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## Gaseous diffusion in porous media. Part 2. - Dry granular materials

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# Gaseous diffusion in porous media.

## Part 2.—Dry granular materials

by J. A. CURRIE, Ph.D., Rothamsted Experimental Station, Harpenden, Herts.

[Paper received 5 January, 1960]

### Abstract

The diffusion of hydrogen through cylindrical samples of porous granular materials, 3 in. long and 2 in. diameter, was measured by the non-steady state technique of Part I<sup>(19)</sup>, and reduced coefficients of diffusion  $D$ , referred to the value  $D_0$  in free air, were calculated for over twenty materials with porosity  $\varepsilon$  between 0.18 and 0.98. Results are comparable with those obtained by other methods, and with those for analogous electrical properties of porous media. Replicate determinations on a given sample agree to within 1%, but larger differences, caused by variations in packing, are observed between duplicate samples of the same porosity. It is shown theoretically that  $D/D_0 = (l/l_e)^2 f \varepsilon$ , where  $f$  and  $l_e/l$  are factors for non-uniformity of cross-section and the increased length of the tortuous path followed by the gas, respectively. The influence on  $D/D_0$  of not only porosity, but also particle shape, was clearly shown and there can therefore be no unique relationship for all materials, as often supposed, between diffusion rates and porosity. The equations of Burger and Bruggeman, both of which include a particle shape factor, were tested on the experimental data and neither was entirely satisfactory. An empirical equation of the form  $D/D_0 = \gamma \varepsilon^\mu$  fits all materials where  $\gamma (\leq 1)$  and  $\mu (\geq 1)$  are constants for a specific type of granular material, and probably represent measures of pore shape. Two particle shape parameters, relative surface area and equivalent settling radius, were measured for a limited number of materials, but at best, only a general trend between these and the experimental values for the Bruggeman shape factor was observed.

### Introduction

DIFFUSION in a porous medium is less rapid than in free air because of the reduced area of available cross-section and increased path length. An effective coefficient of diffusion  $D$  can be measured, and there have been many attempts to find a unique relationship between  $D/D_0$  and the pore space  $\varepsilon$ , where  $D_0$  is the diffusion coefficient in free air. An equation of the type  $D/D_0 = \varepsilon^m$  satisfies the formal requirements at the limiting values of  $\varepsilon = 0$  and  $\varepsilon = 1.0$ , and though Buckingham<sup>(1)</sup> deduced that  $m = 2$  from his work on soils, later workers have sought equations of the form  $D/D_0 = a\varepsilon$  or  $a\varepsilon + b$ , applicable to a restricted range of porosity. Penman,<sup>(2)</sup> using a wide variety of porous materials, gave  $a = 0.66$ ,  $b = 0$  over the range  $0 < \varepsilon < 0.6$ ; van Bavel,<sup>(3)</sup> from a more limited range of dry granular materials, suggested that  $a = 0.58$  was more satisfactory for practical (agronomic) purposes; and Flegg,<sup>(4)</sup> investigating the effect of soil aggregate size on diffusion

rate, obtained values of  $a$  between 0.53 and 0.89 working in the range  $0.35 < \varepsilon < 0.99$ . Dye and Dallavalle,<sup>(5)</sup> using powdered potassium perchlorate, found that in the range  $0.2 < \varepsilon < 0.4$ ,  $a$  varied between 0.73 and 0.90, whereas Rust and others,<sup>(6)</sup> using mixtures of quartz sands, glass beads and silica flour, found  $a = 0.60$ ,  $b = 0.04$  for air dry materials, and  $a = 0.68$ ,  $b = 0.01$  for wetted materials. Of others who have given  $b$  a value other than zero, Blake and Page,<sup>(7)</sup> making measurements on two soils *in situ*, gave  $a = 0.71$ ,  $b = 0.01$ , and  $a = 1.3$ ,  $b = -0.13$ . Taylor<sup>(8)</sup> calculated  $a = 0.97$ ,  $b = -0.09$ ;  $a = 0.78$ ,  $b = -0.08$ ; and  $a = 0.67$ ,  $b = 0.00$  for quartz sand, powdered glass and soil respectively. Though Raney<sup>(9)</sup> has measured diffusion rates in field soils, values of  $a$  or  $b$  cannot be inferred from his data.

