A} + M_{B}})}{P_{.} (V_{A}^{v_{3}} + V_{B}^{v_{3}})^{2} \sqrt{M_{A}.M_{B}}}$$
(4)

x is the index to which the temperature is to be raised to correspond to the data.

The most fundamental equation yet developed is that (11) This equation uses the Lennard-Jones 6-12 potential as the model for the interaction of unlike molecules in spherical non-polar gas pairs. In the first approximation, the result is:

$$D_{AB} = \frac{a T^{3/2} \sqrt{1/M_{A} + 1/M_{B}}}{P T^{2}_{AB} \Gamma V_{AB} \Gamma (T^{*}_{AB})}$$
(5)

where $\left[W_{AB} \stackrel{(U_1)}{\longrightarrow} (T_{AB}^{*}) \right]$ is the collision integral based on the Lennard-Jones 6-12 potential, and is a function of the group

> where k = Boltzmann's Constant C_{AG} = maximum energy of attraction between A, B T_{AB} = Collision diameter for the unlike molecules, A and B.

No accurate values have yet been determined for the maximum energy of attraction or the collision diameters in the case of diffusion.

In order to calculate them, a simplifying assumption is made. It is assumed that the simple combining laws (from kinetic theory) apply to the parameters for the single components:

$$\tau_{AB} = \frac{\tau_{A} + \tau_{B}}{2}$$

$$\varepsilon_{AB} = \sqrt{\varepsilon_{A} \cdot \varepsilon_{B}}$$

Mirschfelder recommends that the required parameters for the single components be obtained from quantum mechanics, viscosity data, or from classical kinetic theory - in the order given.

For the hydrogen-nitrogen gas pair, parameters calculated from viscosity data were employed as no quantum mechanical parameters are available as yet.

In these simplifying assumptions and the use of parameters from viscosity data lies the main disadvantage of the Hirschfelder equation. For example, an error in the ^rAB term is squared when introduced into the Hirschfelder equation and so brings about a larger error.

Values of D_{AB} for the hydrogen-nitrogen system at a total pressure of 1 atmosphere calculated by means of this equation at 25°K intervals from 273-573°K are presented in the appendix, TableVIII. A sample calculation is also presented in the Appendix, page 777. The literature survey following this section presents experimental tests of the validity of this equation in predicting binary diffusion coefficients at one atmosphere pressure and different temperatures. For gas pairs of non-polar spherical molecules, the Hirschfelder equation gives results within 1 - 2% of the experimental results.

Agreement between experiment and the values calculated from the Hirschfelder equation by the method described when applied to the present study would therefore indicate that both the equation and the experimental results obtained were sacceptabley.

LITERATURE SURVEY

A. The Binary Diffusion Coefficient of Gases

Experimental values for the binary diffusion co-efficient of two gases were reported as early as 1907 by both Jackmann⁽¹²⁾ and Loschmidt.⁽¹³⁾ These investigators published values of the diffusion coefficient for pairs of gases which were later reproduced in International Critical Tables and Landolt-Bornstein Tables. Their apparatus consisted of the now-classical Loschmidt apparatus, in which two chambers, each containing a different gas are separated by a slide. The diffusion is allowed to take place when the slide is held open for a given period of time. Their apparatus, by far the most commonly used for this type of work, operates on the unsteadystate principle for which the differential equation for diffusion has been solved. The coefficients published were for the most part at atmospheric pressure and for temperatures close to room temperature. Their value for the gas pair hydrogen-nitrogen was:

 $D_0 = 0.697 \text{ cm}^2/\text{sec}, 1 \text{ atm}, 0^{\circ}\text{C}.$

Later investigators were Waldmann⁽¹⁴⁾ who gave a value for the same gas pair,

$$D_0 = 0.76 \text{ cm}^2/\text{sec}, 1 \text{ atm}, 20^{\circ}\text{C}.$$

and Boardman and Wild⁽¹⁵⁾

 $D_0 = 0.743 \text{ cm}^2/\text{sec}, 1 \text{ atm}, 14^{\circ}C.$

With the type of apparatus used, the investigation of the diffusion coefficient at temperatures slightly above and below room temperature is possible, but the apparatus is not suitable for measurements over wide ranges of temperature.

Diffusion coefficients of vapours are most conveniently determined by the method developed by Winkelmann.⁽¹⁶⁾ Liquid is allowed to evaporate in a vertical glass tube over the top of which a stream of vapour-free gas is passed sufficiently rapidly so that the vapour pressure in the flowing stream is maintained almost at zero. If the apparatus is maintained at a constant temperature, mass transfer will take place from the liquid surface by diffusion alone. The diffusion coefficient can be calculated from the rate of fall of the liquid surface and the concentration gradient. This method is confined to vapours, and does not readily lend itself to diffusion coefficient measurements over a wide temperature range.

B. Diffusion in Porous Solids

Wicke and Kallenbach⁽¹⁷⁾ were among the early investigators on this subject. They counter-diffused nitrogen and carbon dioxide through porous glass and carbon pellets that were cemented in glass tubes. Their results showed that Knudsen diffusion took place in the carbon pellets and bulk diffusion in the **fritted_glass**.

Thiele⁽¹⁸⁾ developed mathematical relationships expressing the rates of diffusion in pores and showing their effect on catalytic reaction rates.

Hoogschagen⁽⁶⁾ mounted catalyst pellets in rubber tubing and let oxygen from air diffuse through them into a closed circulating system from which oxygen was continuously being removed. He proposed the following relationship for the counter-diffusion of gases with equal pressures on both sides of the pellet:

$$N_{A} \sqrt{M_{A}} + N_{B} \sqrt{M_{B}} = 0 - (1)$$

Experimental evidence presented for three gas systems, heliumoxygen, nitrogen-oxygen and carbon-dioxide-oxygen showed that Equation (1) held for the experimental conditions used (1 atm and 20°C). The results also showed that it was difficult to differentiate between Knudsen and bulk diffusion in porous solids for constant total pressure systems; the transfer equation obtained being the same in both cases.

Wheeler⁽²⁾ in his monograph entitled "Reaction Rates and Selectivity in Catalyst Pores", reviewed some of the past work on gas diffusion in porous particles and included some of his own work on Knudsen diffusion in catalyst pellets. He presented a simplified but useful working model of the average porous solid and the mechanism by which a gas reaction can take place inside it. It was demonstrated that qualitative deductions from the theory presented were fully confirmed by the few reliable data available.

Weisz⁽¹⁹⁾ has recently developed a method utilizing a flow-system for effective diffusion measurements on porous solids. He has applied it to silica-alumina catalyst pellets

using the hydrogen-nitrogen gas system. He chose this system as it was the most sensitive for analytical purposes by means of a thermal conductivity cell. The results obtained have been used to develop a general diffusional criterion for catalyst particles. This criterion makes it possible to determine whether a given experimental or practical system will be free of appreciable diffusional effects, independent of the reaction kinetics.

Petersen⁽¹⁾ has developed a mathematical theory of pore constrictions to account for high experimental values of the diffusion ratio obtained in tableted or extruded porous media. Diffusion in a pore of varying cross-section is compared with that occurring in an (equivalent' cylindrical pore. The derivation shows that periodic constrictions in the pore channel may account for the fact that rate of diffusive transport in the 'equivalent' cylindrical pore can be as much as three times greater than that in the constricted pore. This may therefore provide the basis for a reasonable explanation of the high diffusion ratios obtained in practice, but no satisfactory experimental technique has yet been derived to test the above theory.

In the present work, a method similar to that of Weisz⁽¹⁹⁾ has been used to measure the effective diffusion coefficients for various types of porous media. A modified arrangement of the same method was used to measure the temperature dependence of the diffusion coefficient for the hydrogen-nitrogen system in the range 293-573°K.

C. The Electrical Resistivity Ratio

Values of the electrical resistivity ratio, or formation factor as it is sometimes called, have been measured for various non-conducting porous solids over a wide range of porosities.

Different workers have tried to relate this ratio to other properties of the solid, most commonly, the porosity. One of the early workers in this field was the eminent physicist (20) Clerk Maxwell. He derived an expression for the electrical resistivity ratio based on a cubic assemblage of spheres.

$$R/R_0 = (3 - \theta)/2\theta - - - (1)$$

Some experimental data were presented to support the above relationship but in general, values predicted from it are lower than those obtained experimentally.⁽²¹⁾

A theoretical expression by Slawinski⁽²²⁾ for an aggregate of spheres is,

$$R/R_0 = (1.3219 - 0.32190)^2 /0 - (2)$$

More experimental evidence was put forward than previously, and the Slawinski formula tested on other work⁽²¹⁾ shows that the ratios predicted are too low at porosities less than 20%.

Archie⁽²³⁾ on the basis of measuring the electrical resistivity ratios of oil-bearing sands, put forward the empirical formula,

 $R/R_{o} = \theta^{-1.3}$ - - - (3)

for unconsolidated porous media. This was the equation of the best straight line through his experimental points. Later work (20) found the Archie relationship fitted the experimental data well for $\theta = 10 - 25 \%$.

