

ANALYSIS OF DIFFUSION IN MACROPOROUS MEDIA IN TERMS OF A POROSITY, A TORTUOSITY AND A CONSTRICTIVITY FACTOR

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(Received 29 October 1973 and in revised form 21 January 1974)

Abstract—The ratio between the effective bulk diffusion coefficient in macroporous media and the diffusion coefficient in the absence of the porous medium is analysed in terms of the porosity, the tortuosity and the constrictivity. The necessity of distinguishing these three parameters is supported by the description of diffusion in partly saturated homogeneous isotropic monodisperse sphere packings.

The results are generalized to bulk diffusion in all homogeneous isotropic porous media in the porosity range 0–50 per cent.

NOMENCLATURE

A ,	area [m^2];
c ,	molar density [mol m^{-3}];
D_{ij} ,	diffusion coefficient of component i in component j [$\text{m}^2 \text{s}^{-1}$];
D_{eff} ,	effective diffusion coefficient [$\text{m}^2 \text{s}^{-1}$];
L ,	length parameter of porous medium [m];
M_i ,	molecular weight of component i [kg mol^{-1}];
N_i ,	molar flux of component i relative to stationary coordinates [$\text{mol m}^{-2} \text{s}^{-1}$];
Q ,	diffusibility;
q ,	matrix factor;
R_{ij} ,	$= N_i/N_j$;
u ,	liquid content of porous medium [vol. %];
x_i ,	mole fraction of component i ;
α ,	angle;
β ,	ratio of maximum and minimum cross section of a pore space segment;
δ ,	constrictivity;
ε ,	porosity;
σ_i ,	molecular diameter of component i [m];
τ ,	tortuosity.

Subscripts

A, B ,	species A, B ;
S ,	surface;
V ,	volume.

INTRODUCTION

IF DIFFUSION takes place in porous media the effective diffusion coefficient, D_{eff} , is lower than the diffusion coefficient, D_{AB} , in the absence of a porous medium.

Following Hoogschagen [1] we will call the ratio D_{eff}/D_{AB} the diffusibility, Q , of the porous medium.

In order to predict the diffusibility many equations, based on pore space models or empirical correlations, have been proposed; the general tendency being to try to give Q as a unique function of the porosity, ε . The disadvantage of most models is that they contain at least one adjustable parameter that cannot be estimated independently. Hence the sense of developing such models can be disputed [2–4]. Moreover, in general, the experiments do not differentiate between different models [5]. Therefore there is no need for still more complicated models, with still more adjustable parameters, especially if there is no sound physical basis for such models.

The fact remains, however, that the diffusibility can be very different for one porous medium or another. The central theme of this paper will be that to account for this it is necessary to introduce, apart from the influence of the porosity, a tortuosity and a constrictivity factor. None of these terms is new, but the discussion about the influence of these pore space characteristics is highly confusing; especially the term tortuosity is used for almost any concept related to the characterization of the pore space.

These factors must have a sound physical meaning including independent methods to determine them.

Unless otherwise stated, the discussion will be restricted to (bulk, molecular) unidirectional binary gas diffusion in homogeneous, isotropic macroporous media with a continuous pore space. Total pressure or temperature gradients are assumed to be absent.

THEORETICAL CONSIDERATIONS

The diffusion equation

If for a homogeneous and isotropic porous medium it is assumed that the number of collisions of the molecules among themselves is much higher than the number of collisions with the wall (hence bulk diffusion) it can be derived that [6, 7]:

$$N_A = \frac{-cD_{\text{eff}} \text{grad } x_A}{x_A R_{BA} + x_B} \quad (1)$$

with $R_{BA} = -N_B/N_A$. Further, the diffusibility, Q , in

$$D_{\text{eff}} = QD_{AB} \quad (2)$$

is determined only by the structural properties of the porous medium. That is to say the general properties of gas transport derived from the Boltzmann equation do not depend on the special shape of the solid surfaces; only the numerical coefficients change.

Furthermore, according to the derivation of equation (1), R_{BA} is independent of the pore space stereometry and, assuming hard sphere molecules, [6]:

$$R_{BA} \approx \sqrt{\left(\frac{M_A \sigma_B}{M_B \sigma_A}\right)}. \quad (3)$$

Hence the mass transport can be determined *a priori* except for the value of Q . The study of Q is the subject of this paper.

Proposed expressions for Q

The presented expressions for Q can be divided into three classes: (i) empirical correlations, (ii) semi-empirical equations based on a pore model, and (iii) theoretical expressions.

(i) All empirical correlations express Q as a function of ε . Some representative examples are given in Table 1.

Table 1. Empirical correlations for the diffusibility

Author, yr	Dependence of Q on ε	Remarks
Buckingham [8], 1904	ε^2	soils
Penman [9], 1940	0.66ε	soils; $0 < \varepsilon < 0.6$
various, cf. [10], 1948-1952	$a\varepsilon + b$	$a = 0.53 \text{ à } 0.97$ $b = -0.13 \text{ à } 0.04$
Van Bavel [11], 1952	0.58ε	
Currie [10], 1960	$\gamma\varepsilon^\mu$	$0 < \varepsilon < 1$; $\gamma = 0.8-1$
Satterfield [12], 1970	$a\varepsilon$	catalysts: $a = 0.14-0.33$

(ii) The equations falling in this class all take the form $Q = \gamma\varepsilon^\mu$, in which ε^μ is generally said to represent the influence of the smaller cross sectional surface available for diffusion.