Theoretical studies have been by analogy. De Vries<sup>(10)</sup> used the formula derived by Burger<sup>(11)</sup> for the electrical conductivity of an alloy of one metal having inclusions of elliptical particles of another, setting

$$D/D_0 = \varepsilon / \{1 + (k - 1)(1 - \varepsilon)\}$$

where  $k$  is a shape factor. He showed that, for  $k = 1.5$  (the value attributed to spherical particles by Burger), and where porosity is adjusted for a percentage of blocked pores, a relationship is given which is in good agreement with Penman's experimental results for soils. There is, however, no theoretical justification for his assumption that the blocked pore space is given by  $\beta(1 - \varepsilon)\varepsilon$  where  $\beta$  has been assigned the value 0.4. De Vries<sup>(12)</sup> considers in greater detail the applicability of several formulae to the analogous flow of heat through porous media. Of these, that of Burger, already mentioned, and another from Bruggeman,<sup>(13)</sup> are most nearly in accord with experimental data for heat flow. For gaseous diffusion, the Bruggeman equation becomes  $D/D_0 = \varepsilon^m$ , where  $m$  is a shape factor, and though it can be shown that Burger's equation is a special case of the Bruggeman equation, with  $m \simeq k$ , the range of porosity over which they are equivalent is limited. Both formulae indicate that diffusion rate depends not only on porosity, but also on particle shape. This dependence on particle shape has been ignored in many attempts to find a unique relationship for all diffusion data, though it has been noted that certain specific materials gave results somewhat removed from the general trend in others. Penman<sup>(2)</sup> attributed such differences in glass spheres and mica to the variations in diffusion path length with particle shape and also, in mica, to anisotropy of structure. Flegg<sup>(4)</sup> pointed out that the low values of  $D/D_0$  for vermiculite were obtained because "such materials with a plate-like structure are not to be expected to behave in the same way as more granular materials". De Vries,<sup>(10)</sup> though he introduced the concept of shape factor into gaseous

diffusion studies, did not exploit it in his analysis of Penman's results, preferring to use a constant value of  $k = 1.5$  (for spherical particles), and explained deviations from the theoretical in terms of non-continuous air space or "blocked pores". A re-examination of Penman's results shows that—as examples—the behaviour of glass spheres, sand and salt can fit the Burger equation if  $k$  is given the values 1.43, 1.81 and 2.16 respectively.

Marshall<sup>(14, 15, 16)</sup> has adapted a theoretical treatment of viscous flow of liquid in a porous system<sup>(14)</sup> to give  $D/D_0 = \varepsilon^{3/2}$  for gaseous diffusion<sup>(15)</sup> and got approximate agreement<sup>(16)</sup> with the data of Taylor<sup>(8)</sup> for wetted materials. A modification of the original theory by Millington and Quirk<sup>(17)</sup> leads to  $D/D_0 = \varepsilon^{7/6}$ . Millington<sup>(18)</sup> has since proposed that  $D/D_0 = \varepsilon^{4/3}$ .

### Theoretical

**Steady state flux.** Consider unit partial pressure difference maintained across a porous solid of length  $l$ , and cross-section  $A$ . The flux can be written in terms of an effective diffusion coefficient  $D$ , as  $DA/l$ . If now the porous solid is regarded as made up of a system of tortuous tubes of average length  $l_e$  ( $l_e > l$ ), and of total cross-section, normal to the length,  $A_e$  ( $A_e < A$ ), then the flux may also be written as  $D_0 A_e / l_e$ . It seems reasonable to set the porosity as

$$\varepsilon = A_e l_e / Al$$

from which

$$D/D_0 = (l/l_e)^2 \varepsilon \quad (1)$$

**Non-steady state flux.** If a volume  $Aa$  of a gas, initially at concentration  $c_0$ , is allowed to diffuse through a porous solid of volume  $Al$  and length  $l$  in which the initial concentration of the same gas is zero, then the rate of change of concentration at the common interface is given by equation (6) of Part I<sup>(19)</sup> as

$$\partial \ln c / \partial t = -D\alpha_1^2 / \varepsilon \quad (2)$$

where  $\alpha_1$  is the first positive root of

$$\alpha \tan \alpha l = \varepsilon / a \quad \text{or} \quad \alpha_1 l \tan \alpha_1 l = \varepsilon l / a.$$

For the equivalent set of parallel tubes, length  $l_e$ , the decay equation is

$$\partial \ln c / \partial t = -D_0 \alpha_0^2 \quad (3)$$

where  $\alpha_0$  is the first positive root of

$$\alpha \tan \alpha l_e = (1/a)(A_e/A) \quad \text{or} \quad \alpha_0 l_e \tan \alpha_0 l_e = A_e l_e / aA \quad (4)$$

But  $A_e l_e = \varepsilon Al$  and hence the last equation becomes

$$\alpha_0 l_e \tan \alpha_0 l_e = \varepsilon l / a \quad (5)$$

Hence

$$\alpha_0 l_e = \alpha_1 l$$

Also

$$\alpha_0^2 D_0 = \alpha_1^2 D / \varepsilon$$

i.e.

$$D/D_0 = \varepsilon (l/l_e)^2 \quad (6)$$

Equation (6), derived for both steady and non-steady state flow, is applicable only to the ideal porous material in which all the pores are of uniform cross-section throughout their length.