Wyllie and Gregory⁽²¹⁾ reviewed all of this past work and decided that scant attention had been paid to the systematic experimental determination of electrical resistivity ratios for unconsolidated porous media. They embarked on an experimental determination of these ratios for aggregates of spheres, cubes, cylinders, discs and triangular prisms in the porosity range 12 - 56 %. Their results showed that for unconsolidated spheres and sands, the theoretical expressions are obeyed in certain porosity ranges. For artificially-consolidated packings the relationship,

 $R/R_{0} = C \theta^{-K} - - - (4)$

where C, K are constants is obeyed. The constants C, K depend on the type of cementation present.

Cornell and Katz⁽²⁴⁾ have determined electrical resistivity ratios for sandstones, limestones and dolomites in their work on the turbulent flow of gases through porous media. The length of the flow path through the medium was evaluated by means of the ratio in order to predict the nature of turbulent flow through the pores. The results obtained for the porous rocks showed fair scatter when plotted against the permeability and the porosity.

Finally, McMullin and Muccini⁽²⁵⁾ determined the electrical resistivity ratios for a number of varieties of porous solids, both conducting and non-conducting, in order to establish a correlation between the hydraulic radius, the viscous-flow permeability and the electrical resistivity ratio. Their results are presented in the form of a plot of the McMullin equation.

where m - hydraulic radius

p' - viscous-flow permeability

k' - constant

for which their data falls on a reasonably good straight line when plotted logarithmically.

D. The Analogy between Diffusion and Electrical Conductivity in Porous Solids

For a porous non-conducting solid, the value of the diffusion ratio might be expected to be the same as the value of the electrical resistivity ratio.

This is stated by Carman⁽³⁾ and Klinkenberg⁽²⁶⁾ for gas diffusion in porous solids. Schofield and Dakskinamurti⁽²⁷⁾ have verified this statement for liquid diffusion in porous sands.

Klinkenberg⁽²⁶⁾ presents only one experimental determination, the main portion of his work being devoted to the comparison of diffusion ratios and electrical resistivity ratios published by other investigators for similar porous media. For unconsolidated media, the ratio of either the electrical resistivity ratio or the diffusion ratio to the porosity was found to range from 1.40 to 2.60. From the above comparison and a consideration of the differential equations governing both diffusion and electrical conductivity, he concluded that the above analogy should hold true.

Among the references cited by Klinkenberg⁽²⁷⁾ are early workers such as Buckingham⁽²⁸⁾ who investigated the diffusion of carbon dioxide through clays and later workers such as Penman⁽²⁹⁾ and Van Bavel.⁽³⁰⁾ From the results obtained for the diffusion of carbon dioxide, through soil, Penman⁽²⁹⁾ put forward the relationship

$$\frac{1}{Do / De} = 0.6 \Theta - - - (1)$$

Later, Van Bavel⁽³⁰⁾ modified this relation to,

$$\frac{1}{Do / De}$$
 = 0.66 θ = - - (2)

for loose, unconsolidated beds. As the average deviation of the experimental data used is of the order of 5 %, there is not much to choose between either of these two relations. In the plots presented later, the first relation is shown.

E. The Temperature Dependence of the Binary Diffusion Coefficient

In the first approximation to the diffusion coefficient it is only the forces between unlike molecules which occur. This means that the coefficient of diffusion as a function of temperature affords the best method for obtaining the force constants characteristic of the interaction between unlike molecules. At the present time, unfortunately, such experimental data are not available.

Hence we can see the importance and need for the experimental determination of the temperature dependence of the binary diffusion coefficient.

Recent work not mentioned in the above publication has been done by Schafer et al.⁽³¹⁾ They first investigated the temperature dependence of the diffusion coefficients for three gas pairs; hydrogen-nitrogen, carbon dioxide-nitrogen and hydrogencarbon dioxide, at 1 atmosphere and from $197-330^{\circ}$ K, using a modified Loschmidt type apparatus. Their experimental results showed that the diffusion coefficient, for the hydrogen-nitrogen system, was directly proportional to the absolute temperature raised to the 1.81 power. The results were then compared with values of the diffusion coefficient for the same gas pair as predicted from the semi-theoretical equation of Andrussow.⁽¹⁰⁾ The agreement reached was good (within 3%), despite the fact that the Andrussow equation has no term to take into account any concentration dependence of the diffusion coefficient.

In a succeeding paper (3^2) , by the same authors; diffusion coefficients were measured from 200 - 400°K, and at 1 atmosphere, for the gas systems hydrogen-nitrogen, argon-helium and argonnitrogen. The temperature exponent for the hydrogen-nitrogen system appears to be 1.61 for the results presented in this latter paper. The authors offer no explanation for the different value.

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In their latest published paper, Schafer et al,⁽³³⁾ have extended their work to investigating systems of rare gas pains. The diffusion coefficient of neon-argon was measured between 90° K and 473° K, and that of argon-krypton between 200° K and 473° K at 1 atmosphere. For the first system, the temperature dependence of the diffusion coefficient was found to be to the 1.79 power, whilst for the second system, it was found to be to the to the 1.74 power. From this work they concluded that the 'rigid sphere' collision diameters, (simple kinetic theory) derived from diffusion measurements not only are smaller than those derived from viscosity data but they also show a much smaller temperature dependence.

In the work described in the following paragraphs, measurements of the binary diffusion coefficient have been made for various gas pairs. In all cases, these measurements were compared to values of the diffusion coefficient predicted from the theoretical equation of Hirschfelder et al (11) taken to the first approximation. The most common application of this equation attempts to predict the binary diffusion coefficients of gas pairs from parameters obtained from viscosity measurements of the pure components and simple combining rules. The potential function usually used in this equation to evaluate the collision integral is the Lennard-Jones (6/12) potential, although other functionse.g. the Stockmayer potential, are suggested for polar or long molecules.

Amdur and Schatzki⁽³⁴⁾ have measured the diffusion coefficients for the system xenon-xenon and argon-xenon over a temperature range from 195 - 378°K with a claimed experimental accuracy of 1 %. Their lack of agreementwwith predictions of the diffusion coefficient from the Hirschfelder equation is of the order of 0.5%. This discrepancy is ascribed, by the authors, to the inadequacy of the Lennard-Jones 6/12 potential in the evaluation of the collision integrals.

Kilbanova et al⁽³⁵⁾ measured the temperature dependence of the diffusion coefficient for the gas pairs carbon dioxide-air and water vapour-air from 293° K - 1500° K by means of a modified Loschmidt technique. The accuracy attainable in their work has been stated to be quite poor, however.⁽³⁶⁾ Wilke and Lee⁽³⁶⁾ who reviewed their work state that if the authors' value for the diffusion coefficient at 293° K is assumed to be correct, then close agreement, 2%, is reached with predictions from the Hirschfelder equation. This agreement is also stated to be within the limits of experimental precision.

The systems helium-argon, hydrogen-argon, hydrogen-n butane and hydrogen-sulphur hexafluoride were investigated by Streklow⁽³⁸⁾ over the temperature range $245 - 420^{\circ}$ K using a modified Loschmidt type cell to determine the diffusion coefficients. The results, for the first three systems named, showed only fair agreement when compared with predictions from the Hirschfelder equation. (5 - 10%). The results for the diffusion coefficients of the hydrogen-sulphur hexafluoride system were the only ones that agreed closely with the above predictions. In this case, the agreement was within 1%. The

disagreement with theory was stated by the author to be due to the inability of the theoretical potential to predict actual behaviour.

The latest work on this subject has been done by Walker and Westenberg.⁽³⁶⁾ In a new method called the "point source" technique, they injected a trace gas from a fine, hypodermic tube, (essentially a "Point source") into a slow, laminar stream of a second (carrier) gas. Measurements of the trace gas concentration downstream of the source by means of precise gas sampling permitted the binary diffusion coefficient to be determined. By heating the carrier gas, the measurements were extended to high temperatures (1150° K). Results, with a claimed precision of $\pm 1\%$, over the temperature range 300 - 1150° K, and at 1 atmosphere, were presented for the systems helium-nitrogen and carbon dioxide-nitrogen.

The experimental data were discussed in terms of intermolecular potential energies and for the gas pair heliumnitrogen a purely repulsive potential was found to be satisfactory. The data were also fitted with a Lennard-Jones 6-12 potential with equally good results.

In summary, it may be concluded that data on the temperature dependence of the binary diffusion coefficient is not plentiful, and much of it is lacking in accuracy or prefision, or both. The best data for non polar sample molecules appears to agree to within 2 - 3% with that predicted by the Hirschfelder equation as usually applied. Further, the temperature dependence predicted by this same equation for pairs of simple molecules is verified with an accuracy of about 5% by the available data.

SECTION A. DIFFUSION IN POROUS SOLIDS

APPARATUS

A. Diffusion Apparatus

The apparatus is shown in Figure (1). It consisted of two gas trains, one for hydrogen and the other for nitrogen which then contacted opposite faces of the cylindrical solid sample. The hydrogen used was standard commercial grade (99.8% purity), and the nitrogen was premium quality (99.9% purity).