Mostly μ is set equal to 1 and then, introducing q called the matrix factor, the relation between Q and ε

can be given as

$$Q = \frac{\varepsilon}{q}. \quad (4)$$

Many variants of equation (4) are presented in the literature.

(iii) Strictly theoretical equations for Q have been derived for porous media of which the solid phase is dispersed in the form of spheres or other regularly formed solids. In most cases the expressions were derived for the dielectric conductivity of porous media.

In Table 2 some representative equations are given. Recently Neale and Nader [16] have derived that for a homogeneous, isotropic swarm of spheres $Q = 2\varepsilon/(3-\varepsilon)$ for the whole porosity range. This is the same relation as found by Maxwell and others for a limited porosity range. The authors report, however, that the experimental confirmation (by electric conductivity measurements) is satisfactory for $\varepsilon < 0.45$ while excellent for $\varepsilon > 0.45$.

Table 2. Some theoretical diffusibilities for sphere packings

Author, yr	Dependence of Q on ε	Remarks
Maxwell, Rayleigh, cf. [13]	$2\varepsilon/(3-\varepsilon)$	$\varepsilon \rightarrow 1$; ordered packings
Bruggeman [14], 1935	$\varepsilon^{3/2}$	not for monosized spheres
Weissberg [15], 1963	$\varepsilon/(1 - \frac{1}{2} \ln \varepsilon)$	overlapping spheres possible
Neale and Nader [16], 1973	$2\varepsilon/(3-\varepsilon)$	all random homogeneous isotropic sphere packings
Marshall [17], 1959	$\varepsilon^{3/2}$	pseudo theoretical
Millington [18], 1959	$\varepsilon^{4/3}$	pseudo theoretical

When Q is plotted vs ε the different $Q-\varepsilon$ relations can hardly be distinguished from each other; therefore, for comparison, a plot of ε vs $1/q$ has been chosen as given in Fig. 1.

The experimental results reported hitherto permit no conclusion as to which relationship is confirmed best. Most often Bruggeman's equation (curve e in Fig. 1) is preferred for practical applications [1, 19, 20].

It will be argued below that for porous media a function of the kind $Q = f(\varepsilon)$ does not exist. Furthermore it will appear that the pragmatic value of the proposed $Q-\varepsilon$ relations is not very great (cf. curve g in Fig. 1).

The porosity

The molar flux in equation (1) is related to the total cross sectional surface of the porous medium perpendicular to the direction of transport. Thus the diffusibility has to account for the fact that only part of this

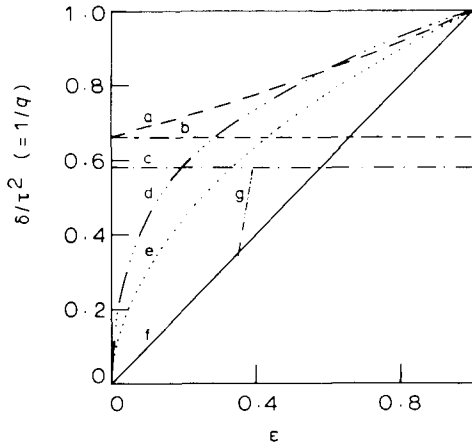


FIG. 1. Some relations between the inverse of the matrix factor and the porosity as given by theoretical and empirical expressions for the diffusibility, cf. Tables 1 and 2. (a) $q^{-1} = 2/(3-\epsilon)$; (b) $q^{-1} = 0.66$; (c) $q^{-1} = 0.58$; (d) $q^{-1} = \epsilon^{1/3}$; (e) $q^{-1} = \epsilon^{1/2}$; (f) $q^{-1} = \epsilon$; (g) experimental results for partly saturated porous media (obtained from Fig. 6).

surface, i.e. the part that intersects the pore space, is available for diffusion. In a homogeneous, isotropic porous medium each plane intersection has the same surface porosity, ϵ_s , which is equal to the volume porosity, ϵ_v .

In the literature there have been several suggestions that $\epsilon_s \neq \epsilon_v$ [18, 21–24]. Such suggestions are incorrect. Although there exist some problems in strictly proving that $\epsilon_s = \epsilon_v$ [25] these are on a level of strictness that does not concern us here.

The reason that for ϵ_s values like $\epsilon_v^{2/3}$ [18], $\epsilon_v^{1/2}$, $\frac{2}{3}\epsilon_v$ [24] have been proposed is that these values have been based on some pore model and because all pore models used are anisotropic ϵ_s will depend on the way the intersecting plane is taken.

Those suggestions that $Q \neq \epsilon^2$ and variants [18, 21, 22] on the ground that "a further restriction on the effective size of each pore sequence by a fraction ϵ is necessary because of the poor fit of one pore to the next" [26] all go back to the permeability pore model of Childs and Collis-George [27].

Such models are based on the assumption that the pore size distributions in two adjacent planes are random relative to each other. This is in general not the case, because the dispersion of the solid and the pore space is not random on a microscopic scale (which has been recognized later on [26, 28]). In fact such a random adjacent plane concept assumes pores of infinite shortness, the extra fraction ϵ in Q then taking account of the combined constrictivity and dead-end pore effect.

