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THE MECHANISM OF TRANSPORT OF MATTER IN POROUS SORBENTS

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INTRODUCTION

Porous sorbents are widely used in industry, both as adsorbents and as a matrix for various additives for absorption, chemisorption, and catalysis. In either case the effectiveness of the sorbent is primarily determined by its capacity and by the sorption velocity, both of which are appreciably dependent on the porous structure of the sorbent. The relationship between sorbent capacity and pore structure has been described in detail in many publications. The work of M. M. Dubinin and his collaborators, in particular, has helped to clarify this relationship. The structure-dependence of the adsorption velocity, on the other hand, has not been so fully investigated. It is nevertheless an important aspect of the technology of sorbents, since the development of a rational pore structure is impossible without a knowledge of the kinetic properties of the sorbent.

A sufficiently clear understanding of the mechanism of matter transport in the pores of a sorbent is a prerequisite to success in the search for the optimum sorbent porosity. This mechanism differs in many respects from that attending the transport of gases and liquids through layers of granular materials, such as soils, which has been considered in detail in a number of monographs[1-6]. For instance, when substances are adsorbed in the pores of a sorbent we notice special effects due to auxiliary modes of transport. Furthermore, the greater inhomogeneity of the pore structure of a sorbent, as compared with that of a layer of granular material, also plays an important part.

A considerable number of publications devoted to the mechanism of transport of gases adsorbed in the pores of sorbents has appeared during the past 10 years in the Russian and more especially in the foreign literature. It does not therefore seem out of place to present a review of the main contributions, preceded for the sake of completeness, by a discussion of the main modes of transport of non-adsorbed gases.

I. TRANSPORT OF NON-ADSORBED GASES

Viscous Flow

A pressure gradient in a porous body gives rise to a flow of gas in the direction of the gradient. The type of motion depends on the ratio of the mean free path of the molecules Λ to the capillary radius r. If $\Lambda/r \ll 1$ the gas flow is viscous; if on the other hand $\Lambda/r \gg 1$ molecular flow sets in. The first case is characterised by collisions of the gas molecules with one another; in the second case collisions between gas molecules and pore walls predominate. Viscous flow may be laminar or turbulent according to the value of the Reynolds number

$$\mathrm{Re} = \frac{wd}{\nu}, \qquad (1)$$

where w is the mean linear velocity of flow, d the pore diameter, and ν the kinematic viscosity.

In cylindrical pipes laminar flow is maintained[7] up to $\mathrm{Re} < 2200$. In granular layers the onset of turbulence takes place at considerably smaller Reynolds numbers because of the tortuous channels and of the periodic narrowing and widening of the pores. The transition from laminar to turbulent flow in this case has been reported by various authors[8-10] in the region $20 < \mathrm{Re} < 200$. Within the grains of sorbents laminar flow occurs[11] up to $\mathrm{Re} \leqslant 4-6$. Further criteria have been put forward, appropriate to the analysis of the motion of gas in porous bodies[12]. The flow of gas through sorbents as commonly used is laminar owing to the smallness of the pore radii.

Darcy's equation,

$$\frac{V}{t} = B \operatorname{grad} p, \qquad (2)$$

expresses the speed of laminar flow of incompressible liquids, and also of gases under conditions when the variations in density can be ignored (small pressure drop). In Eqn. (2) V is the volume of liquid or gas in cm^3, p the pressure in bars, t the time in sec, and B a constant expressing the permeability of the porous medium.

For a single cylindrical capillary, as shown by Hagen[14] and Poiseuille[15]

$$B = \frac{\pi r^4}{8\eta}, \qquad (3)$$

so that the speed of flow of gas is given in this case by

$$\frac{V}{t} = \frac{\pi r^4}{8\eta} \frac{p_1 - p_2}{l}. \qquad (4)$$

In Eqns. (3) and (4) r is the capillary radius, η the gas viscosity, p_1 and p_2 the pressures at the ends of the capillary, and l the length of the capillary.

When the change in density of the gas within the capillary cannot be ignored, Eqn. (4) is modified to

$$\frac{pV}{t} = \frac{\pi r^4}{8\eta} \bar{p} \frac{\Delta p}{l}, \qquad (5)$$

where p is the pressure under which the volume of the effluent gas is measured, $\bar{p} = \frac{p_1 + p_2}{2}$ is the mean pressure, and $\Delta p = p_1 - p_2$.

