l	= crystal size	[mm]	
l'	= length defined by Eq. (6)	[mm]	
Δl	= increment of crystal size	[mm]	
n	= population density	[number/cm$^3\cdot$mm]	
Q	= flow rate	[l/min]	
Q_r	= removal rate	[l/min]	
R	= gas constant	[Kcal/mole$\cdot$°K]	
T	= temperature	[°K]	
t	= time after seeding	[hr]	
u	= solution velocity	[cm/sec]	
V	= volume of crystallizer	[cm^3]	
α	= constant defined by Eq. (2)	[—]	
β	= exponent defined by Eq. (2)	[—]	
ε	= void fraction	[—]	

Literature Cited

1) Abegg, C. F., J. D. Stevens and M. A. Larson: *AIChE J.*, 14, 118 (1968).
2) Clontz, N. A., R. T. Johnson, W. L. McCabe and R. W. Rousseau: *Ind. Eng. Chem., Fundam.*, 11, 368 (1972).
3) Garside, J., J. W. Mullin and N. D. Sibenu: *ibid.*, 13, 299 (1974).
4) Hirota, N., K. Fukui and M. Nakajima: *Kagaku Kogaku, Ronbunshu*, 1, 500 (1975).
5) Nakai, T., K. Miyake and K. Izumitani: *Kagaku Kōgaku*, 38, 829 (1974).
6) Phillips, V. R. and N. Epstein: *AIChE J.*, 20, 678 (1974).
7) Randolph, A. D. and M. A. Larson: *ibid.*, 8, 639 (1962).
8) Randolph, A. D.: *Can. J. Chem. Eng.*, 63, 280 (1964).
9) Sipyagin, V.: *Soviet Physics Crystallography*, 12, 590 (1968).
10) Youngquist, G. R. and A. D. Randolph: *AIChE J.*, 18, 421 (1972).

(Presented at the 40th Annual Meeting of The Soc. of Chem. Engrs., Japan, at Nagoya, April 3, 1975.)

CORRELATIONS OF GASEOUS FLOW AND DIFFU-SIONAL PERMEABILITIES IN POROUS BODIES

MASASHI ASAEDA
*Department of Chemical Engineering,
Hiroshima University, Hiroshima 730*
RYOZO TOEI
*Department of Chemical Engineering,
Kyoto University, Kyoto 606*

Flow and diffusional permeabilities of gases in various unconsolidated and consolidated porous bodies were measured in the pressure range of 6–760 mmHg.

From experimental and theoretical considerations a new method is proposed to obtain the tortuosity factors q or the values of ε/q from flow permeability data. The values are compared with those obtained by the usual diffusion method to obtain good agreement between them.

A single value of tortuosity factor q (or ε/q) was found to be valid for the whole diffusion region and the viscous flow region for such consolidated or unconsolidated porous body as was used in the study, considered to be relatively homogeneous and monodispersed. Dimensionless flow and diffusional permeabilities are well correlated by the theoretical and empirical equations as a function of the modified Knudsen number.

Introduction

It occurs very often in operations of gaseous mass transfer in porous materials such as catalytic reactions, gas-solid reactions, adsorption and desorption, drying, etc., that the usual isobaric diffusion equation can't be applied adequately for estimation of the rates, because in addition to the composition gradients, the total pressure gradient takes place in the porous bodies due to the change of mol number or of mass of diffusing gases by reactions. Diffusion through stagnant gases in porous bodies is inevitably accompanied by the total pressure gradient, which can become so large that it can't be neglected as the transfer mechanism approaches transition or the Knudsen region.

In such cases information about flow of gases in porous bodies becomes important[5] in addition to the effective diffusivities of gases.

Table 1 Physical properties of consolidated and un-consolidated porous samples

	Sample No.	Oil content* [%]	Sample length [cm]	Sectional area [cm²]	Porosity [—]
	UC- 1	0.0	2.53	0.105	0.356
	C- 1	8.9	2.32	0.107	0.432
	C- 2	15.0	”	”	0.420
Glass beads	C- 3	17.5	2.43	0.105	0.380
	C- 4	22.2	2.32	0.107	0.372
	C- 5	23.8	”	”	0.355
	C- 6	39.0	2.43	0.105	0.280
Crushed ceramic	UC- 2	0.0	2.52	0.108	0.390
	C- 7	6.2	2.32	0.107	0.522
	C- 8	10.5	2.43	0.105	0.497
Crushed sea sand	C- 9	15.1	”	0.0975	0.467
	C-10	17.9	”	”	0.451
	C-11	20.0	”	0.105	0.439

* This value is the percentage saturation of the void space of packed beds of solid particles.