The tortuosity

For a homogeneous isotropic porous medium with a continuous pore space the tortuosity and the constrictivity are always both to be recognized. Although it may sometimes seem artificial in the discussions that follow, it will appear that the interpretation of experimentally found diffusibilities is clarified greatly if these two parameters are distinguished.

As far as definitions of the tortuosity, τ , occur in the literature they are always given either with reference to anisotropic cylindrical pore models or using the concept of the shortest distance between two points in the porous medium, which concept has no clear meaning.

The present authors suggest the following approach for the definition of the tortuosity.

Assume the pore space of the porous medium to be completely filled with what we will call diffusion paths. The main direction of the diffusion paths is the same as that of the concentration gradient. In the way the diffusion paths wind through the pore space they can be compared with the streamlines for laminar flow in porous media.

An intersection of the porous medium, perpendicular to the direction of the concentration gradient, of area A will contain an intersection of the pore space of area ϵA . This area ϵA is constituted by the intersections of the diffusion paths, the surface of intersection of a diffusion path being $\Delta(\epsilon A)$. The order of magnitude of the length parameters of the intersections of the diffusion paths is intermediate between those of the free path of the molecules and the dimensions of the pore space segments.* The diffusion paths do not all have equal $\Delta(\epsilon A)$ values, but for each intersection of the porous medium the $\Delta(\epsilon A)$ distribution is the same. The number of diffusion paths is the same in each intersection. Different diffusion paths have different directions relative to the concentration gradient, but the distribution of angles, α , between the direction of the diffusion path and the concentration gradient, is the same in each intersection. At each point of each diffusion path the local Q in this point is linear in $\cos^2 \alpha$: over a distance dl perpendicular to the intersection ϵA the length of the diffusion path is $dl/\cos \alpha$ and the surface for diffusion perpendicular to the direction of the diffusion path is $\Delta(\epsilon A) \cos \alpha$. Thus we can assign to each intersection and hence to the porous medium as a whole a $\cos^2 \alpha$ distribution.

In terms of the above model the matrix factor is a

*A pore space segment is an element of the pore space and has a volume that is of the same order of magnitude as the largest possible inscribed spheres in the pore space. For example, in a densest sphere packing the pore space is constituted by tetragonal and rhombohedral pore space segments. For random particle packings rules can be chosen to divide the pore space in segments in a unique way.

function of the $\cos^2\alpha$ and the $\Delta(\varepsilon A)$ distribution. It will not be possible to specify these distributions; the model was introduced only to clarify the notion of the tortuosity, which is in fact a restricted tortuosity because it is not based on all diffusion paths but only on what we will call the main diffusion paths. The main diffusion paths are the shortest diffusion paths in the porous medium. The tortuosity, τ , can then be defined by stating that τ^{-2} is equal to the average of the values of $\cos^2\alpha$ for the main diffusion paths and hence Q is proportional to τ^{-2} .

It will be clear that τ as defined above is a function of ε . And hence it is not necessary to decide whether τ is equal to $\sqrt{2}$ [29–31] or $\sqrt{3}$ [22, 32]. These values are relevant only to pore models of unconnected cylindrical pores and do not give a physical meaningful characterization of a homogeneous, isotropic, continuous pore space.

The constrictivity

That the main diffusion paths of a pore space segment are not parallel to the concentration gradient has been accounted for by the tortuosity. The constrictivity, δ , accounts for the fact that the cross section of a segment varies over its length. That is to say the constrictivity is defined as $\delta = (D_{\text{eff}}/\varepsilon D_{AB})_{\tau=1}$.

Hence we have for the diffusibility:

$$Q = \frac{\varepsilon\delta}{\tau^2}. \quad (5)$$

The form of the pore space segments varies and is in general not known. However, if these segments are characterized by the ratio of the maximum and the minimum cross section, β , it appears that δ is more or less independent of the segment form. In Fig. 2 some examples are given: Currie [10] calculated δ for sinusoidal segments. Petersen [33] for hyperbolas of revolution and Michaels [3] for a repetition of cylindrical capillaries. Therefore we may assume that in using, e.g. Petersen's curve to find δ the deviation of the true value will be small for most porous media.

Independence of ε , τ and δ

That the diffusibility can be analysed in terms of ε , τ and δ can be verified only if they can be determined independently.

Probably all three variables can be determined from representative photomicrographs of intersections of the porous medium. The porosity can be determined directly; for τ and δ (i.e. β) this is not possible. Especially τ will be too low if determined from the apparent main diffusion paths in a two-dimensional picture.

If ε is known the values of τ and β can be estimated for "reasonable" particle packings. We will return to this point presently.