**Diffusion through tubes of non-uniform cross-section.** The

total effective cross-section may be reduced as a result of constrictions along the length of the tube from  $A_e$  to  $A_e'$ , where  $A_e'/A_e = f$ . The diffusion equation is therefore more correctly derived in the form

$$D/D_0 = (l/l_e)^2 f \varepsilon \quad (7)$$

The value of  $f$  is considered in the Appendix, for one of the simplest possible cases, a sinusoidal form.  $D_0 \varepsilon / D$  is frequently referred to as the tortuosity factor, but it can be clearly seen that, as Carman<sup>(20)</sup> suggested, this is no longer justifiable.

### Determination of $D/D_0$

For a system of fixed geometry (known  $l$  and  $a$ ),  $\alpha_1$  is uniquely determined when  $\varepsilon$  is known; and hence  $\alpha_1^2 / \varepsilon$  {equation (2)} is simply a function of  $\varepsilon$ , say  $\phi(\varepsilon)$ . For a tenfold change in concentration in time  $\Delta t$ , then

$$D = 2.303 / \Delta t \phi(\varepsilon) \quad (8)$$

A graph of  $2.303/\phi(\varepsilon)$  against  $\varepsilon$  was prepared (it is indistinguishable from a straight line) and with  $\varepsilon$  known and  $\Delta t$  measured,  $D$  is easily determined and corrected for temperature and pressure.

The technique for measuring  $\Delta t$  is identical with that described in Part I for the straight tube model. For diffusion measurements on granular materials, the sample was packed into a brass tube where it was supported by a gauze at the lower end. The tube was then inserted into the recess in the fixed lower plate of the apparatus. Porosities were calculated from the internal dimensions of the tube, the weight of the sample and the true particle density where

$$\varepsilon = 1 - \frac{\text{weight of sample}}{\text{volume of tube} \times \text{true density}} \quad (9)$$

The supporting gauze offers a resistance to diffusion proportional to its thickness and inversely proportional to its free cross-sectional area. By the choice of suitable material, this resistance was kept to a minimum. Nylon mesh having a total thickness of 0.1 mm and a free cross-sectional area of about 90% was used whenever possible. For coarse materials, a 1.5 mm hexagonal mesh was used and, for fine powders, a portion of nylon stocking. The resistance of these materials can be shown by calculation to be less than 0.1% of the resistance of a typical sample. For more dense materials, the greater rigidity of a woven wire mesh was preferred and, by calculation, its resistance decreased the value of  $D/D_0$  by 0.25%.

Whenever possible, samples were carefully packed to avoid compression and consequent distortion of particles. Variations in porosity about the expected mean for random packing were achieved by lightly tapping the brass tube. Excessive variations in packing were avoided in the more compressible materials, to prevent orientation of particles and consequent anisotropic structure, but the experimental evidence suggests that this was not always successful. Care was taken to ensure that the sample surface was level with the top of the tube to avoid errors in the values taken for  $a$ ,  $l$  and  $\varepsilon$ .

The value of  $D_0$  used to calculate the ratio  $D/D_0$  was  $0.651 \text{ cm}^2 \text{ s}^{-1}$ , as determined in Part I with the same apparatus. Errors in the original measurements are in the same sense as those occurring in the measurements of  $D$ , and will tend to be minimized in the final expression of the results in the form  $D/D_0$ .

## Experimental results

Fig. 1 shows the values for  $D/D_0$  (Table 1) plotted against the corresponding values of  $\varepsilon$ . At first sight these results seem to fit the equation  $D/D_0 = 0.60\varepsilon$  for  $0 < \varepsilon < 0.8$ . The data for materials having  $\varepsilon > 0.8$  do not conform to the above relationship and cannot be interpreted satisfactorily without reference to the probable effects of particle shape.

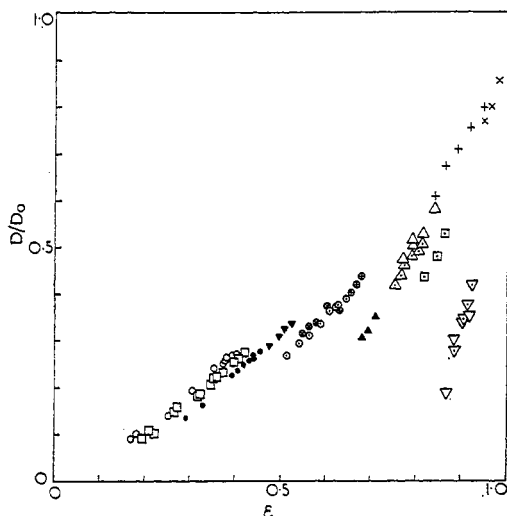


Fig. 1. Dependence of coefficient of diffusion on porosity.  $D/D_0$  and  $\varepsilon$

