

Diffusion of Ideal Gases in Capillaries and Porous Solids

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The steady state diffusion of gases through capillaries or through the pores of a solid when the total pressure in the system is constant is considered. It is shown that the ratio of the molar diffusion rate of the lighter gas to that of the heavier gas must be equal to the square root of the ratio of the molecular weight of the heavier to the lighter.

From simple momentum transfer considerations a diffusion equation is derived to describe the diffusion rate as the nature of the process changes from ordinary mutual diffusion to Knudsen diffusion. This equation is shown to give good agreement with experimental measurements of diffusion rates in porous solids. A structural parameter of the porous solid, the diffusion ratio, is calculated from the experimental results and compared with the experimental value of the same ratio found from electrical resistance ratios and from flow measurements.

The process of gas diffusion through capillaries, or through the fine channels of porous solids, is of considerable importance in operations concerned with chemical reactions in beds of porous particles, in the drying of solids, etc. In the usual case the porous particle is surrounded by a flowing gas stream on all or much of its surface. If the pressure drop due to flow around a single porous particle is counted as negligible, a constant total pressure must exist on the exposed faces of the particle. Transport of gases into or out of the interior void spaces of the solid will then occur by the process of diffusion.

Some aspects of the particular case of diffusion of a binary gas mixture in small channels when the total pressure is maintained constant will be considered here. These considerations form a necessary preliminary to a more general analysis of gas transport in porous solids.

In the following discussion it is assumed that counter diffusion is occurring along a path of small diameter relative to its length, for example through a capillary or the pores of a solid. At the ends of the diffusion path the gas has a uniform composition, that is it is well mixed, and both ends of the path are at the same constant total pressure.

NATURE OF DIFFUSION IN SMALL CHANNELS

Transport of gas through a small channel may occur in a variety of ways. If the equivalent radius of the channel is large relative to the mean free path of the molecules, then transport may take place because of Poiseuille or forced flow if a total pressure gradient exists, by ordinary diffusion if a partial pressure gradient

exists, or by a two dimensional surface flow if one of the molecular species is adsorbed to a considerable degree.

If the radius of the channel is small relative to the mean free path, transport occurs by Knudsen flow or molecular streaming in the presence of either a total pressure or partial pressure gradient. In the present case the transport mechanism will be assumed to be either Knudsen or ordinary diffusion, depending on the relationship between radius and mean free path. It is apparent that a region will exist in which the diffusive process is intermediate in nature between these two extremes. Qualitatively this region appears to extend from values of about 0.1 to 10 r/λ . For most gases at ordinary temperatures and pressures these values correspond to pore radii from 0.005 to 0.5 μ , a range of pore sizes encountered in a great many commercial solid catalysts. Thus this intermediate or transitional diffusive behavior is of considerable practical interest.

In fine pores, of the order of magnitude given above, Wheeler (1, 2) and others have shown that appreciable total pressure differences are required if Poiseuille flow is to be of the same importance as a transport mechanism as is diffusive flow. Therefore, for the usual case of a porous particle bathed in a fluid, the pore channel would have to be of the order of 10- μ radius or greater before any appreciable fraction of the total gas transport could be attributed to forced flow caused by small differences in total pressure. In the particular case of a porous solid immersed in a steady state flowing gas the total pressure differences would usually be small over the length of one particle.

The situation described above has some important consequences. In the usual physical concept of mutual dif-

fusion, bulk flow of the gases is free to occur, but in the present situation such bulk flow is effectively prohibited by the mechanics of flow in the fine pores. Therefore the individual rates of diffusion of the two molecular species may be different, and the usual concept of equimolar counter diffusion for a constant pressure system will be true here only in special circumstances. In general the Fick's first law form of the diffusion equation often used is not correct with respect to a system of fixed coordinates for ordinary diffusion in a small channel when the total pressure is constant at both ends of the diffusion path. It is necessary to know what the relative rates of transport of each gas will be if appropriate diffusion equations are to be applied. In the following section, a proof will be offered that these relative rates are equal to the square root of the inverse of the molecular weight ratio of the two gases, when the total pressure is taken as constant throughout the diffusing system. This relationship has already been demonstrated experimentally, (3, 4), but a complete explanation has not previously been given.