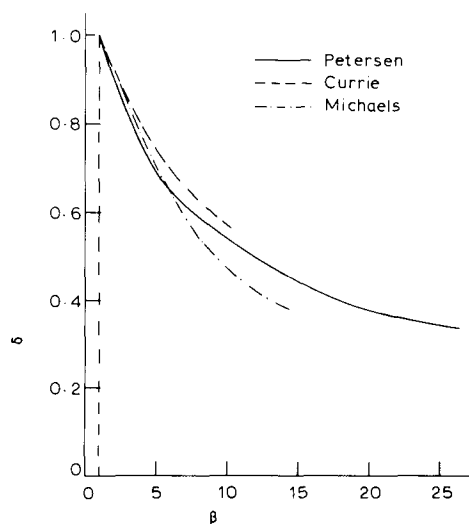


FIG. 2. Constrictivity, δ , as a function of the ratio, β , of the maximum and minimum cross section for different pore forms. Petersen [33]: hyperbola of revolution; Currie [10]: sinusoidal; Michaels [3]: cylindrical capillaries connected in series, length ratio of capillaries is 5.

The value of β and hence of δ can be determined by means of mercury porosimetry: the penetration curve gives the minimum cross section and the retraction scanning curves the maximum cross-section. This method has been verified for random sphere packings [34].

An indirect argument for the distinction between τ and δ is that by comparing diffusion and viscous flow in porous media, the value of τ is the same, but that of δ is different in the two cases.

Or, more general, the tortuosity, like the porosity, is a parameter characterizing the pore space in an absolute sense while the value of the constrictivity depends on the kind of transport phenomenon studied.

EXPERIMENTAL PROCEDURE

Methods and materials

Diffusion experiments were performed under stationary conditions in a modified Wicke-Kallenbach apparatus.

The porous media used for the experiments had a diameter of 21 mm and a length of 14 mm. They consisted of sintered glass beads (i.e. sintered together, but without significant deformation of the spheres); the particle diameter was in the range of 40–400 μm .

The homogeneity of these porous media was measured using an X-ray absorption technique [35]. In some of the experiments to test the measurement technique porous media of sintered bronze spheres were used.

In all experiments helium diffused in a nitrogen atmosphere: one side of the porous medium being swept with pure nitrogen, the other with nitrogen containing 0.5 to 2% vol. of helium.

The same kind of diffusion cell was used as that of Foster *et al.* [24], which cell had been designed to avoid boundary-layer effects and stagnant areas at the surface of the porous medium as much as possible. A disadvantage of the cell is—in our case—the risk of “inflow” of the passing gas.

The velocity of the gas at the surface of the porous medium was in the range 3–13 cm/s.

All experiments were performed at 46.5°C.

Diffusion experiments were also carried out with partly saturated media. For the saturating liquid dichloro acetic acid was chosen based on the following criteria: (i) wettability (ii) low vapour pressure (iii) possibility to determine the homogeneity of the liquid distribution by means of an X-ray absorption technique (iv) easy absorption of the vapour from the gas stream. Different saturations could be obtained using a suction technique, for very low saturations followed by evaporation.

Flow sheet

In Fig. 3 a flow sheet of the experimental apparatus is given. The nitrogen flow, brought to about 4 atm by reducing valve V_1 , is kept on a constant flux by a needle control valve B_1 . This flux is distributed over line (1) and line (2) in about equal proportions by means of the valves A_1 and B_2 .

The helium stream is brought to about 0.2 atm by V_2 . After passing a filter (F) the helium stream is brought on the desired level by means of B_3 . The flow rate is measured by means of the pressure drop (M_1) over a capillary. The pressure difference between the two sides of the porous medium (P) is kept below 0.1 mm H₂O by means of B_2 and A_2 .

The concentration of helium in flow (1) is measured by means of a conductivity cell (K_m , reference K_r). The

gas flows (1) and (2) are measured via rotameters or soap bubble meters (R_1 , R_2).

When the porous medium is partly saturated with dichloro acetic acid the vapour of the latter is absorbed at D with sodium hydroxide.

A complete measurement—including the setting and removal of the porous medium—can be carried out within 15 min.

Reliability and accuracy

The diffusibility of the porous media was calculated using equation (1). For the nitrogen–helium system R_{BA} is about 2.5 [21, 23]. Because the mole fraction of helium is 0.018 at a maximum it is not necessary to know the value of R_{BA} to any great accuracy.

The presence of dichloro acetic acid creates a three component system. Because the mole fraction of the acid vapour was only 0.0013 (no gradient in the pore space) it was assumed that equation (1) remains valid and that the value of D_{AB} remains the same.

The largest error source is the possibility of a total pressure gradient over the porous medium; this can give an error of 3 per cent at a maximum.

In order to test the reliability of the measurement technique eighteen experiments were performed with one and the same porous medium. The standard deviation for the determined diffusibilities was 2.5 per cent. Estimates based on known error sources gave standard deviation 2 per cent, “maximum” error 8 per cent.

These eighteen measurements include a variation of both the total gas flow and the concentration gradient with a factor 4, covering the range of all experimental conditions used.

Furthermore experiments were performed with seven “identical” porous media. The standard deviation for the determined matrix factor was here 5 per cent to be compared with an estimated maximum error of 10 per cent. The difference between the reproducibility for one and the same porous medium and that for numerically different but otherwise—as far as is known—identical porous media is caused by the inaccuracy in establishing the length and the porosity of the porous medium.