The permeability of various bodies may be compared on the basis of the speed of flow under a pressure difference of 1 bar,

$$K = \frac{pV}{t\Delta p} = \frac{\pi r^4}{8\eta} \bar{p} \frac{1}{l}. \qquad (6)$$

The permeability K, when referred to unit cross-section and unit length of sample, is called the specific permeability K_0:

$$K_0 = \frac{K}{F} l. \qquad (7)$$

The specific permeability of a capillary of circular cross-section for compressible gases is given by*

$$K_0 = \frac{r^2}{8\eta} \bar{p}, \qquad (8)$$

* Barrer[16] omits the mean pressure $\bar{p}$ in the expression for K_0.

whereas that of a capillary with a cross-section of arbitrary shape is given by

$$K_0 = \frac{r_m^2}{k r_l} \bar{p}, \qquad (9)$$

where $r_m = \frac{F}{P}$ is the hydraulic radius, F the cross-sectional area, P the perimeter, and k a coefficient determined by the shape of the cross-section of the capillary.

Values of k corresponding to various cross-sectional shapes[17] are given in Table 1.

It can be seen from Eqn. (8) that the permeability to viscous flow decreases sharply as the capillary radius is decreased.

Viscous flow takes place, as pointed out above, for $\Lambda/r \ll 1$. The pores of sorbents range, in dimensions, from those visible with a magnifying glass to those of molecular size. In the coarser pores (radius $r = 10^{-2}-10^{-3}$ cm) viscous flow is possible only for gas pressures not less than 1 mm Hg. The mean free path at atmospheric pressure equals 10^{-5} cm approximately, so that viscous flow under these conditions is observed only in pores with $r > > 10^{-5}$ cm. In the finest pores ($r = 10^{-7}-10^{-6}$ cm) viscous flow under atmospheric pressure is impossible.

TABLE 1. Value of k of Eqn. (9).

Shape of capillary cross-section		k
Circle		2
Square		1.78
Rectangle: height	h	
width	$b=2h$	1.94
	$b=5h$	2.38
	$b=10h$	2.65
Parallel surfaces (fissure)		3.0
Ellipse: semi-axes a and b		
	$a=2b$	2.13
	$a=10b$	2.45

TABLE 2. Factor b for different values of l/r.

$\frac{l}{r}$	0	0,2	0,5	1,0	1,5	2,0	3	5	10	20	50	100	1000	∞
b	1	0,909	0.801	0.672	0.581	0.514	0.421	0.315	0,197	0.114	0.050	0,026	0,0027	$\frac{8r}{3l}$

Molecular Diffusion

At very low gas pressures, or with capillaries of very small radius, the mean free path of the molecules becomes much larger than the capillary radius, and the collisions between the gas molecules and the capillary wall greatly exceed those between the molecules themselves. The molecules colliding with the wall rebound in all directions, and only a small fraction is reflected specularly.

A diffuse reflection of this kind can be due to two causes: (1) no surface is truly flat on a microscopic scale; projections and cavities can be expected to reflect impinging molecules in all directions; (2) all substances are adsorbed to a greater or lesser degree, so that molecules must exist in the adsorbed condition for a certain time after collision; their eventual re-emission results from thermal vibrations and is equally probable in all directions.

Molecular diffusion in capillaries was first investigated by Knudsen[18], who showed that the speed of steady-state molecular diffusion in straight capillaries of circular cross-section is satisfactorily expressed by

$$\frac{pV}{t} = \frac{4\pi r^3}{3}\sqrt{\frac{2RT}{\pi M}}\,\frac{\Delta p}{l}, \qquad (10)$$

where M is the molecular weight of the gas, T the absolute temperature, and R the gas content.

By analogy with Eqn. (8) the specific permeability of a capillary to molecular diffusion can be written

$$K_M = \frac{4r}{3}\sqrt{\frac{2RT}{\pi M}}. \qquad (11)$$

It follows from Eqn. (11) that the permeability of a capillary to molecular diffusion is independent of the gas pressure.

Formula (10) applies to a straight capillary of circular cross-section on the assumption that all colliding molecules are reflected according to the cosine law, that $r/\Lambda = 0$, and $l/r = \infty$. Certain corrections must be introduced when these conditions are not met.

Allowance for specular reflection. If f is the fraction of diffuse reflections and $1 - f$ the fraction of specular reflections, Knudsen's formula becomes

$$\frac{pV}{t} = \frac{4\pi r^3}{3}\sqrt{\frac{2RT}{\pi M}}\,\frac{\Delta p}{l}\,\frac{2-f}{f}. \qquad (12)$$

In many cases of practical importance the value of f approaches unity.