Let us consider the hydrogen gas train in detail. The gas from the storage cylinder was passed through a pressure regulator and a Deomo tube which employed a catalyst to remove any oxygen present. After this purification, the gas was passed through a capillary tube (2" long section of thermometer tubing) to provide a back pressure of approximately 10 inches of mercury to smooth out the flow. In comparison, the pressure drop through the rest of the system, after the capillary tube, was of the order of 1 inch of water.

The hydrogen, after being dried by silica gel in a 10 inch long, 1 inch diameter tube was metered in glass tube flowmeters of the rotameter type. These flowmeters were Matheson Corporation Universal flowmeters, nos. 202, 203 and 204. By selecting a suitable flowmeter size and float material a hydrogen flow ranging from 100 - 5000 ccs/min. or a nitrogen flow ranging from 40 - 2000 ccs/min. at room temperature and atmospheric pressure could be measured. From the flowmeters, the gas passed into the diffusion cell where it contacted one face of the cylindrical sample after which it passed to atmosphere, or to a thermal conductivity cell, through an outlet stop-cpck.

The nitrogen stream followed the same sequence as the hydrogen, except that no oxygen removal step was included.

Identical pressures on each side of the sample were maintained by adjusting the hydrogen outlet stop-cock to show a zero pressure on the differential draught gauge. An Ellison draught gauge was employed with a range of 0 - 1 inch of water over a scale length of 12 inches. Differential pressure readings could be made with an accuracy of ± 0.005 inch water pressure.

The use of hydrogen as one of the gases led to a very sensitive detection system when using a thermal conductivity cell as a detector. This cell was placed downstream from the diffusion cell and could be used to analyse for hydrogen in the nitrogen stream or vice-versa. The thermal conductivity cell used was a Gow-Mac, Model NIS recorder type, four filament unit which was operated with a filament current of 120 m A. The filaments were situated in deep diffusion passages which gave negligible sensitivity to flow rate changes provided the flow rate did not fall below 100 ccs/min.

The wiring diagram for the thermal conductivity cell is shown in Figure 2. A Varian Associates G-10 recorder and a Leeds and Northrup portable precision potentionmeter were used to measure the output millivolt signal of the thermal conductivity cell bridge.



30.a.

30.b.



TO POTENTIOMETER

Figure 2. Thermal Conductivity Coll - Wiring Diagram

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B. Description of Samples

The samples used in this study were obtained in the form of rods of approximately 1" diameter or plates 1" thick and formed into cylinders which were then cut to the required length on a diamond saw.

The Selas Ol, Ol5, O3-1, O3-2 samples were supplied by the Selas Corporation. They were microporous synthetic ceramic rods obtained in 1 inch diameter, 6 inch lengths. The Limestone 36 and 63 samples were obtained from oil well cores. They were a naturally occurring Alberta limestone and were donated by the Imperial Oil Research Department, Calgary. The Sandstone, S1 sample was obtained from the same source and was a naturally occurring sandstone from the Pembina Oil field in Alberta.

The Alundum samples came in the form of a standard plate 12" x 12" x 1" supplied by A.P. Green Fire Brick Co. Ltd., the Canadian representative of the Norton Co. which manufactured the Alundum. It was an extra fine, hard synthetic ceramic solid manufactured for aeration purposes.

The Filtros sample also came in plate form 12" x 12" x l_2^{-1} " supplied by Filtros Inc. The grade was extra dense and it consisted essentially of silica (quartz sand bonded by vitreous silica).

The Carbon sample was supplied by the National Carbon Co. and arrived in the form of a 2 inch diameter rod, 24 inches long. The sample was a porous graphite, Manufacturer's grade 60 C.

C. Diffusion Cell

The diffusion cell is shown in Figures (3) and (10). It consisted of two identical one inch diameter, bell-shaped halves having inlet and outlet tubes, 8 mm in diameter, entering by means of ring seals. The inlet tube entered at right angles to the body of the cell and then was bent 90° down the center line of the cell to within 1/4 inch of the solid sample face, terminating in a slight bell. The outlet tube takes the outlet gas directly from the upper portion of the cell.

Two methods of sample mounting were employed. In the first instance, a Gooch rubber sleeve was drawn over the sample and the ends of the cell halves. In this manner the diffusion rate determinations at room temperature were carried out. For rate measurements at higher temperatures an Araldite AN 130 resin sleeve bonded the sample to the glass ends of the diffusion cell. This resin withstood temperatures up to 300°C.

D. Electrical Resistivity Ratio Apparatus

The electrolyte used for conductivity measurements in this work was 0.10017 N KCl solution. Electrical conductivities for KCl solutions have been very accurately measured. The A/C bridge used was an Industrial Instruments type RC Conductivity Bridge reading directly in ohms. All measurements of resistance were made at 1000 cycles/second. The specific resistivity of the electrolyte used was measured with a dip-cell having a cell constant equal to 1.0.

Figure (4) shows the apparatus for evacuating and saturating the sample with the O.IN KCl electrolyte. The sample was held between the two bell-shaped glass halves by means of a Gooch rubber sleeve. The upper half of the bell-shaped ends was connected to a vacuum system whilst the lower half was connected by a tube with a stop-cock to the electrolytic solution.

The resistance of the sample was measured by means of the apparatus illustrated in Figure (5).

The saturated sample was held between two assemblages each consisting of a platinum disc backed by a saturated cotton wool compress, a copper electrode and a lucite plate. A compressive force of approximately 10 pounds was applied to the whole and the resistance of the sample was measured on the AC bridge.

A similar apparatus to that used by McMullin and Muccini⁽²⁵⁾ was constructed originally. Their method was based on the principle of using a single piece of apparatus to both evacuate and measure the resistance of a sample. This method was found unsatisfactory due to poor vacuum sealing properties and poor electrical contact.



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Figure 5. Apparatus - Electrical Resistivity Ratio

EXPERIMENTAL PROCEDURES

A. Thermal Conductivity Cell Calibration

An experimental calibration had to be made before the thermal conductivity cell could be used. This was done by making up gas mixtures of known composition and passing them through the cell. The method employed was to pass the two streams at constant known flow rates into a tee branch mixer and thence to the thermal conductivity cell for analysis. The composition of the mixture was calculated from the flowmeter readings. The output millivolts were measured on the potentimeter after a constant reading had been obtained on the millivolt recorder. The filament current was set at 120 milliamps.

In this way a series of points, mole fraction against millivolts was obtained.

To measure the hydrogen flow rate more accurately, a rising soap bubble flowmeter was used. This consisted of a vertical burette tube through which the gas flow was passed. The flow rate was directly obtained by timing the rate of rise of soap films up the burette. The calibration results are shown in the appendix, Figures (13) and (14).

B. <u>Measurement of Effective Diffusion Coefficient of Porous</u> Solids

To start a run, the sample was first mounted in position in the diffusion cell. The gas regulating valves were then set to give steady flowmeter readings at the required flow rates.

The thermal conductivity cell was switched on, previously having been zeroed. The draft gage was then set to zero differential pressure by adjusting the outlet hydrogen stream cock. When conditions were steady, a constant reading was obtained on the recorder chart. The output millivoltage of thermal conductivity cell was then accurately measured on the potentimeter connected in parallel with the recorder.

> The following data was recorded for each run:-Run Number Date of Run Type of sample, length, other characteristics Nitrogen flow rate, flowmeter reading, flowmeter number Hydrogen """"""" Ambient temperature Reading on draft gage. (Usually zero) Output millivolts - Thermal conductivity cell.

From this data it was possible to calculate the effective diffusion coefficient, De, for the sample tested. A sample calculation is given in Appendix p. (71).

Several runs, at different gas flow rates, from 300 -1000 cc/minute for both gases were performed on each sample with the average result being taken for calculation purposes.

C. Measurement of Electrical Resistivity Ratio

This ratio was determined for all the samples whose diffusion ratios were obtained. The technique used was to evacuate the sample which was enclosed in a Gooch rubber sleeve, to a pressure of 1 mm for one or two hours. Electrolyte solution was then admitted to the bottom of the sample and allowed to saturate it. After saturation, the sample was withdrawn from the evacuation apparatus and put between the electrodes as shown in Figure (5). The resistance, R, of the sample was then measured on the A.C. bridge. A dip-cell measured the specific resistivity, r_0 , of solution that was used to saturate the sample. Hence the ratio R/R_0 could be calculated. After the resistance of the sample had been determined, the sample was placed in a beaker of distilled water for 24 hours in order to leach out the solution within it. Determinations were also carried out using different lengths of sample to investigate the magnitude of end effects.

D. Measurement of Porosity

The void volume of the sample was found from the weights of the sample before and after saturation of the solid with distilled water following evacuation. The void volume was taken as equal to the difference in the weighings. Caliper measurements gave the bulk volume of the sample, the porosity was then the ratio of the void volume to the bulk volume.