RESULTS AND DISCUSSION

The diffusibility of monodisperse random sphere packings

Pore space segments in random monodisperse packings will resemble those in regular sphere packings. Regular sphere packings are anisotropic, hence Q is direction dependent. Nevertheless values of τ and δ obtained for regular sphere packings will give some idea of those for random packings of round particles. Exact calculations of the diffusibility (by integration over the boundaries of a pore space segment) have been made

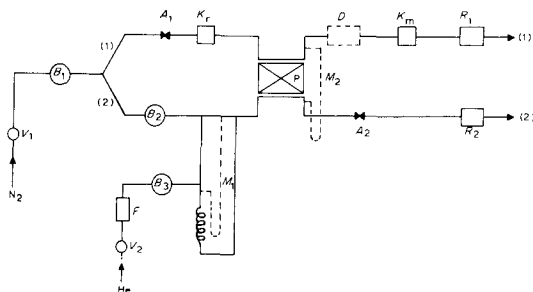


FIG. 3. Flow sheet of diffusion apparatus. See main text for explanation.

by Kessler [36] for different segments in regular packings. His experimental results as well as the estimates made by Adams [19] and Currie [10] correspond to these calculations within 5–10 per cent. According to the estimates of Adams δ is for the cubic ($\epsilon = 48$ per cent) as well as for the hexagonal ($\epsilon = 26$ per cent) packing about 0.75 (using Petersen's curve, cf. Fig. 2). Although Kessler's experimental results suggest that this value can be on the low side we will assume that the value of $\delta = 0.75$ can be used for all random monodisperse sphere packings.

Between the two extreme sphere packings of 26 and 48 per cent porosity the value of τ varies from 1 to 1.3 (and is, again, direction dependent, e.g. when it is said [10, 19] that the tortuosity of a cubic packing is 1, that is of course true only for a transport direction perpendicular to a plane through the sphere centers). Whether or not there is a unique relation between τ and ϵ for random packings, the error in Q will not be very large when we assume a linear change in τ from 1 to 1.3 over the range $\epsilon = 48$ –26 per cent, because the change in τ is anyway small.

Under these assumptions we obtain for the effective diffusivity in the porosity range 38–43 per cent (which covers the porosities normally found for random sphere packings):

$$D_{\text{eff}} = (0.57 \pm 0.04)\epsilon D_{AB}. \quad (6)$$

Our experiments with sphere packings of 40–80, 100–150 and 300–400 μm particles all confirmed equation (6) as do the more numerous and sophisticated experiments of Bennet and Bolch published recently [37]. The compilation of fifteen different sources, given in [37], for diffusion experiments with sphere packings shows a variation in Q from 0.5 ϵ to 0.8 ϵ .

We may conclude that for random monodisperse sphere packings an analysis in terms of ϵ , τ and δ —although in this case perhaps not necessary—corresponds with the experimental results as far as accuracy permits.

It may be remarked that the value for Q derived from equation (6) is—in the specified porosity range—much lower than the value of $2\epsilon/(3-\epsilon)$, which would be the theoretical value according to [16].

The diffusibility of polydisperse packings

Measurements with mixtures of round particles of different diameters confirm equation (6) when they have porosities in the specified range [38]. With mixtures it is, however, possible to obtain much lower porosities [39]. Theoretically one may expect that for such packings in which the smaller particles fill the voids between the larger particles both τ and δ will increase.

We did not find any significant change in q for mixtures having porosities between 30 and 43 per cent. Neither would we expect a significant change for still lower porosities.

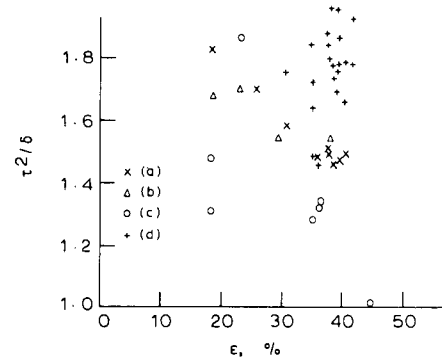


FIG. 4. The matrix factor as a function of the porosity for polydisperse sphere packings. (a) Currie [10]; (b) Vilain and Druelle [40]; (c) Shimizu *et al.* [41]; (d) this work.

The results reported in the literature are not consistent. Currie [10] reported a linear interdependence of q and ϵ , but when his results are compared with those of others (see Fig. 4) the only possible conclusion seems to be that for porosities between 20 and 50 per cent the matrix factor will lie somewhere between 1 and 1.9.

Inhomogeneous porous media

Theoretically we may expect the diffusibility of an inhomogeneous porous medium to be higher than that of a homogeneous porous medium with the same average porosity.

If we assume that the porous medium can be divided in parts that are internally homogeneous, each part has its own ϵ , τ and δ . The summation over the different parts will yield a higher overall Q because of what we might call a macroscopic constrictivity (for inhomogeneities in the transport direction) and a macroscopic tortuosity (for inhomogeneities perpendicular to the transport direction). For example when the porous medium is inhomogeneous in the transport direction only, we have

$$\bar{Q} = \frac{n}{\frac{1}{Q_1} + \frac{1}{Q_2} + \dots + \frac{1}{Q_n}}. \quad (7)$$

Calculation examples, however, show that the inhomogeneity of the porous medium will seldom change the overall diffusibility by more than 10 per cent.

Some experiments were carried out in which the inhomogeneity (expressed in terms of the local porosity) was varied over the length of the porous medium (i.e.

along the transport direction), partly by changing the packing, partly by deformation of the spheres during sintering (the latter might decrease δ in an absolute sense).