- |                         |                           |
|-------------------------|---------------------------|
| ○ Glass spheres         | △ Kaolin (Suprex)         |
| □ Sand                  | △ Kaolin (Peerless No. 2) |
| ● Carborundum           | + Celite                  |
| ▼ Sodium chloride       | × Steel wool              |
| ⊗ Barnfield soil crumbs | □ Perspex flakes          |
| ○ Woburn soil crumbs    | ▽ Vermiculite             |
| ⊙ Highfield soil crumbs | ▽ Mica                    |
| ▲ Pumice                |                           |

**Burger and Bruggeman equations.** Fig. 2, where  $D/D_0\varepsilon$  was plotted against  $\varepsilon$ , shows that within the group of points for each type of particle,  $D/D_0\varepsilon$  is not constant, but is itself a function of porosity as the equations of Burger and Bruggeman predict. It should be borne in mind that these formulae were derived for ellipsoidal particles. Comparison of the diffusion data obtained by experiment with the theoretical values from these equations should therefore be restricted to the glass beads, but on the assumption that all other particles have an equivalent ellipsoidal form, it has been extended to them too. Values for  $k$  and  $m$ , the Burger and Bruggeman shape factors, were computed for all the experimental points where  $k = \{\varepsilon/(1 - \varepsilon)\} \{(D_0/D) - 1\}$  and

$$m = \log (D/D_0) / \log \varepsilon.$$

Table 1 shows the variability of both factors. Each type of material gives a range of values for  $k$  and  $m$ . Materials which give a "rigid" packing over a limited range of porosities, e.g. glass spheres, sands, carborundum and soil crumbs, show a smaller variability than those giving "soft" packings over a much larger range of porosities, e.g. mica, kaolin and celite (a diatomaceous silica). Because of their rigidity of packing, materials of the first type can exhibit only minor variations in pore geometry, whereas those of the second type are prone to compression and particle orientation giving anisotropic structure, and have therefore a much more variable pore

geometry. It must be remembered that  $k$  and  $m$  are particle shape factors, whereas diffusion depends directly on pore shape. When a porous material is packed in such a way

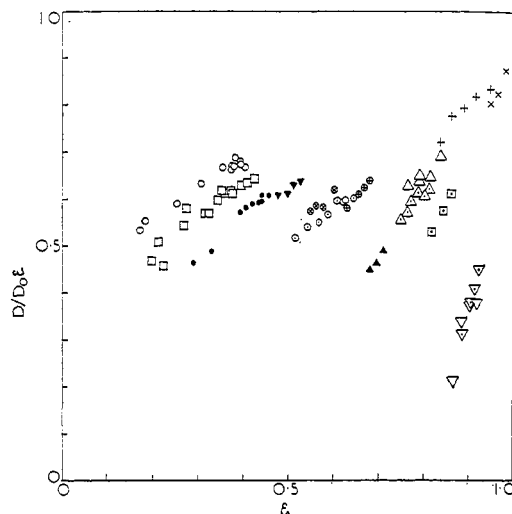


Fig. 2. Dependence of coefficient of diffusion on porosity.  $D/D_0\varepsilon$  and  $\varepsilon$

- |                         |                           |
|-------------------------|---------------------------|
| ○ Glass spheres         | △ Kaolin (Suprex)         |
| □ Sand                  | △ Kaolin (Peerless No. 2) |
| ● Carborundum           | + Celite                  |
| ▼ Sodium chloride       | × Steel wool              |
| ⊗ Barnfield soil crumbs | □ Perspex flakes          |
| ○ Woburn soil crumbs    | ▽ Vermiculite             |
| ⊙ Highfield soil crumbs | ▽ Mica                    |
| ▲ Pumice                |                           |

that the shape of the particles no longer confers a characteristic shape on the pores, a particle shape factor cannot be expected to account for much of the variance in experimental results.

For spheres, sand and carborundum powder, the value of  $k$  is constant for packings of uniform size, but is bigger for packings of mixed sizes; and the value of  $m$  is constant whether the particles are uniform or mixed. The expected value for spheres is  $k = m = 1.5$ , but the values found (Table 1) are  $k = 1.80$ ,  $m = 1.41$ , agreeing well with values that can be deduced from data given by Carman<sup>(20)</sup> for which  $k = 1.73$ ,  $m = 1.39$ , or by Wooding<sup>(21)</sup> (working on the stability of diffusing liquids), from which  $k = 1.88$ ,  $m = 1.45$ . Pearce,<sup>(22)</sup> working on the analogous problem of the electrical properties of oil/water emulsions, showed that an equation, identical with that of Burger, when applied to gaseous diffusion in spherical particles, is excellent for the ordered distributions of spheres and cylinders for which it was produced, but is not adequate for random distributions: and De Vries<sup>(12)</sup> found the Burger equation to be of limited value in predicting the thermal conductivity of a granular system. The difference between the theoretical value of  $k (= 1.5)$  and the observed value ( $1.80$ ) may be partly because of the randomness in the packing of the spheres.