In this paper the results of flow and isobaric diffusion experiments for various consolidated and unconsolidated porous samples in a wide range of total pressure are presented, and the results are discussed on the basis of the theoretical and experimental results described in the previous papers[1,2].

1. Experimental

Packed beds of fine particles of glass beads (average diam. 10.6 microns) and crushed ceramics (equivalent diam. 6.3 microns) were used as unconsolidated porous samples, while consolidated samples included packed beds of glass beads (average diam. about 13 microns) and crushed sand (equivalent diam. about 6 microns), all of which were well mixed with oil (diffusion pump oil was used for its negligible vapor pressure) to various extents before packing. The dimensions and physical properties of the samples are shown in **Table 1**.

The experimental apparatus and procedures are quite similar to those already proposed by the authors[2]. A few improvements were made to the apparatus in order that measurement of isobaric diffusion might be possible under various total pressures (50–760 mmHg).

2. Experimental Results and Discussion
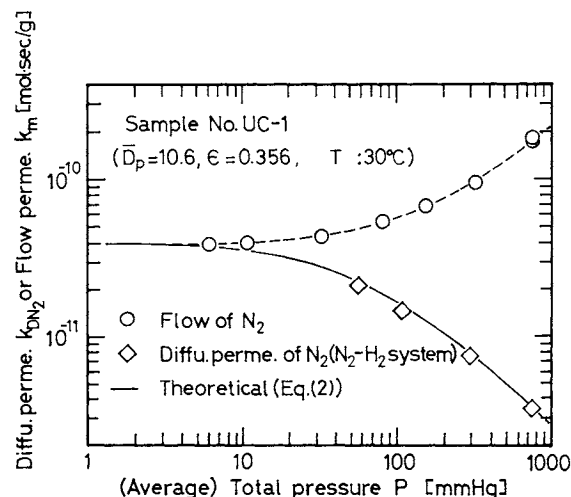
2. 1 unconsolidated packed beds

The flow and diffusional permeabilities are defined as follows[1,2], for flow permeability,

$$k_m = -N/(\Delta P/L) \tag{1}$$
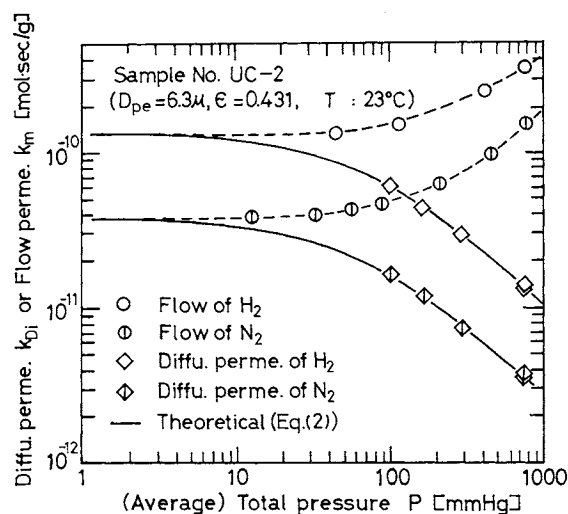
for diffusional permeability,

$$k_{DA} = -N_A/(\Delta p_A/L) = \bar{D}_{eA}/RT \tag{2}$$

where $\bar{D}_{eA}$ is the mean effective diffusivity and can be given by

The theoretical and experimental results of diffusional permeabilities were obtained under the condition $y_{N_2,0}=0$, $y_{N_2,L}=1.0$.