Correction for finite capillary length. Clausing[19] proposed the following formula for the permeability of capillaries of finite length with $l/r < 1000$:

$$\frac{K_l}{l} = b\sqrt{\frac{RT}{2\pi M}}, \qquad (13)$$

where K_l is the specific permeability of a capillary of length l, and b the probability that a molecule will pass through the capillary without being turned back. Values of the Clausing factor are listed in Table 2.

From Eqns. (11) and (13) we find that

$$\frac{K_l}{K_M} = \frac{3}{8}\,b\,\frac{l}{r}. \qquad (14)$$

The ratio K_l/K_M, calculated from Eqn. (14) for several values of l/r, is tabulated in Table 3.

TABLE 3. Ratio K_l/K_M for different values of l/r.

l/r	0,5	1	2	3	5	10	100	1000
K_l/K_M	0,152	0.252	0.384	0,474	0.588	0.737	0,972	0.998

It follows from the data of Table 3 that the values of K_M calculated from formula (11) for capillaries with a small ratio l/r are much too high. Pollard and Present[20] give a detailed discussion of the permeability of short capillaries in the Knudsen region.

Allowance for capillary convolutions. Knudsen's formula (10) is derived for a straight capillary, but the capillaries of porous bodies are far from straight.

Hiby and Pahl[21-24] suggest that tortuous capillaries can be described as a series of straight capillaries for which $2 < l/r < 10$. In the case of systems with a globular structure, the authors replace the channels between the particles by a system of curved capillaries with $l/r = 3$. This lowers the permeability by approximately a factor of 2 (see Table 3) as compared with the straight-capillary model.

Permeability of non-cylindrical capillaries. The specific permeability of capillaries with an arbitrary cross-sectional shape is given[25] by the equation

$$K_M = \frac{8F}{3P}\sqrt{\frac{2RT}{\pi M}}, \qquad (15)$$

where F is the cross-section and P the perimeter of the capillary.

Gas Flow in the Transition Region

A decreased permeability is observed in the transition region (i.e. when the mean free path is approximately equal to the diameter of the capillary). The curve of K vs. $\bar{p}$ shows a minimum, in the region where $r/\Lambda = 0.2-0.3$, whose depth amounts to about 5% of the permeability for molecular diffusion. An example of this behaviour is given in Fig. 1, based on some measurements by Knudsen[18] of the permeability of glass capillaries to carbon dioxide. Similar results have been obtained by Close[26,27], Adzumi[28], Clausing[19], and others. Much effort has been directed towards explaining[29-34] the nature of the minimum in the permeability curve, but the phenomenon is still far from clear.

It follows from Eqn. (6) that the permeability to viscous flow should decrease linearly with pressure down to $p = 0$. In the low pressure region, however, the viscosity coefficient does not remain constant and independent of pressure, as required by Maxwell's molecular-kinetic theory[35], but decreases with pressure.

Meyer[36], who observed a decrease in the viscosity of air at low pressures, invoked gas slip in the neighbourhood of the solid surface to explain the result. He suggested that the coefficient of slip is related to the mean free path by the expression

$$\zeta = \frac{2}{3}\Lambda, \qquad (16)$$

which becomes

$$\zeta = \frac{2}{3}\Lambda\left(\frac{2}{f} - 1\right) \qquad (17)$$

if some of the molecules undergo specular reflection.

The first experimental determination of ζ is due to Kundt and Warburg[37-39]. These authors found a slip coefficient for air, normalised to $p = 760$ mm Hg, of $\zeta = 0.79 \times 10^{-5}$. Millikan[40] obtained $\zeta = 0.77 \times 10^{-5}$ for air and oil by the falling drop method. Further experimental methods for determining ζ are given by Stacy[41], and Skillman and Van Dyke[42].

Kundt and Warburg expressed the Hagen–Poiseuille equation, corrected for slip, in the form

$$\frac{pV}{t} = \frac{\pi r^4}{8\eta}\bar{p}\,\frac{\Delta p}{l}\left(1 + 4\frac{\zeta}{r}\right). \qquad (18)$$

The equation correctly predicts that the slip correction is considerable in the low pressure region, and that the speed of flow accordingly increases. At very low pressures, when molecular flow sets in, Eqn. (18) is obviously inapplicable.