E. Measurement of Pore Size Distribution by Mercury Penetration

The pore size distribution was determined by mercury penetration for certain of the samples by the method of Ritter and Drake⁽⁴⁾ and were done at the Imperial Oil Research laboratories at Calgary, Alta. Basically the method consisted of placing the sample in a pressure vessel of known volume which is evacuated and then flooded with a non-wetting liquid, mercury. As the pressure is increased, it is possible to record for each pressure increment a corresponding amount of mercury absorbed into the sample. In this way, knowing the pore volume, it is possible to obtain a plot of pressure against pore volume filled at each pressure.

By a pressure balance on an individual pore, the following equation is obtained.

$$P_{c} = \frac{2\sigma \cos \phi}{R_{c}} \qquad (1)$$

where P_c = capillary pressure to inject a nonwetting liquid

- σ = interfacial surface tension
- R_c = capillary radius
- ϕ = angle of contact between the mercury and the solid.

This equation has a direct relationship between pressure and pore radius. Hence pressures can be converted to equivalent pore radii and plotted against the percentage pore volume filled. Such a plot is shown in Figure (6) for the Selas 03-2 sample, which was the one used in the measurement of binary diffusion coefficients at elevated temperatures.

RESULTS

The ten porous solids previously described were characterized by porosity, permeability, electrical resistivity ratio and diffusion ratio measurements where possible. Of the above mentioned tests the first two were done mainly by other workers (39)(40) and the latter two were determined in this work.

In addition, some specific tests were made for average pore diameter (by a bubble point method, and mercury penetration method) and for pore size distribution (by mercury penetration only).

From the permeability, bubble point and mercury penetration tests, other quantities such as the specific surface area and the average pore diameter were calculated. Both the measured and the calculated results are tabulated in Table I.

The mercury penetration method was particularly valuable in giving a clear idea of the size and uniformity of the pores of a porous solid, and the nature of the pore size distribution. A typical pore size distribution plot for the Selas 03-2 sample is shown in Figure (6). This plot shows the uniform structure of this particular solid very clearly.

Figure (9) shows a plot of the diffusion ratio, Do/De, against the electrical resistivity ratio, R/Ro, for seven of the solids tested. The full line denotes equivalence of the ratios. The results for the limestone samples have been omitted from this plot as it was felt that the values for the electrical resistivity ratio were in serious error. No electrical resistivity results were obtained for the carbon sample as the apparatus could not be used to test conducting porous solids.

The reciprocals of these ratios are also plotted individually against the porosity, Θ . Figure (7) shows such a plot of the reciprocal diffusion ratio and the porosity, while Figure (8) shows that of the reciprocal electrical resistivity ratio and the porosity. The theoretical line proposed by Penman⁽²⁹⁾

$$\frac{1}{D_o/D_e}, \frac{1}{R/R_o} = 0.60$$

is shown on these plots as a full line.

Sample calculations are also given in the Appendix to show the method of obtaining porosities, electrical resistivity ratios and diffusion ratios from the experimental data. TABLE I

Samples, Description and Results

Sample	Description	Porosity, O	Permeability cgs units x 10 ⁸ a.	Average Pore Size microns	Specific Surface Area m ² /cm3	Effective Diffusion Coefficient De cm ² /sec	Diffusion Ratio ; Do/De	Electrical Resistivity Ratio, R/R ₀
Selas Ol	Microporous synthetic ceramic	0.590	2.424	4.50 b	0.575 b 1.100 d	0.248	3.08	2.61
Selas 015	Filters	0.659	0.717	2.33 b	1.452 b	0.239	3.19	2.90
Selas 03-1	tt	0; 345	0.124	1.31 b	1.336 b	0.109	7.00	6.15
Limestone 36	Natural limestone	0.251	0.0081	0.466 b	1.313 b	0.0213	35.90	11.50
Limestone 63	(Alberta)	0.204	0.0025	0.239 b	2.820 b	0.0114	66.90	8.15
Sandstone S1	Natural Sand stone ((Pemb Alberta	- ina, 0.123	0.0039	0.398 ъ	0.966 ъ	0.0532	13.35	11.60
Alundum Al	Synthetic ceramic aeration sol (Norton Co) extra fine	id 0.403	15.30	14.50 c	0.02890	0.127	6.02	5.65
Filtros F.l.	" (Filtros Cor extra fine	p)) 0,401	5,53	11.60 c	0,0340 C	0.149	5,12	5,10
Carbon Cl	Porous Graph Grade 60 (National Ca Co.)	ite rbon 0.159	0.0257		0.0588 c	0.0128	59.60	<u></u>
	 a. Results from References (39) and (40) b. By Mercury penetration c. By Kozeny Equation. d. By B-E-T Method 							



40.a.



Figure 7. Porosi

ot of Reciprocal Diffusion Ratio

40.D



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40.c.



40.d.

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DISCUSSION OF RESULTS - SECTION A

The results obtained for the porosity, the electrical resistivity ratio, and the diffusion ratio were found to be consistent and reproducible to within 1-2%. The electrical resistivity ratios and the diffusion ratios were also found to be independent of sample length. The values of these ratios, although not directly comparable to the values of any previous workers, were of the same order of magnitude as those found for somewhat similar solids.

The average pore sizes obtained from the mercury penetration tests were considered more accurate than those calculated from permeability tests even though the Poiseuille equation for viscous gas flow was closely obeyed in all of the solids tested.

The correlation plot, Figure (9), of the electrical resistivity ratio and the diffusion ratio show deviations from exact equivalence of up to 25% for some samples. The limestone samples show very large deviations that are out of the range of this plot. However, in this latter case, this is felt to be experimental error due to the solubility and hence conductivity of these samples.

If the analogy between the diffusion ratio and the electrical resistivity ratio is to be truly useful, it should hold for all inert, non-conducting porous solids and should be independent of the average pore size, the pore size distribution and the pore structure. An explanation for those cases in which

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large deviations occur is hard to offer. Values of the pore size, the (pore size)² and the percentage deviation of the two ratios from equivalence are presented in Table II. These data indicate clearly that the greatest deviations occurred in those samples having the smallest average pore sizes.

With the data at hand, it is not possible to say whether the lack of correlation in these samples is due entirely to some form of experimental error occurring in pore sizes below a certain value or whether it is caused by some unsuspected natural effect.

Further evidence, from the work of Selby,⁽⁴¹⁾ shows that results for the electrical resistivity ratio, obtained on several of the same samples under more careful experimental conditions, have negligible difference from those found in this study. This would suggest that it is unlikely that experimental error is a cause of the deviations observed.

Figures (7) and (8) show the individual reciprocal electrical resistivity and diffusion ratios plotted against the porosity. No definite relationship is observed for the solids used in this study; the results, on the average, falling below the line predicted by Penman⁽²⁹⁾ for unconsolidated solids. Again, the solids having the closest agreement with the Penman line are those with the largest average pore sizes.

It may be possible that as the average pore size decreases, materials of the kind used in our investigations (fine particles fused or cemented together to form the porous solid) change in character from mainly unconsolidated to more

Deviations from the Analogy, and Pore Sizes of the Samples $(Pore Size)^2$ Pore Size, % Deviation Deviation Sample Microns 4.50 0.47 16.5 Selas Ol 20.25 0.29 9.5 Selas 015 2.33 5.42 0.85 1.72 12.9 Selas 03-1 1.31 Selas 03-2 2.30 2.89 1.52 25.2 0.466 0.218 24.40 Limestone 36 Limestone 63 0.057 58.80 0.239 Sandstone 51 0.398 0.158 2.74 21.2 6.3 14.50 0.37 Alumdum Al 210.0 11.60 134.2 0.02 0.4 Filtros Fl

TABLE II

highly consolidated. This may be accompanied by a change in the behavior of the transport properties within the pores of the solid.

EXPERIMENTAL ERRORS

A. Electrical Resistivity Ratio

It is felt that the maximum errors made in determining the porosity and the electrical resistivity ratio are less than \pm 1%. The porosity can be determined accurately by the method used here, and the errors in the electrical resistivity ratio, primarily the value of the conductivity of the electrolyte solution and the value of the sample resistance, are felt to be small. The electrolyte solution was made up by accurately weighing out the required amount of pure KCl (A.C.S. specifications) and dissolving it in a 2 litre volumetric flask. The specific resistivity of this solution was measured independently by a dip-type conductivity cell and was found to check with published values.

Subsequent results for the electrical resistivity ratio, obtained by R. Selby⁽⁴¹⁾ on some of the samples, showed negligible difference when compared with the results presented here.

This later work was performed under more careful experimental conditions, the samples were evacuated to a pressure of 0.1 mm pf mercury as compared to 1 mm of mercury in this work.

B. Measurement of Gas Composition

The calibration plot for the hydrogen and nitrogen gas compositions (expressed as mole fractions) against the thermal

conductivity cell millivolt readings were used in the calculation of the diffusion rates.

The calibration plot for the hydrogen gas composition is estimated to give the composition of the stream with a maximum error of $\pm 2\%$ and an average error of 1% and the calibration plot for the nitrogen gas composition is estimated to give the composition of this stream with a maximum error of $\pm 4\%$ and an average error of 2%.