INDIVIDUAL RATES OF DIFFUSION IN CONSTANT PRESSURE SYSTEMS

Suppose a gas mixture is diffusing through a fine capillary, and the pressure and composition are maintained at constant steady state values at each end of the capillary.

If $r \gg \lambda$, then ordinary diffusion occurs, and from the simple momentum transfer theory of Maxwell

$$-\frac{D_{AB}P}{RT} \frac{dp_A}{dx} = N_A p_B - N_B p_A \quad (1)$$

The above equation which is not confined to the constant total pressure case cannot be used without some knowledge of the value of N_A/N_B . Although constant total pressure is usually taken to imply that equimolar counter diffusion exists, the conditions described earlier allow a constant total pressure to be maintained without the necessity for equimolar counter diffusion also occurring.

If binary diffusion of gases at constant total pressure is considered in

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any individual capillary, then an overall momentum balance written between the two ends of the capillary shows that, in general, a net shearing stress exists at the wall of the channel. This shearing stress is very small and will not exceed a value of more than a few dynes per squared centimeter in ordinary situations. It is apparent that as the capillary radius decreases, such small shearing forces must be of decreasing significance in determining the total transport rate. Therefore in capillaries of sufficiently small diameter the net axial momentum transported to the wall per unit area per unit time can be set equal to zero in a good approximation. Calculations show that this approximation would be valid, for example, for all but the coarsest of porous solids normally encountered in practice.

Therefore if the limitation is imposed that, effectively, the net axial momentum transported to the wall per unit area per unit time is zero, and if diffuse molecular reflection is assumed, then these conditions can be written for an arbitrarily small element of wall surface as

$$m_A u_A n_A \frac{\bar{v}_A}{4} + m_B u_B n_B \frac{\bar{v}_B}{4} = 0 \quad (2)$$

where \bar{v}_A and \bar{v}_B are the average velocities of gases A and B. Inasmuch as

$$\frac{\bar{v}_A}{\bar{v}_B} = \left(\frac{M_B}{M_A} \right)^{1/2} \quad (3)$$

it follows from Equations (2) and (3) that

$$\frac{G_A}{G_B} = \frac{u_A n_A}{u_B n_B} = - \left(\frac{M_B}{M_A} \right)^{1/2} \quad (4)$$

where G_A and G_B refer to the rate of diffusive transport of those molecules striking the wall. This equation has also been given by Hoogschagen (3).

Of these molecules which strike the wall some have obviously made their last intermolecular collisions very close to the wall, while others will have come from a greater distance. However the probability of any significant number of these molecules coming from a distance that is very much greater than the mean free path is negligible. Therefore all the molecules striking the wall can be thought of as coming from a volume element that is thin in comparison with the radius of the capillary.

Not all molecules in such a volume element strike the wall. However it is reasonable to suppose that the molecules which leave the volume element in other directions after collision have the same average diffusive rate as those which strike the wall. Therefore Equation (4) should apply to all the molecules that have already collided in the volume element.

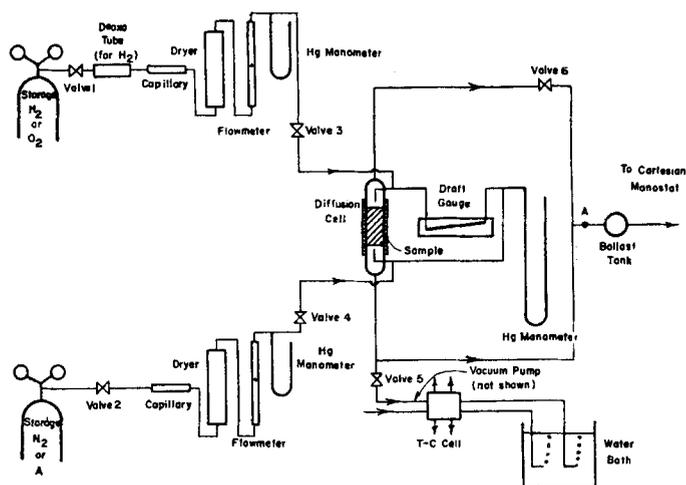


Fig. 1. Apparatus for measuring diffusion rates in porous solids at varying total pressures.