Fig. 1 Experimental results of flow and diffusional permeabilities of N₂ gas (N₂–H₂ system) in packed bed of spherical particles

Diffusional permeabilities were obtained under the condition $y_{N_2,0}=0$, $y_{N_2,L}=1.0$.
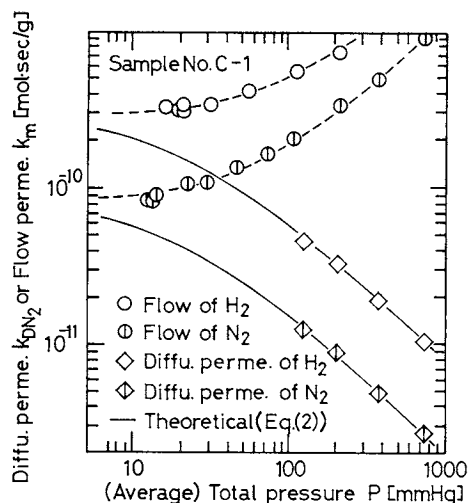
Fig. 2 Experimental results of flow and diffusional permeabilities of H₂ and N₂ gases in a packed bed of nonspherical particles

$$\bar{D}_{eA} = D_{AB} \cdot \frac{\varepsilon}{q} \cdot \frac{1}{\alpha(y_{A0} - y_{AL})} \ln \left\{ \frac{1 + \alpha y_{AL} + D_{AB}/D_{KA}}{1 + \alpha y_{A0} + D_{AB}/D_{KA}} \right\} \tag{3}$$

where D_{KA} is the Knudsen diffusion coefficient of component A, which can be given by the following equation for packed beds of particles of equivalent diameter, D_p[1]

$$D_{KA} = \left(\frac{RT}{2\pi M_A} \right)^{1/2} \cdot \frac{4\varepsilon D_p}{3(1-\varepsilon)\Phi} = \frac{q}{\varepsilon} \cdot RT k_{m0} \tag{4}$$

The experimental results of flow and diffusional permeabilities k_m, k_{Di} for unconsolidated porous samples are shown in **Figs. 1 and 2**.

Diffusional permeabilities were obtained under the condition $y_{N_2,0}=0$, $y_{N_2,L}=1.0$.

Fig. 3 Experimental results of flow and diffusional permeabilities of H_2 and N_2 gases in a consolidated porous body

Figure 1 shows the experimental results of flow permeabilities of N_2 gas and diffusional permeabilities of N_2 gas for N_2–H_2 gaseous diffusion in an unconsolidated sample of glass beads bed (sample No. UC-1). The broken lines in the figure are the flow permeabilities given by the following empirical equation, which is obtained from the experimental results for packed beds of spherical particles of various diameters[1],

$$\frac{k_m}{k_{m0}} = \left\{ 1 + \left(\frac{0.14}{Kn}\right)^{6/5}\right\}^{5/6} \tag{5}$$

where k_{m0} is the flow permeability in the Knudsen region and Kn is the modified Knudsen number in packed beds, which is defined in the previous paper[1] as the ratio of the number of molecule-particle collisions to that of intermolecular collisions, or

$$Kn = \left(\frac{\pi RT}{8M}\right)^{1/2} \cdot \frac{1-\varepsilon}{\varepsilon} \cdot \frac{\eta S}{P} \tag{6}$$

where S is the specific surface given by $S=6/D_p$ for a sphere.

The experimental results for the packed bed of non-spherical particles of crushed ceramic (sample No. UC-2) are shown in Fig. 2, where flow and diffusional permeabilities are shown against total pressure P for each kind of gas (N_2–H_2 system). The solid lines in Figs. 1 and 2 are the theoretical ones calculated by Eq. (2) with $\bar{D}_{eA}$ given by Eq. (3). The tortuosity factor q in these calculations was taken to be 1.41 for the packed bed of spheres and 1.70 for the crushed ceramic bed, respectively. There can be seen from these figures a good accordance between calculated and experimental results, which shows that for relatively homogeneous unconsolidated porous media the same tortuosity factor can be used in the whole

diffusion region (from the Knudsen to the usual molecular diffusion regions).