The main variables were the accurate control and measurement of the quantities of the two gas streams that made up the mixture of known composition for calibration purposes.

The smaller of the two streams forming the mixture could be held accurate to within 2% by manipulation of the cylinder reducing valve. This stream was measured directly by the rising scap-film method.

The larger stream could be kept flowing at a constant and steady rate, the error in this case was the measurement of the flow rate using the Matheson gas rotameters. The ball float in these rotameters could be read with an accuracy of 1%. (i.e., 5ml/min in a total flow of 500 ml/min at room temperature and one atmosphere pressure.)

The electrical measuring circuit and the instruments used with it were felt to have a much smaller error.

The larger errors in the case of the nitrogen analysis were due to the relative insensitivity of the thermal conductivity cell to small amounts of nitrogen in a hydrogen stream as compared to the sensitivity with hydrogen in a mitrogen stream.

C. Measurement of Diffusion Rates

In the actual calculation of the experimental diffusion ratios, a significant source of error was the accurate determination of the flow rates of the two streams of gas, hydrogen and nitrogen, one on either side of the porous sample, in order to calculate the volume of gas diffused. As shown above, the flow-rate measurement error for large flow rates (400-1000 ml/min) was estimated to be of the order of 1%.

The other main error was introduced by the use of the composition calibration chart to determine the mole fraction of one of the gases in the other gas stream. In

the case of hydrogen, the maximum error was of the order of \pm 2% as pointed out previously. In the case of nitrogen the maximum error was larger, \pm 4%.

As the diffusion ratio was always calculated on the basis of hydrogen as the diffusing gas, the magnitude of the maximum error involved was of the order of 3%; the average error ofiinddvidual.determinations of diffusion rate being about 1.5%.

D. Effect of Forced Flow

Clearly it is necessary to keep the differential pressure drop at the zero mark (equal pressure on both sides of the sample) during the course of each experimental run. In the present work, this differential could be maintained at less than 0.005 inch of water pressure. The results given in

TABLE III

Effect of Forced Flow on the Volume of Hydrogen

Passed Through a Sample

Sample: Selas 03-2, 1" 294°K, 1 atmosphere.

Pressure Drop in inches of water	Volume Hydrogen passed, cm ³ /sec.	Deviation (1) % Deviation		
	·.	•		
+ 0.3	0.299	0.044	17.3	
+ 0.2	0.278	0.023	9.0	
+ 0.1	0.266	0.011	4.3	
0.0	0.255			
- 0.1	0.245	0.010	3•9	
- 0.2	0.229	0.026	10.2	
- 0.3	0.220	0.035	13.7	

(N.B. Positiye Sign - Hydrogen Side Pressure.)

(Single Values, not average of several runs)

(1. Additional gas flow, cm³/sec, due to differential pressure drop)

Table III indicate that at this level, the error due to absolute pressure differences should be negligible.

To determine the effect of a differential pressure across the solid sample on the transport through the porous sample, a definite external pressure was applied in turn to both the hydrogen side of the porous sample and to the nitrogen side. These pressures were set by throttling the outlet stopcocks of the stream in question so as to indicate a constant pressure on the differential draught gauge.

The results, shown in Table III, indicate a definite increase or decrease in the volume of gas diffused for as little as a tenth of an inch of waterppressure.

This effect of the pressure is due to the presence of Poiseuille flow in the direction of the applied pressure.

CONCLUSIONS AND RECOMMENDATIONS - SECTION A

The analogy between the electrical resistivity ratio and the diffusion ratio holds for the solids tested in this study to within 20%. The largest deviations are observed in those solids having the smallest mean pore sizes.

It is not possible, at present, to explain why these large deviations exist in the smaller pore sizes.

Further work on solids with both larger and smaller mean pore diameters than those used in this study (0.2 - 11.6 micron diameter) would be worthwhile. In particular, the smaller sizes are of interest in catalytic work.

The hydrogen-nitrogen system appears to be quite satisfactory as a test system for the measurement of the effective diffusion coefficient of porous solids. 50

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SECTION B

THE TEMPERATURE DEPENDENCE OF THE DIFFUSION COEFFICIENT FOR THE HYDROGEN-NITROGEN SYSTEM

APPARATUS

The apparatus is shown schematically in Figure (1). The diffusion ratio apparatus used earlier was modified by placing the diffusion cell and inlet preheater coils inside a constant temperature oven. A new method of sample mounting was also necessary as the Gooch rubber sleeve used previously fails above $100^{\circ}C$.

The oven used was a Fisher Textemp oven with a 1000 watt heater capacity controlled by a Cenco bimetallie thermoregulator. A fan mounted in the upper part of the oven circulated the air within it. This arrangement gave a $\pm 1^{\circ}$ C temperature control up to the highest temperature reached. (300°C). A special door consisting of two sheets of 1/4 inch thick boiler plate bolted together 1 inch apart with insulation between was constructed for the oven. This door was designed so that the diffusion cell was mounted in position on the inside face of the door and all access lines for the inlet and outlet gas streams and the pressure connections were made through the door. This construction allowed the entire assembly to be easily removed from the oven.

The inlet coils were two 50 foot lengths of 1/8 inch copper tubing wound on a frame projecting from the inside face of the door. They were joined to the diffusion cell by means

of machined Teflon sleeves, 1 inch long. A further 50 foot length of 1/4 inch copper tubing was added to the outlet nitrogen stream to cool the gas to room temperature before it entered the thermal conductivity cell.

A 2 inches long by 1 inch diameter nominal size cylinder of the 03-2 Selas sample was selected for the temperature work. It had a narrow range of pore sizes (from 0.5 microns to 2.0 microns diameter) as shown in Figure (6). Other properties of this solid are given in Table I. It also gave conveniently measurable gas concentrations at the maximum temperature. $(300^{\circ}C)$.

Figure (10) shows the method of sample mounting for the temperature dependence work. A layer of Araldite epoxy resin AN 130 was first bonded onto the sample. This layer was then joined to the glass ends of the diffusion cell by a "butt weld" of the same resin. The Araldite sleeve, which was airtight, allowed the work to be cafried out to a maximum temperature of 300°C at which point the resin started to decompose.


Figure 10. - Diffusion Cell

EXPERIMENTAL PROCEDURES

Temperature Dependence of the Binary Diffusion Coefficient

The runs at high temperatures were done in much the same manner as the runs at room temperature. Before the gases were allowed to flow the oven was maintained at a fixed temperature for at least 15 minutes. Due to the large pressure drop caused by the 50 feet of inlet preheater tubing, (approximately 2-4 inches mercury pressure) the flowmeters were calibrated at a pressure of 6 inches of mercury. This pressure was maintained by regulating a fine needle valve situated downstream from the flowmeters.

Some difficulty was experienced in the field of gas temperature measurement. Due to radiation error and the very low gas flow rates, normal methods of gas temperature measurement such an thermocouples, shielded thermocouples, etc., proved ineffective.

In the end, the gas temperature was obtained by measuring the pressure drop across a length of capillary tubing through which the gas flowed. A l inch length of quartz capillary of approximately 1 mm bore was chosen as it had a low coefficient of thermal expansion and thus would be less subject to dimensional changes as temperatures varied. For viscous flow through a capillary, the Hagen-Poiseuille equation applies, and provided the rate of flow is kept constant, the pressure drop is directly proportional to the kinematic viscosity,

 P/ρ of the gas.

The variation of the kinematic viscosity with the temperature for gases is obtained from standard references. Hence it is possible to gauge the temperature of a gas ffom a knowledge of its pressure drop through a capillary. Values of the necessary properties for nitrogen and hydrogen are plotted in Appendix, Figure 16.

This method of temperature measurement was found to be accurate enough for our purposes, that is to $\pm 3^{\circ}$ C. The gas temperature was always found to be within $\pm 3^{\circ}$ C of the oven temperature, as shown in Figure 11. Therefore, it can be concluded that the length of heat transfer tubing used (50' of 1/8" copper tubing) was adequate to heat the gases to oven temperature. The oven temperature itself was known with an accuracy of $\pm 1^{\circ}$ C.

The maximum temperature at which the runs were carried out was 300°C. At this temperature, the Araldite resin, used to cement the sample and the diffusion cell together, showed the first signs of decomposition.

Calibration runs were also carried out at room temperature since the geometric (L/A) factor for the cemented sample might be expected to be different to that of the sample when sheathed in a Gooch rubber sleeve. The Sherwood and-Pigford⁽⁵⁾ equation, already derived (p. 12) can be written:

$$\frac{D_{AG.P}}{R'.T.L} l_{m} \frac{1-c}{1-c} \left(\frac{p_{H_{2}}}{1}\right)_{1} = c \frac{N_{H_{2}}}{A} - - -(1)$$

Assuming the perfect gas laws apply

$$N_{H_2} = \frac{P.V_{H_2}}{R'T}$$
 --- (2)

Equation (1) can now be rewritten:

or

$$D_{AB} = \alpha \cdot \frac{V_{H_2}}{l_m \frac{1-c \left(\frac{p_{H_2}}{r}\right)_i}{1-c \left(\frac{p_{H_2}}{r}\right)_2}} - - - (4)$$

where \propto is a calibration factor incorporating C, L, and A.