Obviously the above argument can be extended to any surface element, and Equation (4) applied to the entire surface. It can be said then that a layer in the form of a thin film exists adjacent to the wall such that all molecules colliding in this layer travel either back into the interior of the capillary or strike the wall. If a second similar thin layer is considered adjacent and parallel to the wall layer, then it is also required that there be no net shearing stress between these two layers; that is there must be no net momentum transfer through any surface element. If the average differences in the axial diffusive transport velocities of species A and B passing through this element of the surface from the wall side and from the direction of the capillary interior are du_A and du_B , then the above condition is met by writing

$$m_A n_A \bar{v}_A du_A = - m_B n_B \bar{v}_B du_B \quad (5)$$

This equation can be rearranged to give

$$\frac{dG_A}{dG_B} = - \left(\frac{M_B}{M_A} \right)^{1/2} \quad (6)$$

Therefore G_A and G_B must have the same ratio as that in the layer adjacent to the wall. Also it is apparent that Equation (6) will apply to a surface element on the inner side of the thin cylindrical layer. When one extends the above argument, Equation (4) can be generalized for all the gas in the entire cross section of the capillary. It is not required that G_A and G_B have constant values in the direction normal to flow, but only that the ratio of the two transport rates must always be the same.

If the capillary radius is such that $r \ll \lambda$, then Knudsen diffusion will prevail, and it is evident from the well-known Knudsen diffusion equa-

tion that the relative rates of diffusion of two gases are given also by Equation (4).

From these arguments gas-diffusion processes at constant total pressure can be summarized as follows. In large channels equimolar counter diffusion must occur, and as channel radius decreases, the ratio of diffusion rates of the two species changes and finally approaches the ratio $(M_A/M_B)^{1/2}$ well before the point at which the radius is of the order of a mean free path length. With further decrease in channel radius the ratio of diffusion rates remains at this value as the transport process changes in nature from ordinary to Knudsen diffusion.

RATE OF DIFFUSION IN THE TRANSITION ZONE

If the conditions of diffusion are such that $r \approx \lambda$, then the diffusion process will have a mixed character. As yet the only expressions which have been presented for describing the rate of diffusion in this region are either semiempirical in character, such as those of Wheeler (1, 2), or are complex and of limited applicability, such as that of Pollard and Present (5), for self-diffusion.

Apparently, elementary momentum transport theory in gases has not yet been applied to this transition region. In this region the frequency of wall collisions relative to intermolecular collisions must increase. Therefore the total pressure drop for gas A in a binary mixture of A and B can be considered as being due to the sum of two momentum transfer processes, the rate of momentum transfer to the wall, and the rate of transfer of momentum arising from unlike molecular collisions.

Therefore in a section of capillary tube of length L one can write

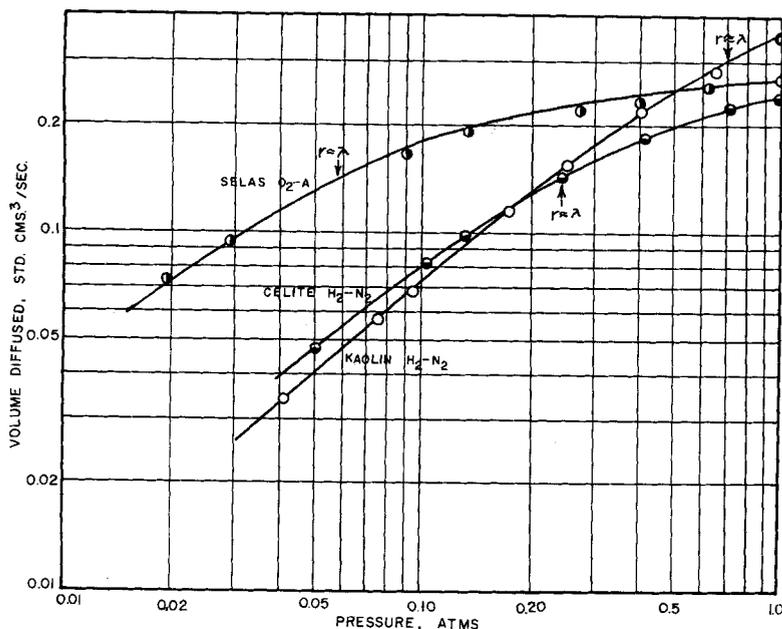


Fig. 2. Diffusion of oxygen or hydrogen through porous solids in the transition region: open circle, half open circle, half open circle dark on right side experimental, curve Equation (9).