As for the flow in the viscous region ($Kn \ll 1$) Eq. (5) becomes

$$k_m/k_{m0} \approx 0.14/Kn \tag{7}$$

From this equation the Blake-Kozeny equation can be derived to give the Kozeny constant as

$$\kappa = \frac{\pi \Phi q}{(16)(0.14)} \approx 3.06q \tag{8}$$

This equation gives the values of the Kozeny constant, $\kappa=4.31$ for packed beds of spheres of relatively homogeneous diameter ($q=1.41$) and 5.20 for the packed bed of non-spherical particles ($q=1.70$). The corresponding values of κ reported for unconsolidated packed beds of spherical and non-spherical particles are 4.17 and $5.0^{[3,4]}$, respectively. For unconsolidated packed beds of non-spherical particles the scatter of the reported values of κ is within $\pm 15\%$ around the value of $\kappa=5.0$, which seems to correspond to the scatter of tortuosity factor around the value of $q=1.7$. From these considerations it seems possible to use a single tortuosity factor in the whole region of flow and diffusion of gases in unconsolidated porous bodies, although the flow permeability in the transition region has not yet been obtained theoretically.

2. 2 consolidated porous bodies

An example of experimental results for a consolidated porous medium (glass bead-bed of 8.9% oil content) is shown in **Fig. 3**. The tendency of transformation of flow permeability curves with pressure is quite similar to that of unconsolidated packed beds. Accordingly, it is also possible to obtain the equivalent diameter by the method proposed previously[1]. But equivalent diameter of consolidated porous bodies seems to lose its physical meaning because the solid part is no longer isolated. Instead, it will be useful to obtain the pressure at which the Knudsen number becomes 1.0, for example*. Putting the pressure at $Kn=1.0$, $P_{Kn=1}$, into Eq. (6) the flow permeability the Knudsen region can be written as

$$k_{m0} = \frac{2\eta}{M\Phi P_{Kn=1}} \cdot \frac{\varepsilon}{q} \tag{9}$$

From this equation and the experimental flow permeability data the value of ε/q can be determined** (flow permeability method). According to this method, for example, the value of ε/q was calculated to be 0.195 for the sample C-1.

---

* The experimental flow permeability curves are compared with the experimental results in Fig. 5 of the previous paper[1] or with the curve by Eq. (5) to obtain the pressure corresponding to $Kn=1.0$

** The value of ε/q may be preferable to the tortuosity factor q for consolidated porous media, because much of the pore space in highly consolidated media would represent blind alleys which could take no part in flow or diffusion.

Table 2 Observed values for consolidated porous samples

Sample No.	Pressure at $Kn=1$ $P_{Kn=1}$ [mmHg]	Knudsen permeability of N_2 gas k_{mON_2} [mol·sec/g]	$(\varepsilon/q)_F$* (−)	$(\varepsilon/q)_D$** [−]	q [−]	S*** [cm²/cm³]
C- 1	9.7	8.4×10^{-11}	0.195	0.191	2.24	3010
C- 2	10.8	6.4	0.160	0.159	2.63	3200
C- 3	8.2	7.4	0.148	0.150	2.55	2050
C- 4	8.8	4.7	0.101	0.0997	3.71	2130
C- 5	9.2	4.2	0.0820	0.0848	4.26	2070
C- 6	7.1	0.78	0.0137	0.0136	20.5	1130
C- 7	12.0	8.4	0.230	0.262	2.12	5355
C- 8	12.5	8.0	0.229	0.236	2.14	5010
C- 9	11.5	6.8	0.179	0.201	2.46	4120
C-10	11.3	7.9	0.213	0.207	2.15	3790
C-11	11.8	6.0	0.162	0.171	2.64	3770

* The values are obtained from Eq. (9) and the observed results of flow permeabilities (flow permeability method).

** The values are obtained from Eq. (3) and the observed diffusional permeabilities at relatively high pressure, where the Knudsen diffusion term in Eq. (3) is negligibly small (diffusional permeability method).

*** The specific surface (the total surface/the volume of solid portion) for a sphere of diameter 13 microns, S_0, is 4615 cm²/cm³.

The value of ε/q can also be obtained by the usual method, applying Eq. (3) to the observed results in the molecular diffusion region (diffusional permeability method). The value for the above sample is 0.191, which is very close to the one from the flow permeability method. The solid lines in Fig. 3 are the theoretical ones calculated by Eq. (2) with $\bar{D}_{eA}$ from Eq. (3).