The porosity distribution for two extreme cases is given in Fig. 5. The values of Q as a function of the porosity variation are given in Table 3. As can be seen the influence of the inhomogeneity is negligible.

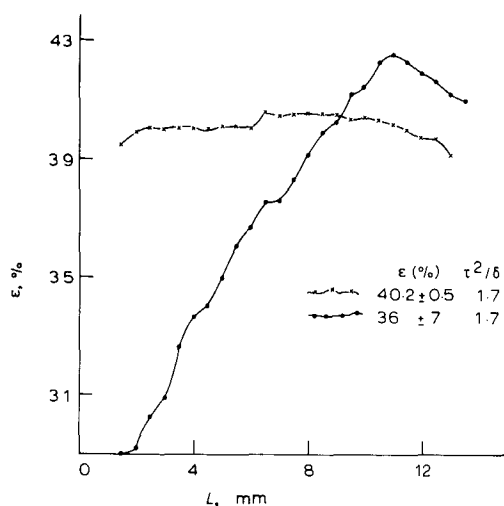


FIG. 5. Porosity distribution along the transport direction for a homogeneous and a heterogeneous porous medium.

Table 3. Matrix factor for inhomogeneous sphere packings

Porosity (%)	Matrix factor
36 ± 7	1.72
38.4 ± 3.7	1.85
41.9 ± 2.4	1.77
30.5 ± 1.5	1.75
35.6 ± 0.9	1.84
40.2 ± 0.5	1.65
39.2 ± 0.2	1.77

Hence the reported "important influence of the nature of the packing" on Q [9-11] is not confirmed; it is more probable that the high standard deviation for experiments with numerically different porous media is the cause of bad reproducibility (cf. also Fig. 4).

The diffusibility of partly saturated sphere packings (pendular liquid)

When a packing of particles, initially completely saturated with a wetting liquid, is drained some liquid will remain behind around the contact points of the

particles. These isolated rings of liquid have been called pendular liquid in distinction of funicular liquid, in which case the liquid phase in the porous medium is continuous. The change of the funicular to the pendular phase for round particles is at about 8 per cent of the liquid content [42, 43].

Some experimental results for the matrix factor in the "pendular state" are given in Fig. 6. It appears that q changes linearly with the liquid content, u . The homogeneity of the liquid distribution appeared to have no significant influence.

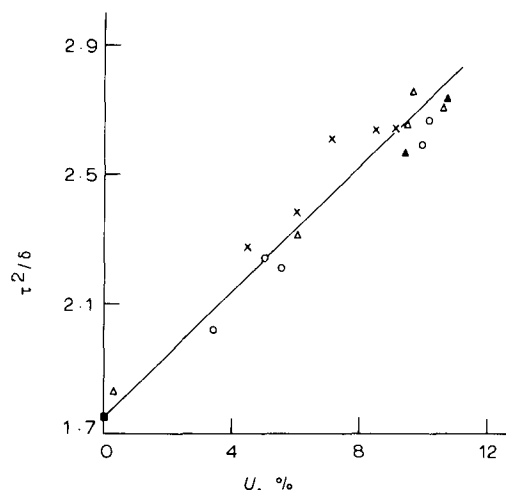


FIG. 6. The matrix factor for a partly saturated porous medium as a function of the liquid content (pendular state). Different symbols (○, △, ×, ▲) indicate experiments with different porous media; for easy comparison the results were corrected in such a way that the points for τ^2/δ at $u = 0$ per cent coincide for the different porous media.

We may emphasize that the (gas phase) porosity changes only from, for example, 38 to 34 per cent when u goes from 0 to 10 per cent. This implies that none of the functions depicted in Fig. 1 are appropriate in describing diffusion in the pendular state (cf. curve g in Fig. 1). Although the absolute values for Q in the pendular state as found by Currie [44] are about 10 per cent lower than ours, it can be deduced from his data that he also observed a linear relationship between q and u in the pendular state; moreover with the same slope as we do (Currie himself analyses his results, for pendular as well as funicular liquid, in terms of the empirical correlation $Q = \gamma \epsilon^u$).

The change in q as a function of u can be wholly attributed to a change in δ , cf. Fig. 7. The liquid in the pendular rings will not or hardly change the position of the main diffusion paths and hence τ will remain constant. On the other hand it can be seen

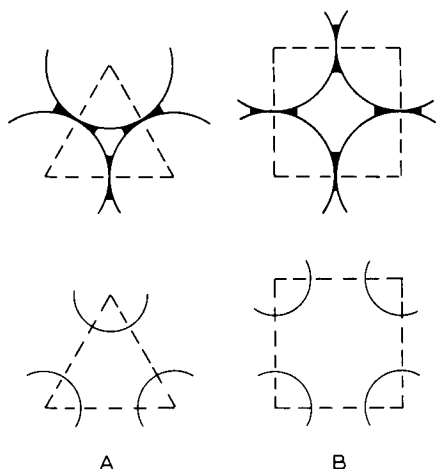


FIG. 7. Intersections of regular sphere packings with pendular liquid. (A) tetrahedral cell; (B) cubic cell.

that the pendular liquid does change the minimum cross section while for the greater part of a pore space segment the cross-sectional area remains the same.