$$-dp_A \cdot \pi r^2 = \frac{n_A m_A u_A \bar{v}_A}{4} (2\pi r) dL + n_A n_B (u_A - u_B) \frac{kT}{mD_{AB}} (\pi r^2) dL \quad (7)$$

where the first term on the right-hand side describes the rate of momentum transfer to the wall, and the second term is the Maxwell expression for the rate of momentum transfer between unlike colliding molecules.

The expression defining a Knudsen diffusion coefficient for a circular tube can be introduced into the above equation; that is $D_{KA} = 2/3 r \bar{v}_A$. In addition, since the total pressure is constant, $p_A + p_B/P = 1.0 = y_A + y_B$, where y_A and y_B are the respective mole fractions of A and B.

When one introduces these relationships and simplifies, Equation (6) becomes

$$G_A dL = - \frac{P dy_A}{kT} \left/ \left(\frac{1 - \alpha y_A}{D_{AB}} + \frac{1}{D_{KA}} \right) \right. \quad (8)$$

where $G_A = u_A n_A$, $G_B = u_B n_B$, and $\alpha = 1 + G_B/G_A$.

This equation can be readily integrated for the steady state to give an expression for N_A , the total rate of transport of A, in moles per unit time per unit area:

$$N_A = \frac{P}{RTL} \frac{D_{AB}}{\alpha} \ln \left\{ \frac{(1 - \alpha y_{A_2}) + D_{AB}/D_{KA}}{(1 - \alpha y_{A_1}) + D_{AB}/D_{KA}} \right\} \quad (9)$$

where y_{A_1} and y_{A_2} refer to the two ends of the diffusion path, and α is now $1 + (N_B)/(N_A)$.

The above equation must reduce to the expression for ordinary diffusion in one limit ($r \gg \lambda$) and to the expression for Knudsen diffusion in the other limit ($r \ll \lambda$). For ordinary diffusion at constant pressure in the steady state the integrated Maxwell equation is

$$N_A = \frac{D_{AB} P}{RTL \alpha} \ln \left\{ \frac{1 - \alpha y_{A_2}}{1 - \alpha y_{A_1}} \right\} \quad (10)$$

Similarly, for Knudsen diffusion, Equation (11) applies:

$$N_A = \frac{D_{KA} P}{RTL} (y_{A_1} - y_{A_2}) \quad (11)$$

For ordinary diffusion $D_{KA} \gg D_{AB}$, and the ratio D_{AB}/D_{KA} is very small. It is apparent that Equations (9) and (10) then become identical. On the other hand for Knudsen diffusion $D_{KA} \ll D_{AB}$, and the ratio D_{AB}/D_{KA} becomes a large number. The logarithmic term in (9) therefore approaches a value of unity, and the logarithm can be replaced by the first term of its series expansion. If the ratio $D_{AB}/D_{KA} \gg 1 - \alpha y_A$, as would be expected, then Equations (9) and (11) become identical.