The Bruggeman equation was derived for a random distribution of spheres, and though the agreement between theory ( $m = 1.5$ ) and observation ( $m = 1.41$ ) is much better than for the  $k$  values, there is a consistent difference yet to be accounted for. It is unlikely to arise from particle size distribution, as suggested by Pearce, because for spheres,  $m$  changes very little over a range of mixtures having the ratios of maximum to minimum diameter of 10 : 1, and there

Table 1. Values for  $\varepsilon$ ,  $D/D_0$ ,  $k$  and  $m$ 

[Figures in first column are particle diameters (in mm)]

Material	$\varepsilon$	$D/D_0$	$k$	$m$	Material	$\varepsilon$	$D/D_0$	$k$	$m$
Spheres					Highfield soil crumbs				
0.75-0.80	0.405	0.271	1.83	1.44	1-2	0.680	0.436	2.75	2.15
0.75-0.80	0.396	0.267	1.80	1.42		0.669	0.419	2.80	2.16
0.75-0.80	0.381	0.256	1.79	1.41		0.656	0.401	2.85	2.17
0.38	0.395	0.269	1.77	1.41		0.630	0.367	2.93	2.17
0.38	0.383	0.263	1.74	1.39	Talc (powdered)	0.768	0.473	3.67	2.84
5-6	0.375	0.249	1.80	1.42		0.747	0.420	4.08	2.97
5-6	0.376	0.252	1.79	1.41		0.727	0.399	4.01	2.88
Mixtures	0.255	0.150	1.94	1.39		0.708	0.404	3.56	2.62
Mixtures	0.355	0.240	1.74	1.38	Kaolin: Suprex	0.813	0.506	4.07	3.28
Mixtures	0.183	0.101	1.99	1.35		0.804	0.490	4.27	3.27
Mixtures	0.307	0.194	1.84	1.38		0.788	0.483	3.98	3.05
Sand						0.773	0.461	3.98	3.01
0.25-0.50	0.424	0.274	1.95	1.51		0.765	0.438	4.18	3.08
0.25-0.50	0.402	0.254	1.97	1.50		0.752	0.419	4.19	3.05
0.25-0.50	0.375	0.231	1.99	1.50	Peerless 2	0.839	0.582	3.74	3.09
0.25-0.50	0.355	0.221	1.94	1.46		0.813	0.527	3.91	3.09
2-3	0.411	0.262	1.97	1.50		0.791	0.503	3.74	2.93
1-2	0.361	0.222	1.98	1.48		0.790	0.513	3.58	2.83
$\frac{1}{2}$ -1	0.399	0.253	1.97	1.50		0.767	0.482	3.53	2.75
$\frac{1}{2}$ -1	0.377	0.231	2.01	1.50	Celite	0.950	0.795	4.88	4.47
Mixtures	0.321	0.182	2.12	1.50		0.945	0.784	4.73	4.30
Mixtures	0.269	0.147	2.14	1.46		0.940	0.786	4.26	3.88
Mixtures	0.346	0.207	2.03	1.48		0.918	0.753	3.67	3.22
Mixtures	0.325	0.186	2.11	1.50		0.891	0.708	3.37	2.99
Mixtures	0.274	0.159	2.00	1.47		0.864	0.672	3.10	2.72
Mixtures	0.223	0.103	2.51	1.51		0.840	0.607	3.40	3.00
Mixtures	0.197	0.092	2.42	1.56	Vermiculite				
Mixtures	0.212	0.108	2.22	1.43	(< 2)	0.924	0.419	16.79	10.98
Spheres/sand						0.915	0.377	17.79	11.06
Mixtures	0.171	0.091	2.06	1.44		0.905	0.346	18.00	10.85
Carborundum	0.442	0.269	2.15	1.61		0.886	0.278	20.18	10.57
	0.442	0.263	2.22	1.64	Mica				
	0.434	0.257	2.22	1.63	(powdered)	0.919	0.351	20.98	12.38
	0.421	0.248	2.21	1.61		0.904	0.341	18.20	10.67
	0.407	0.237	2.21	1.60		0.885	0.302	17.79	9.79
	0.456	0.269	2.27	1.67		0.867	0.186	28.53	11.78
	0.456	0.285	2.10	1.59	Pumice				
Mixtures	0.394	0.226	2.23	1.60	2	0.710	0.350	4.55	3.07
	0.330	0.162	2.55	1.64		0.695	0.323	4.77	3.11
	0.293	0.135	2.66	1.63		0.681	0.308	4.80	3.07
Sodium chloride	0.527	0.336	2.20	1.70	Perspex flakes				
(irregular crystals)	0.512	0.323	2.21	1.69	1-2	0.863	0.528	5.63	4.33
	0.499	0.308	2.24	1.69		0.846	0.480	5.95	4.39
	0.476	0.289	2.23	1.69		0.819	0.436	5.86	4.16
Sodium metasilicate	0.530	0.339	2.20	1.70		0.802	0.435	5.26	3.77
(fragmented material)	0.502	0.314	2.20	1.68	Steel wool				
	0.470	0.292	2.15	1.63	Domestic	0.984	0.853	10.57	9.87
	0.463	0.281	2.21	1.65		0.967	0.798	7.42	6.53
Woburn soil crumbs	0.645	0.389	2.85	2.15		0.951	0.767	5.90	5.28
2-3	0.623	0.371	2.80	2.10	Plaster of Paris	0.492	0.230	3.24	2.07
	0.609	0.364	2.72	2.04	Polyurethane plastic foam	0.974	0.662	19.13	15.71
0.2-0.5	0.627	0.375	2.80	2.10	Brass turnings	0.691	0.457	2.66	2.12
0-2.0	0.589	0.335	2.84	2.07	Ceramic beads	0.535	0.304	2.63	1.90
	0.563	0.310	2.87	2.04					
	0.541	0.293	2.84	2.00	Hypo*			1.88	1.47
	0.515	0.267	2.91	1.99	Magnesium sulphate*			2.23	1.65
Barnfield soil crumbs					Sucrose*			1.91	1.51
1-2	0.603	0.374	2.54	1.94	Sodium citrate*			1.90	1.49
	0.578	0.338	2.59	1.98	Sulphate of ammonia*			2.12	1.57
	0.562	0.330	2.60	1.92					
	0.548	0.315	2.64	1.92					