Knudsen's semi-empirical equation satisfactorily describes the velocity of gas transfer over a wide range of pressures, embracing both viscous flow and molecular diffusion:

$$\frac{pV}{t} = \left(\frac{\pi r^4}{8\eta}\bar{p} + \frac{1 + c_1 p}{1 + c_2 p}\cdot\frac{4\pi r^3}{3}\sqrt{\frac{RT}{\pi M}}\right)\frac{\Delta p}{l}, \qquad (19)$$

where

$$c_1 = 2.00\frac{r}{\eta}\sqrt{\frac{\rho}{p}},$$

$$c_2 = 2.47\frac{r}{\eta}\sqrt{\frac{\rho}{p}},$$

and ρ is the density of the gas.

According to Wicke[34] both types of transport (laminar flow and molecular diffusion) take place in a sufficiently long capillary; as the pressure continuously drops along the length of the capillary, it is possible for the flow to become molecular. Wicke obtained a formula analogous to Eqn. (19) by considering the flow in the transition region as two currents in series (viscous and molecular).

Porous sorbents contain channels of every conceivable size and therefore support the transitional mode of flow over a wide range of pressures.

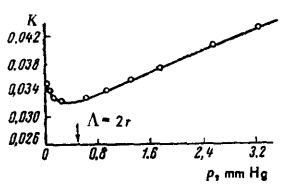


Fig. 1. Permeability of a glass capillary to carbon dioxide, after Knudsen[18].

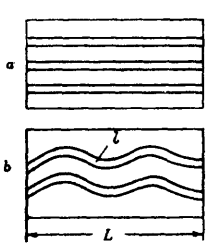


Fig. 2. Simplest model of a porous medium. $l = K_1 L$.

Model of a Porous Body. Mixed Transport

The questions discussed above relate to the flow of gas in a single capillary. Sorbents, with their multitude of pores of different sizes and arbitrary cross-sections, variously interconnected, present a much more complicated picture. Quantitative discussions of the process of matter transport in real porous bodies must therefore rely on some simplified model of the sorbent structure.

Leibenzon, in his study of the permeation of gas through soils[1], used as preliminary models of the porous system a bundle of straight, cylindrical, parallel capillaries of uniform radius ("ideal soil") or a layer of spherical particles of uniform size ("fictitious soil"). The "ideal soil" concept (Fig. 2) was applied to studies of the sorption process by Damköhler[43], Barrer[44], Flood[45], Dacey[46], and others. One of the deficiencies of this model is the fact that its transverse permeability, unlike that of an actual system, is zero.

Adzumi[48] modified the "ideal-soil" model by assuming a system of cylindrical, parallel capillaries of non-uniform diameter. Each capillary consists of a series of capillaries of different lengths and diameters, joined end-to-end. Adzumi's model of a porous body is shown schematically in Fig. 3.

Wicke[49,50] and Dubinin[51], in their studies of sorption by active carbons, assumed a pore structure consisting of branching chains of coarse pores, freely interconnected. Micropores are taken to be ramifications of the coarse pores, as shown in Fig. 4.

Wiggs assumes that zones of high and of low conductivity are present in the particles of sorbents[52]. Their relative extent, and mutual disposition, depend on the preparative conditions, and may vary. A schematic view of Wiggs' model is given in Fig. 5.

A globular structure characterises silica gel[53-55]. Obviously, the "fictitious soil" model is more suitable in this case.

Deryagin and Bakanov's theoretical study[33] of the flow of gas in the transition region is based on a model of a highly-porous medium consisting of a system of randomly distributed spheres, rigidly fixed but not in contact with each other.

Sorbent particles may contain fissures due to the shrinkage and disintegration of the material during preparation, or embody elements of the structure of the parent material, as is the case with wood charcoals[56]. This makes the structure of real sorbents even more complicated; a quantitative calculation of the influence of such structural features on the kinetics of the sorption process is exceedingly difficult.

On the basis of simple considerations, Adzumi derived an expression of the following form for the permeability of his model of a porous medium:

$$K = \frac{\varepsilon}{8\eta}\bar{p}\frac{n}{\sum\limits^{m}\frac{l}{r^4}} + \gamma\frac{4\pi}{3}\sqrt{\frac{2RT}{\pi M}}\frac{n}{\sum\limits^{m}\frac{l}{r^3}}, \qquad (20)$$

where n is the number of capillaries connected in parallel, m the number connected in series, and γ is a constant.