If it is desired to define a single mean or average diffusion coefficient D_N for the transition zone by means of the usual simple diffusion equation, that is

$$N_A = \frac{D_N P}{RTL} (y_{A_1} - y_{A_2}) \quad (12)$$

then Equations (9) and (11) can be equated to give

$$D_N = \frac{D_{AB}}{\alpha (y_{A_1} - y_{A_2})} \ln \left\{ \frac{1 - \alpha y_{A_2} + D_{AB}/D_{KA}}{1 - \alpha y_{A_1} + D_{AB}/D_{KA}} \right\} \quad (13)$$

If the quantity $X_2 = 1 - \alpha y_{A_2} + D_{AB}/D_{KA}$ is introduced, together with a similar definition for X_1 , then (13) can be written as

$$D_N = \frac{D_{AB}}{X_{LM}} \quad (14)$$

where X_{LM} is the logarithmic mean average defined by

$$X_{LM} = \frac{X_2 - X_1}{\ln X_2/X_1} = \frac{\alpha (y_{A_1} - y_{A_2})}{\ln \left\{ \frac{1 - \alpha y_{A_2} + D_{AB}/D_{KA}}{1 - \alpha y_{A_1} + D_{AB}/D_{KA}} \right\}} \quad (15)$$

In employing the quantity $\alpha = 1 + (N_B)/(N_A)$, it should be remembered that N_B/N_A is positive for concurrent diffusion and negative for counter diffusion. The apparent dependence of this mean diffusion coefficient on the composition arises because of the different functional form of the two diffusion equations applying in this case.

In the special case of self-diffusion, or if two counter diffusing gases have equal molecular weights, $\alpha = 0$. Equation (8) then integrates to

$$N_A = \frac{P}{RTL} (y_{A_1} - y_{A_2}) \frac{1}{\left(\frac{1}{D_{AB}} + \frac{1}{D_{KA}} \right)} \quad (16)$$

Equating this with Equation (12) one sees that

$$\frac{1}{D_N} = \frac{1}{D_{KA}} + \frac{1}{D_{AB}} \quad (17)$$

an expression which has been presented for the transition zone by Bosanquet (6). It was shown by Polard and Present (5) that Equation (17) gives almost the same values as their more complex expression for self-diffusion in the transition zone.

APPLICATION TO DIFFUSION IN POROUS SOLIDS

In applying Equation (9) to a porous solid the transfer rate is conveniently based on unit geometric cross-sectional area of the solid, and the diffusion path length is taken to be the actual length of the solid. The diffusion coefficients then become effective values, which differ from the true values by a geometric factor which describes the increased path length due to tortuosity of the pores, and the reduction in cross-sectional area because of the limited porosity of the solid.

It might be expected that Equation (9) would not apply precisely to a porous solid because the pores are never of a completely uniform size, nor are they, in general, circular in shape. These factors would influence

TABLE 1

Sample	Test gas,		Porosity, %	Effective diff. coeffs.,*		True $D_{AB}P$	Diff. ratio	Elec. res. ratio	Equivalent pore radius microns		Diff. ratio, Equation (22)	
	A	B		$D_{AB}P$	D_{KA}				1	2		
Selas 015 microporous porcelain (Selas Corp.)	O ₂ -A		61.4	0.072	1.31	0.200	2.78	2.90	3.64	1.17	1.24	2.73
Selas 03-2	H ₂ -N ₂		28.6	0.085	0.54	0.763	8.98	8.00	4.85	0.60	0.47	8.78
Celite catalyst support (diatomaceous earth, Johns-Manville Co.)	H ₂ -N ₂		56.1	0.0945	0.555	0.763	8.08	8.87	4.49	0.48	0.39	7.70
Kaolin-unglazed porcelain (Coors Porcelain Co.)	H ₂ -N ₂		34.7	0.053	0.117	0.763	14.4	19.3	1.69	0.16	0.144	13.4

* All diffusion coefficients at 20°C. in sq. cm./sec.

1. By mercury penetration.

2. Calculated from true value of D_{KA} .

Diffusion ratio is ratio of true to effective value of D_{AB} .

the coefficient D_K , primarily because of its specific dependence on the pore shape and dimensions. However if the solid had a fairly uniform pore structure, reasonable average values might be obtained for these coefficients. Obviously, the best values might be expected to result from the use of experimental diffusion data, rather than from other less direct measurements (for example permeability tests).