\* Mean of ten determinations at different  $\varepsilon$  values.

is even less variation in  $m$  for carborundum powder mixtures in which the diameter ratio changed from 100 to 1.

### Empirical relation

When  $\log D/D_0$  is plotted against  $\log \epsilon$  (Fig. 3), the set of points for a given material lie on a straight line. A general

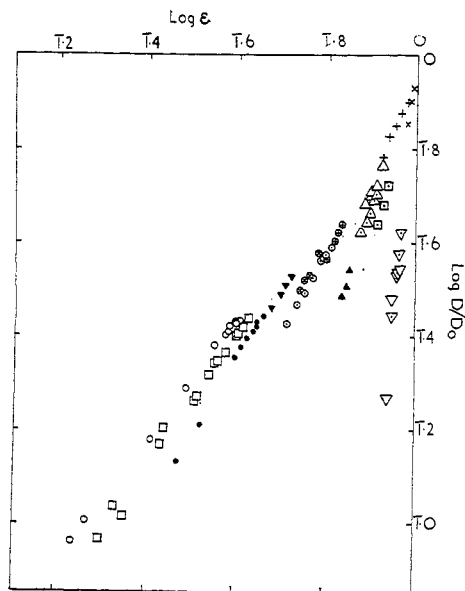


Fig. 3. Dependence of coefficient of diffusion on porosity.  $\log(D/D_0)$  and  $\log \epsilon$

- |                         |                           |
|-------------------------|---------------------------|
| ○ Glass spheres         | △ Kaolin (Suprex)         |
| □ Sand                  | △ Kaolin (Peerless No. 2) |
| ● Carborundum           | + Celite                  |
| ▼ Sodium chloride       | × Steel wool              |
| ⊗ Barnfield soil crumbs | □ Perspex flakes          |
| ⊙ Woburn soil crumbs    | ▽ Vermiculite             |
| ⊕ Highfield soil crumbs | ▽ Mica                    |
| ▲ Pumice                |                           |

equation of the form  $D/D_0 = \gamma \epsilon^\mu$  fits all the materials tested, with  $\gamma = 1$ ,  $\mu = m$ , as limiting values. The values of  $\gamma$  lie between 1.0 and 0.8, and  $\mu$  is always less than  $m$ . Very roughly,  $\gamma$  increases with the mean porosity for each type of material, and though errors in the measurement of either  $D/D_0$  or  $\epsilon$  might cause deviations from  $\gamma = 1$  there is no known or suspected source of experimental error important enough to account for the magnitude of the deviations. Further, Wyllie and Gregory<sup>(23)</sup> working with unconsolidated media, gave data fitted by the equation  $D/D_0 = \gamma \epsilon^\mu$  with  $\gamma < 1$ ; and all the data summarized by Carman<sup>(20)</sup> for glass spheres can be fitted with  $\gamma = 0.81$ , though they come from different workers using different techniques.

### The shape factor

The value of  $\mu$  is probably a measure of pore shape, and in the hope that this might be related to particle shape, two attempts were made to define and measure a particle shape factor. Using regularly shaped crystals, a *relative surface area* ( $S_r$ ) was calculated from measured dimensions, defined as the ratio of the surface area to that of a sphere of the same volume. From diffusion measurements on these materials values of  $m$  were determined and in Fig. 4,  $m$  is plotted against  $S_r$ . On the same diagram are the theoretical Bruggeman curves for ellipsoids having relative semi-axes 1 : 1 :  $n$ , with  $n > 1$  and  $n < 1$ ; though the wide divergence of these curves clearly indicates that surface area is not an adequate index to shape, the six sets of experimental data plotted do show a clear trend of  $m$  increasing with relative surface area.