Assuming that τ remains constant the experimental results show a change in δ from 0.75 to 0.48 over the range $u = 0$ –10 per cent. This can be compared—following Adam's method of calculation [19]—with a maximum change in δ for the cubic, tetrahedral, and rhombohedral pore space segments (containing pendular liquid) of 0.7–0.75 to 0.49–0.57.

We may conclude therefore that the variation of the matrix factor in the pendular state is due to a variation in the constrictivity and for the latter:

$$\delta = 0.75 - 0.027u, \quad 0 < u < 10. \quad (8)$$

The diffusibility in partly saturated sphere packings (funicular liquid)

Regarding the diffusion in porous media with funicular liquid only a semiquantitative account is possible. The reason for this is that the liquid distribution in the porous medium depends strongly on the "history" of the liquid. If we think of the pore space as consisting of "cells" and "connections" then at a certain liquid content certain cells and connections will be filled with liquid. But which cells and which connections cannot be said *a priori*. It may be emphasized that a simple analysis in terms of a so called pore size distribution is only confusing and disguises the important statistical and historical aspects of the problem as well as the fact that there do not exist isolated menisci (corresponding with "pores") in the porous medium. It is, however, not the purpose of this paper to discuss the problems of the statics and dynamics of capillary liquid in porous media. It is enough to realize that at

the same u , Q can vary considerably depending on the liquid distribution in the porous medium.

The constrictivity will not decrease further in the funicular state. The minimum cross section corresponds with touching pendular rings (cf. Fig. 7). At higher liquid contents the now annular ring in the minimum cross-section will become unstable soon and will collapse, thus closing a connection. If anything, one would expect δ to increase because, the minimum cross-section remaining constant, the maximum cross-section can only decrease with increasing liquid content.

At low u in the funicular state one can expect first a small and when u increases a stronger increase in τ caused by the closing of cell connections one after another. At higher liquid contents the more or less random distribution of the liquid will cause two effects:

- (i) An inhomogeneity effect which can be thought of as a macroscopic tortuosity. For this kind of tortuosity an analysis in terms of a random adjacent plane concept seems appropriate.
- (ii) The occurrence of "dead-end pores": a gas phase region in the porous medium that is only accessible from one side.

Some experimental results for q in the funicular state are given in Fig. 8 and Fig. 9. Figure 8 is for a very homogeneous porous medium. The almost constant q between 8 and 15 per cent corresponds with the physical picture outlined above, but this may be accidental.

From Fig. 9 it can be seen that the scatter is much larger than can be accounted for by the accuracy of the measurement technique. The scatter has to be attributed to the irreproducibility of the procedure by

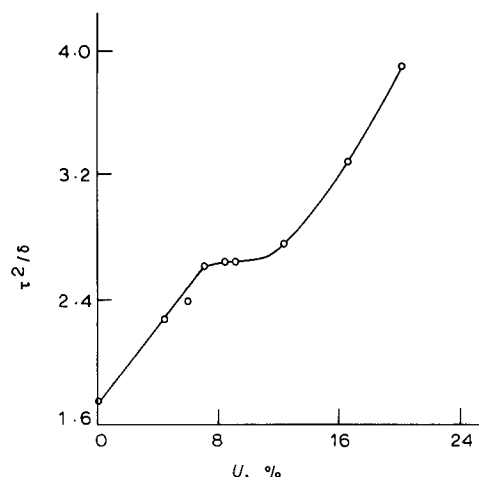


FIG. 8. Matrix factor for a very homogeneous partly saturated porous medium as a function of the liquid content.

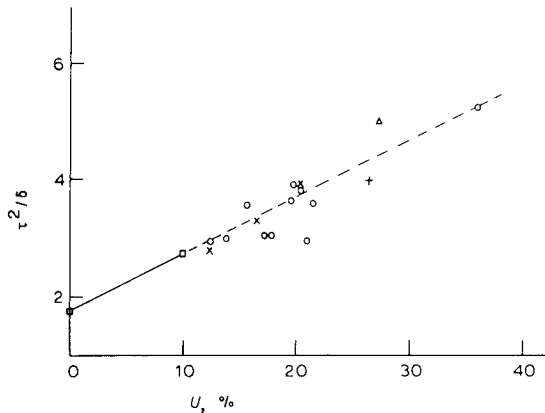


FIG. 9. Matrix factor for partly saturated sphere packings as a function of the liquid content (funicular state). The line from 0 to 10 per cent has been taken from Fig. 6. Different symbols (\circ , \times , \triangle , $+$) indicate experiments with different porous media.

which the porous media were drained. Some experiments were performed at a liquid content of 60 per cent. The results in this case were completely unpredictable: the matrix factor varying between 12 and ∞ . This is in conformity with the reported variation in the liquid content at which Q becomes zero [45, 46].

In concordance with the account given above published results for the diffusibility of partly saturated sphere packings are not consistent. Currie [44] obtained for q about the same values as we did. However both Vilain and Druelle [40] and Reist [38] obtained lower values.

Some generalizations to more complex porous media

In many cases one is not concerned with diffusion in partly saturated porous media. Nevertheless the results for partly saturated sphere packings are relevant to the interpretation of the diffusibility of porous media with a more complex pore space. One can think for example of catalysts and the kind of media encountered in geology.