The calibration factor, \propto , is experimentally determined for a given porous sample at room temperature. It can then be used to determine, D_{AB}, at a higher temperature, provided L, A remain constant.

An example illustrating this method of calculating the binary diffusion coefficient at higher temperatures is given in the Sample Calculations p.75.

Measurements were also carried out at room temperature to determine the comparative rates of diffusion of hydrogen and nitrogen. A Selas 03-2, 1 inch diameter, 1 inch long sample was used for the test. Both outlet gas streams were analyzed by means of thermal conductivity cells. Two cells were required, one calibrated for hydrogen in nitrogen and the other calibrated for nitrogen in hydrogen.

600 GAS TEMPERATURE CALCULATED, T Η 2 0 -N 2 G 0 200 0 4.00 600 TEMPERATURE, OVEN F

Figure 11. Plot of Oven Temperature and Calculated Gas Temperature 55.a.

RESULTS - SECTION B

A. Measurement of Gas Temperatures

Figure (11) shows the variation of the gas temperature with the oven temperature for both gases. The gas temperatures were measured by means of the capillary thermometer that has previously been described. The plot shows that the difference between the gas temperature and the oven temperature did not exceed 3° C, even at the maximum temperature (300° C). The readings obtained are given in Table IV.

B. Temperature Dependence of the Diffusion Coefficient

Values of the binary diffusion coefficient for the hydrogen-nitrogen system ane plotted logarithmically against the absolute temperature in Figure (12) and shown in Table V. The binary diffusion coefficient at higher temperatures was obtained from the volume of hydrogen that diffused through the sample and a calibration factor that was established at room temperature. A sample calculation showing the procedure is in the Appendix p. 75.

Using the method of least squares, the temperature dependence line. for the diffusion coefficient is found to have a slope of 1.6821, the standard percentage deviation of the points from this line being 1.91 percent.

A summary of all the published diffusion coefficient data for the hydrogen-nitrogen system at 1 atmosphere total

pressure and various temperatures is given in Table VI. These data are plotted in Figure (12); the solid line represents the diffusion coefficient for the hydrogen-nitrogen system calculated by means of the Hirschfelder equation taken to the first approximation, using force constants derived from viscosity data.

A sample calculation illustrating this application of the Hirschfelder equation is given in the Appendix p. 77.

C. Comparison of Diffusion Rates for Hydrogen and Nitrogen

The relationship for equal pressure counter-diffusion of gases across an interface given by Hoogschagen⁽⁶⁾ and mentioned earlier in the theory section was tested. This relationship states that the rates of the counter-diffusion of two gases at constant tetal pressure through a porous solid are inversely proportional to the square roots of their molecular weights.

The Selas 03-2 sample was selected for the test and the results obtained are presented in Table VII. The values of a number of individual runs are given, together with the average value. It can be seen that the observed ratio of the rates of counter-diffusion of hydrogen and nitrogen through the Selas 03-2 sample agrees closely with that predicted by the Hoogschagen relationship.

With the experimental error possible in the determination of the volume of nitrogen diffused (discussed in Section A) it is fair to say that the relationship

$$N_A \sqrt{M_A} + N_B \sqrt{M_B} = 0 - - - - (1)$$

holds well for this gas system, at least at ordinary temperatures and pressures.

In the original work performed by Hoogschagen, discrepancies of similar and greater magnitude were reported in comparing the rates of counter-diffusion of other binary gas systems through porous solids.

TABLE IV

GAS TEMPERATURE MEASUREMENTS

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	HYDROGEN	انو د نگ ^ر زاده بر مورد « بودینی همین <u>ت می بالد</u> باند اور و بر و		NITROGEN	
Oven Temperature ^T oven (° _F)	Calculated Temperature ^T calc (^O F)	Kinematic Viscosity ۲/ Q cm ² /sec	Oven Temperature T _{oven} (°F)	Calculated Temperature Tcalc (^O F)	Kinematic Viscosity P/Q cm ² /sec
70	70	1.065	70	70	0.162
120	£1 7	1.20	160	159	0.195
190	185	1.48	250	245	0.242
256	254	1.76	260	257	0.256
306	304	1.94	342	335	0.310
360	350	2.13	390	391	0.346
392	406	2.32	430	432	0.377
420	422	2.40	470	461	0.397
460	464	2.68	526	527	0.445
490	490	2.82			
510	515	2.96			

TABLE V

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Diffusion Coefficient Results, Hydrogen-Nitrogen, 1 atm, 20-300°C.

Absolute Temperature T (°K)	Diffusion Coefficient, DAB cm ² /sec	Diffusion Coefficient, cm ² /sec. (Hirschfelder Eqn.)	Pe De	rcentage viation %
294	0.763	0.763		
296.5	0.781	0.776	+	0.64
322	0.903	0.891	+	1.26
355	1.051	1.050	+	0.03
373	1.161	1.142	+	1.66
398	1.289	1.273	+	1.28
411	1.370	1.343	t	1.97
422	1.384	1.404		1.43
450	1.541	1.542	_	0.06
455	1.547	1.594	-	2.97
483	1.751	1.763	-	0.66
506	1.883	1.906	_	1.21
508	1.909	1.918	-	0.47
536	2.120	2.097	+	1.10
539	2.171	2.119	+	2.42
573	2.417	2.346	+	3.03
				• •

TABLE VI

Diffusion Coefficient Results of Other

Investigators,

Hydrogen-Nitrogen, 1 atm.

Absolute Temperature	Diffusion Coefficient	Investigator
	<u> </u>	
273	0.697	Jackmann (12)
293	0.760	Waldmann (14)
287	0.743	Boardman and Wild (15)
252	0.620	Schafer, Corte and Moesta (31)
273	0.697	11
290	0.780	11
298	0.815	11
308	0.858	11
195	0.355	Schafer and Moesta (33)
234	0.507	11
282	0.676	H
331	0.871	n
355	1.000	11
398	1.175	11

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TABLE VII

Comparison of Diffusion Rates for Hydrogen and Nitrogen, 1 atm.

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Sample: Selas 03-2, 1 inch

			· · · · · ·		
т (°к)	Volume Hydrogen diffused cm3/sec	Volume Nitrogen diffused cm3/sec	Ratio	Theoretical Ratio	
294	0.258	0.075	3.44	3.742	-
294	0.250	0,062	4.03	3.742	
294	0.255	0.068	3.75	3.742	

Average 3.77

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(N.B. Single Values)



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DISCUSSION OF RESULTS

A. Measurement of Gas Temperatures

The calculated gas temperature, for both of the gases, is plotted against the measured oven temperature in Figure (11). The results can be seen to fall both above and below the 45° line, with an average divergence of $\pm 3^{\circ}$ C. These divergences would appear to be due to experimental error in gauging the pressure drop, and in maintaining a constant flow rate through the capillary.

The oil manometer used for the pressure drop measurements had a reading error of approximately <u>+</u> 1.5%.

A larger error in this method of temperature measurement is due to the difficulty in maintaining a flow rate through the preheater coils at a value which varies by less than 3%. This method will give the absolute temperature with a probable accuracy of $\pm 3\%$.

In view of the results obtained, it was concluded that the gas temperature was within 1 or 2⁰ C of the oven temperature reached. Therefore, the oven temperature was taken to be the temperature at which the diffusion took place.

B. Temperature Dependence of the Bulk Diffusion Coefficient

The true diffusion coefficient was calculated from the runs at high temperature using the calibration factor determined at room temperature as described earlier.

The experimental values of the diffusion coefficient obtained in this way for the hydrogen-nitrogen system over a temperature range from 20° C to 300° C are listed in Table V together with the calculated values from the Hirschfelder equation. A least squares line drawn through these points when plotted logarithmically would have a slope equal to 1.6821. The standard deviation of the points from the line is 0.026 cm²/sec which would represent a percentage standard deviation equal to 1.91 percent.

Very good agreement is found between the experimental values obtained and the values predicted from the Hirschfelder equation. The maximum percentage deviation is approximately 3% which is small in view of the possible estimated error.

Errors involved in the measurement of diffusion rates have already been discussed in detail. In addition there is a possible error in these results due to a small uncertainty in temperature measurement. This is estimated to cause a maximum error of no more than $\pm 2\%$ in the value of Do calculated.

The estimated maximum error at the highest temperature reached would amount to approximately 5% with all these factors being taken into consideration.

The results given by the Hirschfelder equation are tabulated in Table VIII, Appendix, and the experimental data obtained by other workers for this particular system are shown in Table VI. All these values are plotted logarithmically in Figure (12), the full line being the plot of the values from

the Hirschfelder equation. This line has a slope of 1.6815.

It is therefore seen that the data obtained in this work correspond closely to the Hirschfelder equation to the first approximation. Comparison with the data of previous workers is also fairly good. Isolated values which have been obtained experimentally by Jackmann, Waldmann, and Boardman and Wild also agree with predictions from the Hirschfelder equation.