The second factor tested was the *relative "Stokes" radius*, and measurement was restricted to those particles big enough for their volumes to be estimated accurately. The settling velocity of the materials was measured in a 160 cm column of mineral oil, and the equivalent radius calculated from

$$r = V(\rho - \sigma)g/6\pi\eta v \quad (10)$$

where  $V$  and  $\rho$  are the volume and density of a particle settling with velocity  $v$  in a liquid of density  $\sigma$  and viscosity  $\eta$ .

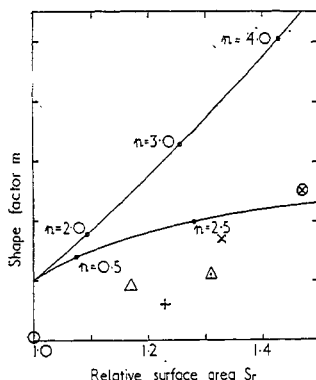


Fig. 4. Relationship between the Bruggeman shape factor  $m$  and the relative surface area of the particles. Theoretical curves are shown for ellipsoids having relative half axes 1 : 1 :  $n$

- |                      |
|----------------------|
| ○ Spheres            |
| △ Sodium citrate     |
| + Hypo               |
| × Ammonium sulphate  |
| ⊗ Magnesium sulphate |
| △ Sucrose            |

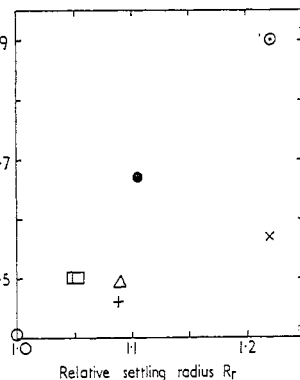


Fig. 5. Relationship between the Bruggeman shape factor  $m$  and the relative particle settling radius

- |                       |
|-----------------------|
| ○ Spheres             |
| △ Sodium citrate      |
| + Hypo                |
| □ Sand                |
| × Ammonium sulphate   |
| ● Sodium metasilicate |
| ○ Insulating beads    |

The relative Stokes radius  $R_r$  was calculated as  $r/r_s$  where  $r_s$  is the radius of a sphere having the same volume as the settling particle. The result of plotting  $m$  against  $R_r$  (Fig. 5) shows a trend, but no unique relationship, and the points for the rod-like materials lie below those for the more compact materials.

### Conclusions

The coefficient of diffusion through a porous medium is clearly a function of both internal geometry and porosity. Neither of the theoretical equations considered is satisfactory for predicting diffusion rates through porous materials. Both the equations of Burger and of Bruggeman include only a single shape factor, that for particle shape. An equation having two shape factors is required because a single shape factor cannot satisfactorily define both particle shape and the spacial distribution of the particles. An empirical equation of the type  $D/D_0 = \gamma\epsilon^\mu$  appears to be satisfactory for all the granular materials investigated,  $\gamma$  and  $\mu$  being functions of the material. The equation is not expected to apply to wetted materials in which the geometry of the gas-filled pores will be appreciably altered by the liquid phase.

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### Appendix

*Diffusion through tubes of non-uniform cross-section.* The value of  $f$ , the factor for tubes of non-uniform cross-section, is derived for a porous medium consisting of tubes of sinusoidal form, ignoring the shape of streamlines.

Set the area as

$$A' = p + q \sin \theta \quad (11)$$

The length of unit cell  $l$  is from  $\theta = -\pi$  to  $\theta = +\pi$ .

$$x/l = \theta/2\pi \quad \text{and} \quad dx = (l/2\pi)d\theta$$

The impedance of unit pore

$$I = \int_0^l \frac{dx}{A'} \\ = l(p^2 - q^2)^{1/2} \quad (12)$$

and the volume of unit pore

$$V = \int_0^l A' dx \\ = lp \quad (13)$$

$(p^2 - q^2)^{1/2}$  represents the effective free cross-section of the tube available for diffusion ( $=\Delta A_e$ ).

For a straight tube  $q = 0$

whence  $I = l/p$

and  $V = lp$

$p$  therefore represents the cross-section of the straight tube of equal volume, that is of equal porosity ( $=\Delta A_e$ ).