The rates of counter diffusion of hydrogen and nitrogen, or of oxygen and argon, were measured through a number of porous solids. A constant pressure steady state flow technique was used, similar to that employed by Weisz (7) but with larger cylindrical samples and somewhat higher flow rates. The apparatus is shown schematically in Figure 1. The major modification in the apparatus consisted of combining the outlet streams from the two halves of the diffusion cell and removing the combined flow through a manostat and a vacuum system. Analysis of the outlet streams was accomplished by withdrawing a small sample continuously from either stream through a separate pump (not shown). The sample stream was usually only 10 to 20% of the total flow. With this arrangement it was possible to operate the diffusion cell at any absolute pressure from 1.0 down to about 0.01 atm. Analysis was by means of a modified thermal-conductivity cell described elsewhere (8).

In all tests pure gases were used on each face of the solid, and outlet concentrations were low. Therefore the total partial pressure difference for a diffusing gas was always in the range of 95 to 99% of the absolute pressure. Results were expressed as the rate of diffusion of hydrogen, or of oxygen, depending on the gas pair used.

Experimentally measured values were substituted in Equation (9) from runs at the highest and lowest pressures and the resulting equations solved simultaneously for values of D_{KA} and $D_{AB}P$. From the high-pressure results

the value of the ordinary diffusion coefficient was obtained, and the value of the Knudsen coefficient was taken from the low-pressure values. Inasmuch as the geometric length and area of the porous solid were used in these calculations, the value of the ordinary diffusion coefficient so found was an effective value. The true value of this coefficient was obtained from the literature. If it is assumed that the geometric parameter given by the ratio of the true value to the effective value of the ordinary diffusion coefficient also applies to Knudsen diffusion, then the true and effective Knudsen diffusion coefficients are also known; that is

$$\left(\frac{D_{AB}}{D_{KA}}\right)_{\text{Effective}} = \left(\frac{D_{AB}}{D_{KA}}\right)_{\text{True}} \quad (18)$$

The diffusion coefficients obtained as described above were used to calculate the diffusion rate at intermediate pressures. The results are shown in Figure 2 for three different types of porous solid and for both gas pairs. The solid line represents the calculated values in accordance with Equation (9), and the points give experimentally measured values. The properties of the three solids are given in Table 1. The Selas and porcelain (kaolin) samples had a narrow range of pore sizes, while the celite had a fairly uniform distribution of pore diameters over a much wider range.

An inspection of the results shows that Equation (9) satisfactorily describes the rate of diffusion through these solids. Curves plotted in the fashion shown in Figure 2 should become asymptotic to a 45-deg. line at the low-pressure end and approach a constant value in the high-pressure range. The approximate location where $r = \lambda$ is also shown on each plot.

It should be possible to calculate an equivalent pore radius for diffusion from the values of the Knudsen diffusion coefficient obtained. This value is also given in Table 1 and is compared with the value obtained by mer-

cury penetration measurement. The agreement again is good.

The statement has also been made (9) that electrical resistivity ratio in a porous solid should be analogous to the ratio of the true ordinary diffusion coefficient to the effective coefficient. The resistance ratios were measured for these solids, and the values of the two ratios are compared in Table 1. Agreement is satisfactory in view of the difficulty of measuring the electrical resistance for fine pored solids.

In another paper (10) the authors have shown that it should be possible to calculate an effective Knudsen diffusion coefficient from flow tests in which the specific flow rate is obtained as a function of the mean total pressure. Extrapolation of the straight-line plot obtained to zero pressure can be taken to give the value of the slip flow coefficient. On the basis of the flow equation presented by the authors it was shown that the ratio of the slope A to the zero pressure intercept B is given by

$$\frac{A}{B} = \frac{3\bar{r}}{4\pi\eta v} \quad (19)$$

It was further shown that the limiting Knudsen molecular flow $C\Delta p$ is given by the equation

$$C\Delta p = \frac{4B\Delta p}{\pi} = D_{K_e} A \frac{\Delta p}{kTL_s} \quad (20)$$

The right-hand side of the above equation serves as a definition of D_{K_e} , the effective Knudsen diffusion coefficient. Rearranging the above equation one gets

$$D_{K_e} = \frac{4BkTL_s}{\pi A_s} \quad (21)$$

Combining this equation with $D_{KA} = 2/3 \bar{r} v$, and with Equation (19), one obtains the result for the diffusion ratio based on Knudsen flow:

$$\frac{D_{KA}}{D_{K_e}} = \frac{16\pi}{9} \frac{A}{B^2} \frac{\eta A_s}{mL_s} \quad (22)$$

Table 1 includes the values of the diffusion ratio calculated in this way from flow rate vs. mean total pressure plots. The agreement is well within the probable experimental error.