The values of ε/q obtained by these two methods for the consolidated porous samples listed in Table 1 are compared in **Table 2**, which shows good agreement between these values. From these results, it is concluded that the same tortuosity factor q or the value ε/q can be used also for flow and diffusion in consolidated porous bodies which can be considered to be relatively homogeneous.

If the contribution of blind alleys to porosity is negligibly small, the values of the tortuosity factor q and the specific surface S (the total wetted surface/the volume of solid portion) may have their usual physical meanings. These characteristic properties of porous media become frequently important in studies of transport phenomena in or through porous media. The value of tortuosity factor can be easily obtained by the method proposed above, and the specific surface S can also be calculated by Eq. (6) with the value of $P_{Kn=1}$. The values of q and S for the consolidated porous samples used in this work are calculated and shown in Table 2. The value of tortuosity factor is found to increase with the increase of oil content or of the degree of consolidation, while the specific surface S decreases as the degree of consolidation increases. It is noticeable that the estimation of S with Eq. (6) needs no empirical constant such as the Kozeny constant κ in the Blake-Kozeny equation, which cannot be applied to consolidated porous media. The BET method usually gives overly large values of S, as point-
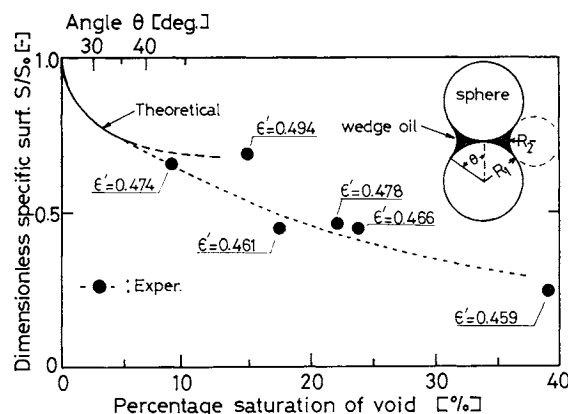
Values of ε' mean the porosities when the oil is taken off. $S_0 = 4615$ cm²/cm³, number of average contact points per sphere; 6.7.

Fig. 4 Dimensionless specific surface of consolidated porous media

ed out by Carman[3]. In **Fig. 4** are shown the dimensionless specific surface values for consolidated porous samples consisting of glass beads (diameter 13 microns) and wedge oil. The theoretical line in the figure was obtained by supposing that the oil was held only around contact points of spheres (see Fig. 4). The expressions of the volume of liquid held around a contact point and the average number of contact points are given elsewhere[6,7]. The ratio of the surface area decrease to the surface area of a sphere, $\Delta S/S_0$, is given by

$$\frac{\Delta S}{S_0} = \frac{1-\cos\theta}{2\cos\theta}\left\{\left(\frac{\pi}{2}-\theta\right)\tan\theta - (1-\cos\theta)\right\}$$

$$-\frac{1}{2}(1-\cos\theta) \tag{10}$$

The theoretical line was obtained for a packed bed of spheres of $\varepsilon'=0.47$, which is the porosity when the volume of oil is disregarded. The dashed part of the
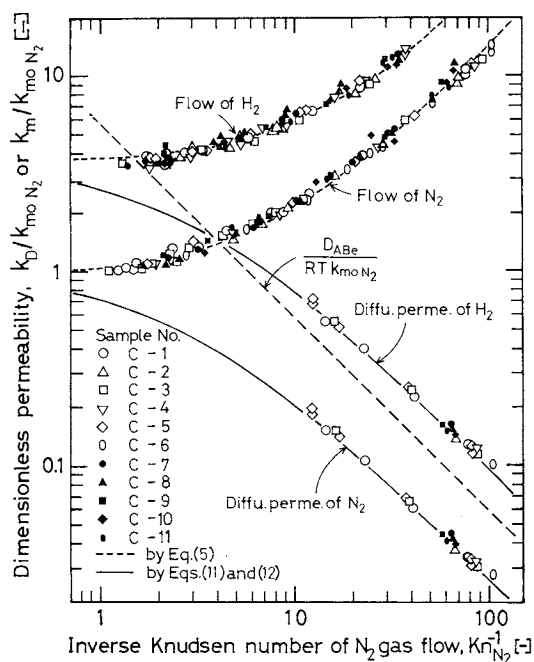
Fig. 5 Correlations of flow and diffusional permeabilities for monodispersed porous bodies