In conductivity as well as in diffusion experiments values of q up to 20 and higher have been reported. Because the matrix factor is, in general, analysed only in terms of the tortuosity this may lead to conclusions like that of Carman that [31] "The physical meaning of these high tortuosities is not at all clear". What will, however, be clear is that a value of 10 or even 20 for q is not so strange, given the considerations presented above. If we take for δ a minimum value of 0.35 (cf. Fig. 2) and τ at low porosities at a maximum of $\sqrt{3}$ it is anyway reasonable to expect a value of 10 for q , even for a homogeneous isotropic porous medium.

Much higher values can be expected for inhomogeneous porous media or porous media in which dead-

end pores are present that are not accounted for via the porosity used in equation (5). In analogy with the results for the funicular state one may expect that especially for low porosities the influence of dead-end pores can be considerable.

It is of interest to note that it is a well known fact in geology that the electric conductivity (and hence the diffusion) in porous stones depends strongly on the measure of "cementation" [47, 48], e.g. in conductivity measurements a value of 22 for q was obtained on a porous medium (having a porosity of about 15 per cent) that had been constructed by adding a cementing agent to a mixture of glass beads [47]. As in the pendular state the cementing agent will first concentrate at the contact points of the particles and then start to close connections.

CONCLUSIONS

(i) The diffusibility, Q , of a homogeneous isotropic porous medium can be analysed in terms of three parameters, all having a sound physical basis: the porosity, ϵ , the tortuosity, τ , and the constrictivity, δ .

(ii) Q is proportional to ϵ . The porosity is the specific volume available for diffusion. Arguments contending the surface porosity to be different from the volume porosity for isotropic media are invalid.

(iii) Q is proportional to τ^{-2} . The tortuosity can be defined in terms of the average main diffusion path. For homogeneous isotropic media τ is a function of ϵ , and can take values between 1 and $\sqrt{3}$. For most particle packings τ will be close to 1.15.

(iv) Q is proportional to δ . The constrictivity can be defined in terms of the ratio of the maximum and minimum cross-sectional area of a pore space segment. For homogeneous isotropic round particle packings δ is about 0.75 (lower boundary).

(v) The importance of distinguishing between τ and δ is supported, *inter alia*, by the functionalism in describing diffusion in partly saturated sphere packings; by the possibility of estimating τ and/or δ *a priori*; and by the possibility of determining δ independently by means of mercury porosimetry.

(vi) None of the proposed $Q-\epsilon$ relations is suitable for describing the diffusibility of partly saturated porous media.

(vii) For sphere packings containing pendular liquid τ is independent of the liquid content, u , and δ changes linearly with u .

(viii) For porous media containing funicular liquid no *a priori* statements can be made about Q because the liquid distribution depends strongly on its history and small inhomogeneities in the porous medium.

Acknowledgement We thank Ir. O. R. Booi for performing most of the experimental work in the final year of his studies.

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ANALYSE DE LA DIFFUSION GAZEUSE DANS DES MILIEUX MACROPOREUX A
L'AIDE D'UN FACTEUR DE POROSITE, DE TORTUOSITE ET DE RETRECISSEMENT

Résumé— Le rapport entre le coefficient de diffusion effectif dans des milieux macroporeux et le coefficient de diffusion en absence de milieu poreux est décrit en fonction de la porosité, de la tortuosité et d'un facteur de rétrécissement.

La nécessité de discerner ces trois paramètres est soutenue par la description de la diffusion dans des empilements homogènes, isotropiques, et partiellement saturés de billes de verre monodispersés. Les résultats sont généralisés à tous les milieux poreux homogènes et isotropiques pour les porosités de 0 à 50 pour cent.

ANALYSE DER DIFFUSION IN SCHÜTTUNGEN UND
PORIGEN GÜTERN MITTELS DER POROSITÄT,
EINES UMWEGFAKTORS UND EINES ERWEITERUNGSFAKTORS

Zusammenfassung—Das Verhältnis zwischen dem Diffusionswiderstand eines porigen Gutes und der Diffusionszahl wird beschrieben als eine Funktion der Porosität, eines Umwegfaktors und eines Erweiterungsfaktors. Die Notwendigkeit, diese drei Parameter zu unterscheiden, ist durch die Funktion für die Beschreibung der Diffusion in homogenen, isotropen, teilweise gesättigten Schüttungen von monodispersen Glaskugeln bedingt.

Die Resultate werden im Hinblick auf die Diffusion in allen homogenen, isotropen, porigen Gütern mit Porositäten von 0–50% verallgemeinert.

АНАЛИЗ ДИФФУЗИИ В КАПИЛЛЯРНО-ПОРИСТЫХ ТЕЛАХ ПРИ ПОМОЩИ
СТРУКТУРНЫХ ХАРАКТЕРИСТИК: ПОРИСТОСТИ, ПРОСВЕТА И ИЗВИЛИСТОСТИ

Аннотация — Соотношение между эффективным коэффициентом диффузии газа в капиллярно-пористых телах и коэффициентом диффузии при отсутствии пористого тела анализируется при помощи структурных характеристик: пористости, просвета и извилистости. Необходимо различать эти три параметра для описания диффузии в частично насыщенных, однородных, изотропных монодисперсных упаковках сферических частиц.

Результаты обобщаются для всех однородных изотропных пористых тел в области пористости от 0-50%.