But by definition

$$f = A_e'/A_e \\ = \Sigma(p^2 - q^2)^{1/2}/\Sigma p \\ = \frac{(\text{maximum} \times \text{minimum cross-section})^{1/2}}{\text{mean cross-section}} \quad (14)$$

Table 2. Range of values of  $f$  for different ratios of area

Maximum/Minimum cross-sectional area	$f$
1.0	1.0
2.0	0.944
3.0	0.867
4.0	0.800
5.0	0.746
6.0	0.701
7.0	0.662
8.0	0.629
9.0	0.600
10.0	0.575
100.0	0.218

Table 3. Comparison between values for  $D/D_0$  for spherical particles

	Closest packing	Cubic packing
Porosity $\epsilon$	0.26	0.48
$(l/l_e)^{2*}$	0.66	1.00
$f^*$	0.87	0.76
$D/D_0$		
Equation (7)	0.149	0.365
Burger ( $k = 1.5$ )	0.190	0.381
Burger ( $k = 1.8$ )	0.163	0.339
Bruggeman ( $m = 1.5$ )	0.133	0.333
Bruggeman ( $m = 1.4$ )	0.151	0.358

\* Calculated from the geometry of the system.



Table 2 shows the range of values of  $f$  for different ratios of maximum to minimum cross-sectional area.

It is of interest to make the following comparison (Table 3) between values for  $D/D_0$  for spherical particles obtained using equation (7) and from the Burger and Bruggeman equations using theoretical and experimental shape factors.

For both cubic and hexagonal packing, the value for  $D/D_0$  given by equation (7) lies between the theoretical values given by the equations of Burger and Bruggeman, where  $k = m = 1.5$ . The best agreement is observed in both systems between the values given by equation (7) and the Bruggeman equation, where  $m = 1.4$ , the experimental value,

## Contact electrification of semiconductors

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[Paper first received 13 October, 1959, and in final form 20 April, 1960]

### Abstract

*Recently published experimental findings on the electrification of rutile powder by sliding down a metal chute can be explained by an extension of the present author's theory of the separation electrification of metals. The mechanism of the electrification of insulators must, in most cases, be quite different.*

### Introduction

THE mutual electrification of metals resulting from light contact without rubbing, followed by separation, has received a quantitative explanation based on the quantum-mechanical theory of electron levels in metals.<sup>(1)</sup> Different procedures for the investigation of the electrification of insulators used by Peterson,<sup>(2)</sup> Wagner<sup>(3)</sup> and by the present author,<sup>(4, 5)</sup> have led to differing experimental results. The significance of these results has been discussed by Loeb,<sup>(6)</sup> and by the author.<sup>(7)</sup> Experiments on semiconductors by Cooke<sup>(8)</sup> and Jewell-Thomas<sup>(9)</sup> have recently been reported by Donald.<sup>(10)</sup> These experiments led to a remarkable empirical law, that applied also to insulators, the significance of which was not understood at the time. The purpose of the present paper is to show that the quantum-mechanical theory of semiconductors predicts the law for semiconductor/metal contact, but makes it difficult to understand how it comes about that the law has been found to apply to insulator/metal contact as well, and difficult also to reconcile the findings of Cooke and Jewell-Thomas with those of Peterson and Wagner.

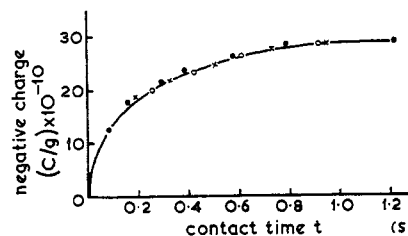
The law found by Cooke and Jewell-Thomas for particles sliding down a chute refers to the dependence of the charge acquired by given particles sliding down a given chute when the chute length and inclination are varied. The charge was found to depend only on the time it took the particles to descend the chute, different combinations of chute length and inclination that gave the same time of descent giving the same charge. That this was so for the semiconductor rutile may be seen from Fig. 1, taken from Donald's paper, in which charge is plotted against time of descent for different chute lengths and inclinations. The form of dependence of charge on time is established by Fig. 2, also taken from Donald's paper, in which  $\log \{C_m/(C_m - C)\}$  is plotted against  $t$ ,  $C_m$  being the maximum charge attained for  $t = \infty$ , and  $C$  the

charge at time  $t$ . It is seen that  $\log \{C_m/(C_m - C)\}$  is proportional to  $t$ , from which it follows that

$$C = C_m \{1 - \exp(-t/T)\} \quad (1)$$

where  $T$  is a relaxation time.

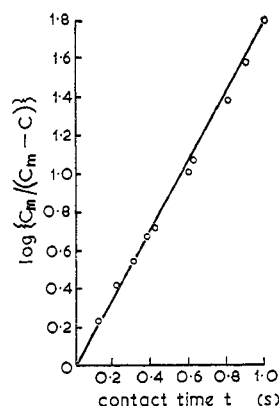
The law is the same as the law of the charging of a capacitor to which a potential is suddenly applied through a resistance.



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Fig. 1. Charging of rutile for different chute lengths and inclinations

○ = 40° × = 35° ● = 30°



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Fig. 2. Graph of function  $\log \{C_m/(C_m - C)\}$  against contact time  $t$  for rutile 100/120 mesh on nickel chute,  $R = 0.074$  in. ( $C_m = 29.0 \times 10^{-10}$  C/g)