theoretical curve shows the region where the unification of the wedge liquid around the neighbouring contact points becomes appreciable and the theoretical estimation is not applicable. Considering that the experimental curve approaches the theoretical one in the region of low oil content and that the observed values are lower than the theoretical because of the unification of wedge oils, the above method seems to give adequate values of specific surfaces of consolidated porous media. Using the specific surface S by this method, the hydraulic diameter of porous media, $D_h = \varepsilon/S(1-\varepsilon)$, can be obtained and the Reynolds number can be defined as $Re = 2D_h G/\eta$, which was always less than the order of 10^{-4} in the viscous region in this work.

2.3 correlations between flow and diffusional permeabilities

It was shown in the previous paper[1] that flow permeabilities can be well correlated by the modified Knudsen number (Eq. (6)) for packed beds of particles. As for diffusion, it is also possible to express the diffusional permeability as a function of the Knudsen number, Kn_i, for flow of component i.

The diffusional permeability of component i, Eq.(2), is to be divided by the flow or diffusional permeability in the Knudsen region, k_{m0i}, to obtain the dimensionless diffusional permeability;

$$\frac{k_{Di}}{k_{m0i}} = \frac{\bar{D}_{ei}}{(\varepsilon/q)D_{Ki}} = \frac{1}{\alpha_{ij}(y_{i0} - y_{iL})} \cdot \frac{PD_{ij}\Phi M_i}{2RT\eta_i} \cdot Kn_i$$

$$\times \ln\left\{\frac{1 - \alpha_{ij}y_{iL} + (PD_{ij}\Phi M_i/2RT\eta_i)\cdot Kn_i}{1 - \alpha_{ij}y_{i0} + (PD_{ij}\Phi M_i/2RT\eta_i)\cdot Kn_i}\right\}$$

$$(11)$$

and

$$\frac{k_{Dj}}{k_{m0i}} = \left(\frac{M_i}{M_j}\right)^{1/2} \cdot \frac{k_{Di}}{k_{m0i}}$$

$$(12)$$

where $\alpha_{ij} = 1 - (M_i/M_j)^{1/2}$, $i,j = A,B$ $(i \neq j)$ and Kn_i is the Knudsen number of component i under the same total pressure. And the following relation holds between Kn_A and Kn_B,

$$Kn_A = \left(\frac{M_B}{M_A}\right)^{1/2} \cdot \frac{\eta_A}{\eta_B} \cdot Kn_B$$

$$(13)$$

Equations (11) and (12) show that the dimensionless diffusional permeabilities depend on the Knudsen number for flow of one of the components, on the physical properties of the diffusing gaseous components, and on the diffusion conditions (y_{i0}, y_{iL}) but not on the total pressure or on the representative dimension of pore structure explicitly.

These relations are shown in **Fig. 5**, where the experimental results of flow and diffusional permeabilities for H_2–N_2 system in the samples in Table 1 are also shown against the inverse Knudsen number for N_2 gas flow, $Kn_{N_2}^{-1}$. The Knudsen number of flow of gas in consolidated porous bodies is obtained by the method in section 2.2, or by comparing the experimental results of N_2 gas flow in each sample with Eq. (5). The solid and broken lines in this figure are the theoretical and empirical ones by Eqs. (11), (12) and (5), respectively. Good acord can be seen between the theoretical and observed results. This shows that the flow and diffusional permeabilities of gases in monodispersed porous bodies can be correlated by the Knudsen number.