Other temperature work has already been mentioned in the literature survey. In their first paper, Schafer, Corte and Moesta⁽³¹⁾ have investigated the diffusion coefficient at five different temperatures from - 80° to 60°C. Their points show a temperature dependence of 1.81 for the diffusion of a 56% hydrogen-nitrogen mixture. In later work, Schafer and Moesta⁽³²⁾ investigated the temperature dependence for hydrogen-nitfogen mixtures diffusing at different concentrations. These points were averaged for the purpose of comparison in Figure (12) by taking the mean of their diffusions coefficients at 0, 20, 40, 60, 80, and 100% mole fraction of nitrogen and these average values are plotted in Figure (12). Closer examination shows these points to have lower values than those of the previous work. The temperature dependence, in the latter work, shows an exponent of 1.61. Schafer's work therefore has two sets of results which fall on either side of the Hirschfelder line, and of the data obtained in this study.

This is good evidence that the present data are at

least as accurate as those of Schafer and his co-workers. The Hirschfelder equation, with force constants from viscosity data and taken to the first approximation, predicts the diffusion coefficient for non-polar spherical gas pairs up to 300° C with an accuracy of 1-2%, (11). Our data, which shows a temperature dependence slope of 1.6821 compared to the slope of 1.6815 from the Hirschfelder line, may therefore give the diffusion coefficient of the hydrogen-nitrogen system to as great a degree of accuracy as the theoretical equation. This would indicate that the calibration factor obtained at room temperature is sufficiently accurate at least to 300° C.

CONCLUSIONS AND RECOMMENDATIONS

The results from the temperature dependence study of the diffusion coefficient of the hydrogen-nitrogen system appear to be encouraging. It would therefore be interesting to investigate other systems of both polar and non-polar gas pairs to see whether the Hirschfelder equation to the first approximation is obeyed equally well over the same or greater temperature range.

Should a cement with better heat resisting properties than the Araldite AN 130 be found, it could be used to extend the investigation to temperatures higher than those reached in this work ($300^{\circ}C$). Alternatively, it may be possible to enclose the porous solid in glass.

The apparatus and method used appear to be sufficiently reliable to give good results.

The hydrogen-nitrogen system would be entirely suitable for the calibration of a diffusion sample, which could then be used on other gas pairs with undetermined diffusion coefficients.

BIBLIOGRAPHY

1.	Petersen, E.E., A.I.Ch.E. Journal., <u>4</u> , 343, (1958)
2.	Wheeler, A., in "Advances in Catalysis and Related Subjects", Vol. 3, 249-327, Academic Press, New York, 1951.
3•	Carman, P.G., "Flow of Gases through Porous Solids", Academic Press, New York, 1956.
4.	Ritter, H.L., and Drake, I.C., Ind. Eng. Chem., Anal Ed., <u>17</u> , 787, (1945).
5.	Sherwood, T.K., and Pigford, R.L. "Absorption and Extraction", 2nd Ed., McGraw-Hill, New York, 1952.
6.	Hoogschagen, J., Ind. Eng. Chem., <u>47</u> 906 (1955).
7.	Maxwell, J.C., "Scientific Papers", Vol. 2, Cambridge University Press, New York, 1890.
8.	Gilliland, E.R., Ind. Eng. Chem., <u>26</u> , 681 (1934).
9.	Sutherland, A., Phil. Mag., <u>36</u> , 507 (1893).
10.	Andrussow, L., Z. Elektrochem., <u>54</u> , 566 (1950).
11.	Hirschfelder, J.O., Curtiss, C.F., and Bird, B. "Molecular Theory of Gases and Liquids", Wiley, N.Y., 1954.
12.	Jackmann, International Critical Tables, Vol. 5, 1928, p. 62, McGraw-Hill, New York.
13.	Loschmidt, International Critical Tables, Vol. 5, 1928, p. 62, McGraw-Hill, New York.
14.	Waldmann, L., Naturwissenschaften, <u>32</u> , 223 (1944).
15.	Boardman, L.E., and Wild, N.E., Proc. Roy. Sec. (London), <u>A162</u> , 511(1937).
16.	Winkelmann, A., Ann. Physik., <u>22</u> , 1,152, (1994)
17.	Wicke, E., and Kallenbach, R., Kolloid, Z., <u>97</u> , 135 (1941).
18.	Thiele, E.W., Ind. Eng. Chem., <u>31</u> , 916 (1939).

Bibliography (Cont.)

19.	Weisz, P.B., Z. Phys. Chem., 11 Band, Heft 1/2, 1, (1957).
20.	Maxwell, see Fricke, H., and Morse, S., Phy. Rev., <u>25</u> , 361 (1925).
21.	Wyllie, M., and Gregory, A. Trans AIME., <u>198</u> , 103, (1953).
22.	Slawinski, A.J. Chem. Phys., <u>23</u> , 710 (1926).
23.	Archie, G., Trans AIME., <u>146</u> , 54 (1942).
24.	Cornell, D., and Katz, D.L. Ind. Eng. Chem. <u>45</u> , 2145 (1953).
25.	McMullin, R., and Muccini, G. A.I.Ch.E. Journal;, <u>2</u> 393 (1956).
26.	Klinkenberg, L.J., Bull Geol Soc. Amer., <u>62</u> , 559 (1951).
27.	Schofield, R.K., and Dakshinamurti, C., Disc Faraday Soc., <u>3</u> 56 (1948).
28.	Buckingham, E., U.S. Dept. Agri., Bur. Soils, Bull. <u>25</u> , (1904).
29.	Penman, H.L., J. Agric. Sci., <u>30</u> , 437, 570, (1940).
30.	Van Bavel, C.H.M., Soil Sci., <u>73</u> , 91, (1942).
31.	Schafer, K., Corte, H., and Moesta, H.,Z. Elektrochem, 55, 662, (1951).
32.	Schafer, K., and Moesta, H., Z. Electrochem., <u>58</u> 743 (1954).
33.	Schafer, K., and Schumann, K., Z. Elektrochem., <u>61</u> 247 (1957).
34.	Amdur, I., and Schatzki, T.F., J. Chem. Phys., <u>27</u> , 1049, (1957).
35.	Kilbanova, Pomerantsev, and Frank-Kamenetskii, J. Tech. Phys., (U.S.S.R.) <u>12</u> , 14, (1942).
36.	Walker, R.E., and Westenberg, A.A., J. Chem. Phys., 29, 1139, (1958).

- 37. Wilke, C.R., and Lee, C.Y., Ind. Eng. Chem., <u>47</u>, 1253, (1955).
- 38. Strehlow, R.A., J. Chem. Phys., <u>21</u>, 2101 (1953).
- 39. Bertram, D., B.A.Sc. Thesis in Chemical Engineering, University of British Columbia, 1958.
- 40. Novak, G., B.A.Sc. Thesis in Chemical Engineering, University of British Columbia, 1957.
- 41. Selby, R., Private Communication to Dr. D.S. Scott, Department of Chemical Engineering, University of British Columbia, 1958.

APPENDIX

TABLE VIII

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Diffusion Coefficient for the Hydrogen-Nitrogen System, 1 atm, as a Function of Temperature using the Hirschfelder Equation to the First Approximation

T (°C)	<u>T</u> (⁰ K)	<u>(T) 3/2</u>	T 12	₩ (1) ⁽¹⁾	Do, cm 2/sec
0	273	4511	4.96	0.8430	0.6742
25	298	5144	5.42	0.8300	0.7814
50	323	5805	5.87	0.8167	0.8961
75	358	6492	6.32	0.8056	1.0159
100	373	7204	6.78	0.7951	1.1423
125	398	7941	7.23	0.7857	1.2741
150	423	8700	7.69	0.7773	1.4111
175	458	9482	8.14	0.7693	1.5540
200	473	10290	8.60	0.7622	1.7019
225	498	11113	9.05	0.7556	1.8542
250	523	11960	9.51	0.7490	2.0131
275	5 5 8	12827	9.96	0.7424	2.1783
300	573	13716	10.41	0.7372	2.3460

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SAMPLE CALCULATION

1. Porasity

Sample	Selas 03.2	
Length	2.47 cm	
Average Diameter	2.62 cm	
Average Cross Sectional Area	5.39 cm^2	
Bulk Volume	13.31 cm ³	
Weight wet (saturated with distilled water	26.60 g	
Weight dry	22.80 g	
. Difference	3.80 gms	•
Assuming a density of 1 gm/cm	³ for water,	

void volume = 3.80 cm³

Porosity	=	3.80	=	. 2855
		13.31		

SAMPLE CALCULATION

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2. Electrical Resistivity Ratio

Sample	Selas	03.2
Length		2.47 cm
Average Cross Sectional Area		5.39 cm^2
Length/Average Cross Sectional	Area	0.458 cm^{-1}
ro, specific resistivity of saturating solution		82.0 ohm cm
R_0 , = $r_0.L / A$ =		37.56 ohms.
R, resistance of saturated samp	ple	321.0 ohms
Electrical Resistivity Rat	tio = _	<u>321.0</u> = 8.55 37.56

Effective Diffusion Coefficient and Diffusion Ratio

Sample	Selas 03.2
Average Cross Sectional Area, A,	5.39 cm^2
Length, L,	2.47 cm
(L/A)	0.458 cm^{-1}
Temperature	294 ^o K
Differential pressure drop (draug gauge)	ght 0.00 inch water
Nitrogen flow rate, FN2,	9.15 cm ³ /sec
Output mV	29.45 mV
Hydrogen mole fraction in outlet stream, 2	N2 KH2, 00273 mf

Calculation:

By means of a material balance, we can calculate the volume of hydrogen diffused, $V_{\rm H2}$ (This material balance takes the form of a molar or volume balance for a constant pressure system.)