DISCUSSION

The form of Equations (9) and (13) indicate a rather slow convergence to the asymptotic values at high and low pressures. Therefore a mixed mode of diffusion does occur to an appreciable degree over a wide range of values of the ratio r/λ . On the basis of the results for the porous solids this would appear to be a somewhat greater range than the hundredfold value given earlier. The convergence of Equations (9) or (13) is intermediate between the simple form of Equation (17) and the more rapidly converging intuitive equation proposed by Wheeler (2), given as

$$D_N = D_{AB} (1 - e^{-D_{AB}/D_{KA}}) \quad (23)$$

A more rigorous test of Equation (9) would require experiments of the same kind as those performed on the porous solids but with true capillaries of known dimensions. Such work is currently under way.

However it would appear that the diffusion equation presented here gives an adequate description of the transition zone of diffusion for binary gas mixtures and can be applied with good accuracy to porous solids.

ACKNOWLEDGMENT

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NOTATION

A_s, L_s	= geometric area and length of porous sample
D_{AB}	= binary mutual diffusion coefficient for gases A and B, sq. cm./sec.
D_{KA}	= Knudsen diffusion coefficient for gas A, sq. cm./sec.
D_N	= mean diffusion coefficient
G	= molecular transport rate, molecules/(sec.) (sq. cm.)
k	= Boltzmann constant
L, x	= length of diffusional path, cm.
m	= mass of a molecule
M	= molecular weight
n	= molecular concentration, molecules/cc.
N	= molar transport rate, moles/(sec.) (sq. cm.)
p	= partial pressure
P	= absolute pressure
r	= radius
\bar{r}	= equivalent pore radius
R	= gas constant
T	= absolute temperature
u	= diffusional velocity in the axial direction, cm./sec., referred to a fixed set of coordinates

\bar{v}	= average molecular speed
y	= mole fraction
λ	= mean free path
η	= gas viscosity
Δp	= pressure differential causing flow

Subscripts

A, B	= gas A and gas B, respectively
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Thermodynamic Properties of Polar Gases in the Dilute Phase

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A procedure is proposed, based in part on theory and in part on experimental data, for predicting the effect of polarity on the thermodynamic properties of polar, organic gases in the dilute phase. This correlation was used to predict compressibility factors Z , and the change of enthalpy with pressure, in the vapor phase.

By use of this correlation the computed compressibilities indicated an average absolute deviation of 1.0% from available experimental data, which includes reduced pressures up to 0.9 and temperatures to 1.0. Similar comparisons were made for the effect of pressure on enthalpy.

Reasonable progress has been made in developing prediction methods for thermodynamic properties of nonpolar gases, particularly pure components. However progress has been slight for polar substances where electrical properties may exert a significant effect. The objective of this paper is to present a prediction method for classes of organic, polar compounds.

PREVIOUS CORRELATIONS

The original method of Hougen and

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Watson (5) assumed that volume and energy were the two parameters characterizing a gas. Thus the reduced volume V/V_0 or the reduced pressure P/P_0 was used with the reduced temperature T/T_0 to provide the two variables which determined the compressibility factor:

$$Z = PV/RT \quad (1)$$

Experimental compressibility factor data have shown that Z is not the same function of the reduced pressure and reduced temperature for every compound. Thus more parameters are needed; these parameters must repre-

sent the forces which are present in some compounds but not in others at the same conditions of reduced pressure and temperature.

These forces are usually due to one of the following causes: deviation from spherical molecular shape, or the degree of acentricity; high electrical forces such as manifested by the dipole moment and the existence of hydrogen bonding; and quantum forces which are important in hydrogen and helium.

This latter effect will not be considered here, since it is important in only the compounds mentioned. All compounds are effected by the first effect with the exception of the inert gases, which are spherical. For this