It is sometimes necessary to know if the Knudsen diffusion term in the diffusion equation must be taken into account under a certain total pressure or to which region the mechanism of diffusion belongs under pressure. A usual but rather ambiguous method to find this information is to compare the representative pore diameter with the mean free path of the gas mixture. This method is clearly based on the pore model of porous media, which cannot always cover the whole flow and diffusion region in porous media. A more definite way is to compare the effective diffusivity D_{ABe} with the effective Knudsen diffusivity $D_{KB}\varepsilon/q$. From the discussion above the ratio $D_{ABe}/(\varepsilon/q \cdot D_{KB})$ $(= D_{ABe}/RTk_{m0B})$ can be given by

$$\frac{D_{ABe}}{RTk_{m0B}} = \frac{PD_{AB}\Phi M_B}{2RT\eta_B} \cdot Kn_B$$

$$(14)$$

which is a function of the Knudsen number but not of ε/q, and is also shown in Fig. 5.

It can be seen from the above discussion or simply from Fig. 5 that the mechanisms of flow and diffusion can be classified by the Knudsen number and that the diffusional permeability can be estimated simply from

218

the flow permeability data and vice versa. It should be noted, however, that the relation obtained above can be applied to monodispersed porous media but not to bidispersed ones which have macro- and micropores.

Conclusion

From the theoretical and experimental results of flow and diffusion of gases in relatively homogeneous, monodispersed, consolidated and unconsolidated porous media the following results are obtained:

1) A method is proposed to obtain the value of tortuosity factor or the values of ε/q of porous bodies from the experimental results of flow permeabilities. The values by this method coincide well with those obtained by the usual diffusion method. Also, a new method to obtain the specific surface of consolidated porous media is proposed.

2) Applying the equations proposed here and in the previous paper, the same tortuosity factor or the value of ε/q can be used not only for the whole diffusion region but also for the viscous flow region.

3) Dimensionless flow and diffusional permeabilities are shown to be expressed as a function of the modified Knudsen number. And the theoretical and experimental equations are found to correlate the flow and diffusional permeabilities.

Acknowledgments

Nomenclature

D_{AB}	= diffusivity for binary gaseous mixtures	[cm²/sec]
$\bar{D}_{eA}$	= mean effective diffusivity defined by Eq. (3)	[cm²/sec]
D_K	= Knudsen diffusivity	[cm²/sec]
D_p	= equivalent diameter of particle	[cm]
Kn	= modified Knudsen number defined by Eq. (6)	[—]
k_D	= diffusional permeability defined by Eq. (2)	[mol·sec/g]
k_m	= flow permeability	[mol·sec/g]
k_{m0}	= flow permeability in Knudsen region	[mol·sec/g]
L	= sample length	[cm]
M	= molecular weight	[g/mol]
N	= mole flux	[mol/cm²·sec]
P	= (average) total pressure	[dyne/cm²]
ΔP	= pressure difference	[dyne/cm²]
q	= tortuosity factor	[—]
R	= gas constant	[erg/mol·°K]
S	= specific surface	[cm²/cm³]
S_0	= specific surface of a sphere	[cm²/cm³]
T	= temperature	[°K]
y	= mole fraction	[—]
α_{ij}	= $1-(M_i/M_j)^{1/2}$	[—]
ε	= porosity	[—]
Φ	= constant ($\doteqdot 2.18$)	[—]
η	= viscosity	[g/cm·sec]
κ	= Kozeny constant	[—]

⟨Subscripts⟩

A,B	= component A and B, respectively (B refers to heavier component)
e	= effective or equivalent value
i,j	= component i and j, respectively
$0,L$	= at one side and at the other side of sample, respectively

Literature Cited

1) Asaeda, M., S. Yoneda and R. Toei: *J. Chem. Eng. Japan*, **7**, 93 (1974).
2) Asaeda, M., M. Nakano and R. Toei: *ibid.*, **7**, 173 (1974).
3) Carman, P. C.: "Flow of Gases through Porous Media", Academic Press (1956).
4) Krischer, O.: Die wissenschaftlichen Grundlagen der Trocknungstechnik", p. 184, Springer-Verlag (1963).
5) Mason, E. A., A. P. Malinauskas and R. B. Evans II: *J. Chem. Phys.*, **46**, 3199 (1967).
6) Okazaki, M.: Doctor Thesis, Kyoto Univ., Kyoto (1975).
7) Pietsch, W. and H. Rumpf: *Chem. Ing. Tech.*, **39**, 885 (1967)