A material balance on the nitrogen stream gives:

To

$$F_{N_2} - V_{N_2} = (F_{N_2 + H_1}) \cdot X_{N_2} - - - (1)$$

$$V_{H_2} = (F_{N_2 + H_2}) \cdot X_{H_2} - - - (2)$$

$$X_{N_2} + X_{H_2} = 1 - - - (3)$$

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- - - (3)

We make use of the theoretical expression of Hoogschagen for diffusion through a porous solid:

$$\frac{N_{N_2}}{N_{H_3}} = \frac{V_{N_2}}{V_{H_2}} = \frac{\sqrt{M_{H_2}}}{\sqrt{M_{N_2}}} = 0.2682$$
In our case,

$$FN_2 = 9.15 \text{ cm}^3/\text{sec}$$

$$XH_2 = 0.0273 \text{ m.f.}$$

$$XN_2 = 0.9729 \text{ m.f.}$$

$$\frac{VN_2}{VH_2} = 0.2682$$

$$VH_2$$
Solving for VH2, we get:
9.15 - VH2 x 0.2682 = VH2 x 0.9727
0.0273

0.255 cm³/sec VH2 =

We can now apply the Sherwood and Pigford equation developed in the Introduction and Theory section, p. 12.

$$\frac{D_e P}{R'TL} ln \frac{1-c \left(\frac{p_{H_2}}{T}\right)_2}{1-c \left(\frac{p_{H_2}}{T}\right)_1} = c \frac{N_{H_2}}{A}$$

assuming the perfect gas laws apply,

$$N H_2 = \frac{P V_{H_2}}{R'T}$$

and

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$$C = 1 - \frac{N_{N_2}}{N_{H_2}} = 1 - \left(\frac{M_{H_2}}{M_{N_2}}\right)^{\frac{1}{2}} = 0.7318$$

we have,

$$D_{e} = c \frac{L}{A} \cdot \frac{V_{H_{2}}}{l_{n} \frac{l - c \left(\frac{p}{l_{2}}\right)_{2}}{l - c \left(\frac{p}{l_{2}}\right)_{1}}}$$

$$\left(\frac{p_{H_{2}}}{l_{1}}\right)_{2} = 0.0273 \text{ atm}$$

$$\left(\frac{p_{H_{2}}}{l_{1}}\right)_{1} = 0.9944 \text{ atm}$$

$$l_{n} \frac{l - 0.7318 \left(0.0273\right)}{l - 0.7318 \left(0.9944\right)} = 1.2807$$

$$D_{E} = \frac{0.7318 \times 0.255 \times 0.458}{1.2807}$$

$$D_{E} = 0.0667 \text{ cm}^{2}/\text{sec}$$

taking Do = $0.763 \text{ cm}^2/\text{sec}$ at 294°K

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$$\frac{Do}{DE}$$
 = $\frac{0.763}{0.0667}$ = 11.44

SAMPLE CALCULATION

Calibration Run at 294°K

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Differential Pressure Drop (draught gauge)	0.00 inch water
Nitrogen flow rate	5.45 cm ³ /sec
Output millivolts	28.35
Hydrogen mole fraction	0.0263 m.f.

 $V_{\rm H2}$ is determined by a material balance similar to that carried out in the previous section.

V_{H2}

0.146 cm³/sec

The Sherwood and Pigford equation can be written if A,L remain constant:

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$$D_{AB} = \alpha \frac{V_{H_2}}{l_n \frac{1-c(\frac{p_{H_2}}{c})_2}{1-c(\frac{p_{H_2}}{c})_1}}$$

where \propto is a calibration factor.

(P _{H2})2	=		0.0263		
(PH2)1	•		0.9950		
and ln	<u>1-0.</u> 1-0.	<u>7318</u> 7318	<u>x (0.0263)</u> x (0.9950)	=	1.283
Do at 29	94 ⁰ K	=			0.763 cm ² /sec
•••	\prec	=	Do VH2/1.283		
	X	=	<u>0.763 x 1.3</u> 0.146	<u>283</u>	
	X	=	6.710		

Diffusion Coefficients at Higher Temperatures:

Sample	03.2
Length	5.19 cm
Room Temperature	294 ⁰ K
Oven Temperature	573 ⁰ к
Differential Pressure Drop (draught gauge)	0.00 inch water
Nitrogen flow rate (at room temp.)	6.50 cm ³ /sec
Output millivolts	39.15 mV
Hydrogen mole fraction in outlet N2 stream (at room temp.)	0.0359 m.f.

The volume of hydrogen diffused is measured at room temperature. This volume, as calculated from the above data, must be corrected to the true conditions of diffusion.

 $V_{\rm H2}$ (294°K) = 0.2396 cm³/sec. Assuming that the perfect gas laws apply,

 $\frac{VatT_{1}}{VatT_{2}} = \frac{T_{1}}{T_{2}}$ or $\frac{V_{H2} (573^{\circ}K)}{V_{H2} (294^{\circ}K)} = \frac{573}{294} = 1.949$ so $V_{H2} (573^{\circ}K) = 0.4670 \text{ cm}^{3}/\text{sec}$ We can now apply the Sherwood and Pigford equation: with $\propto = 6.71$ Do $(573^{\circ}K) = 6.71 \frac{V_{H_{2}} (573^{\circ}K)}{U_{H_{2}} (573^{\circ}K)}$ $\int_{1-c} (\frac{p_{H_{2}}}{1-c} (\frac{p_{H_{2}}}{1-c})_{1}$

(p _H	2)1	= 0.9917		
(p _H	2)2	= 0.0359		
ln	($\frac{1-0.7318}{1-0.7318}$ (0.0359) 1-0.7318 (0.9917))	-	1.267
Do	=	<u>6.71 x 0.467</u> 1.267		
Do	=	2.473 cm ² /sec.		

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(573[°]K**)**

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<u>SAMPLE CALCULATION</u> Diffusion Coefficient, Hirschfelder Equation. Data on force constants from Hirschfelder, Curtiss et al, (11) "Molecular Theory of Gases and Liquids."

The coefficient of diffusion of a binary gas mixture may be obtained from the following equation which is taken to the first approximation:

$$\begin{bmatrix} D_{12} \end{bmatrix}_{1} = 0.0026280 \frac{\sqrt{T^{3}(M_{1} + M_{2})/2M_{1}M_{2}}}{\not P \cdot \sigma_{12}^{2} \cdot W_{12}^{(1,1)}(T_{12}^{*})}$$
(1)

where $[D_{12}]$ = diffusion coefficient in cm²/sec

p = pressure in atmospheres

T = temperature in O_K

 $T_{12}^{*} = kT / \epsilon 12$

 M_1, M_2 = molecular weights of species 1, 2

 $\sigma_{12}, \mathcal{E}_{12}/\mathcal{R}$ = molecular potential energy parameters characteristic of 1-2 interaction in \mathcal{A} and $\mathcal{O}K$ respectively.

To obtain the coefficient of diffusion for the gas pair $H_2 - N_2$ at 273⁰K and 1 atm, we use the above formula.

From Table IA, we find (letting H₂ be component 1) that:

 $\mathcal{E}_{1/R} = 38.0 \,^{\circ} \mathrm{K}$, $\mathcal{E}_{2/R} = 79.8 \,^{\circ} \mathrm{K}$, $\sigma_{1} = 2.915 \,^{\circ} \mathrm{A}$, $\sigma_{2} = 3.749 \,^{\circ} \mathrm{A}$,

These parameters are obtained from viscosity data, From the simple combining rules;

$$\sigma_{12} = \frac{1}{2} (\sigma_1 + \sigma_2)$$

$$\epsilon_{12} = (\epsilon_1 \cdot \epsilon_2)^{V_2}$$

we obtain,

$$\sigma_{12} = 3.332 \text{ Å}$$

 $\sigma_{12} = 55.07 ^{\circ} \text{K}$

For the temperature 273°K,

 $=\frac{kT}{2}$ T12 * = 4.96 C12 The molecular weights are - 2.016 H₂ 14.02 N₂ -

From Table (I M), we obtain

 $W_{12}^{(1,1)}$ (4.96) **=** 0.8436

The first approximation to $\begin{bmatrix} D_{12} \end{bmatrix}$,

computed from Equation (1)

is
$$0.6742 \text{ cm}^2/\text{sec.}$$



8B.a.





81.b.



₿**₿.**с.