In the case of sorbents with pores of a single kind both the effective pore radius and the number of pores per unit area of sample can be calculated from Eqn.(20). Assuming

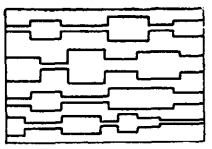


Fig. 3. Azumi's model of a porous medium[48].

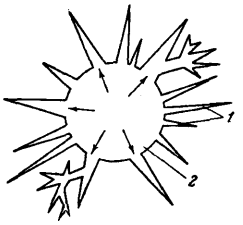


Fig. 4. Network of transport pores and adsorption pores, after Wicke[49,50]. 1) adsorption pores; 2) transport pores.

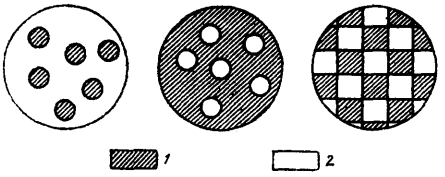


Fig. 5. Pore structure of a sorbent, after Wiggs[52]: 1) poorly conducting regions; 2) highly conducting regions.

uniform pores of length l and radius r, the equation can be written

$$K = A_0\bar{p} + \gamma B_0, \qquad (21)$$

where $A_0 = \frac{\pi r^4}{8\eta l}n$ and $B_0 = \frac{4\pi}{3}\sqrt{\frac{2RT}{\pi M}}\frac{r^3}{l}n$.

The quantities A_0 and B_0 can easily be obtained from a study of the variation of K with pressure $\bar{p}$. Assuming $\gamma \cong 1$, we have

$$r = \frac{A_0}{B_0} \text{ and } n = \frac{B_0^4}{A_0^3}.$$

The surface area of the pores (S) can then be derived from the value of r by means of the formula

$$S = \frac{2\varepsilon}{r}, \qquad (22)$$

where ϵ is the relative pore volume in cm^3/cm^3.

The determination of the specific area of powders is based on considerations similar to the above[57-75]. The method has been critically appraised, and its limitations

discussed, in a number of papers. The whole problem has been re-examined quite recently[76].

The K - $\bar{p}$ curves for porous media frequently show no minimum[32]. According to Pollard and Present[20], this is due to a large number of short capillaries ($l < 2\Lambda$), whose permeability is less than that calculated from Knudsen's formula. Consequently, the limit of K for $p = 0$ is in fact lower than usually supposed. As shown theoretically by Deryagin and Bakanov[33], the K - $\bar{p}$ curve for highly porous bodies (porosity $\epsilon > 0.7$) must have a minimum.

Dacey and Fendley[46] report that the adsorption of argon and of methane, in quantities greater than 5% by weight, alters the pore structure of saran charcoal. The flow of helium in a given pressure region, which was molecular before the adsorption of argon, became viscous after argon adsorption. No such effects were noticed with argon adsorptions less than 3%.

When the sorbent pores are initially filled with some foreign gas, e.g. air, and no pressure gradient exists, the transport of another gas depends on volume diffusion in the pores, a case of frequent practical occurrence. The diffusion will be of the common, or of the Knudsen type, according to the value of the ratio Λ/r. The diffusion equations, and their solution for various geometries, are discussed in a number of monographs[77-79].

II. TRANSPORT OF ADSORBED GASES

The concept of adsorbed and non-adsorbed gases is somewhat arbitrary. We know that all gases and vapours are adsorbed on solid surfaces to a greater or lesser extent. From this point of view, non-adsorbed gases do not exist. The adsorbability of a given substance depends on the conditions under which the adsorption proceeds. Nitrogen, for instance, is hardly adsorbed at ordinary temperatures, but its adsorption at low temperatures may be considerable. We will define a non-adsorbed gas as one whose adsorption under the relevant conditions is so small as not to affect significantly the speed of flow through the porous medium.

The permeability of porous bodies to non-adsorbed gases is most frequently described using Adzumi's equation:

$$K = \frac{A}{\eta}\bar{p} + B\sqrt{\frac{T}{M}}, \qquad (23)$$

where A and B are structural parameters, related to the size, number, and shape of the pores.

Good agreement between calculation and experiment is usually obtained when the constants A and B, derived from experiments on one non-adsorbed gas, are used to predict the flow characteristics of another non-adsorbed gas. However, if the same procedure is applied to adsorbed gases the calculated values are invariably low. These observations are reported by many independent workers[31,80-86].

Several hypotheses have been advanced to explain the increased speed of flow of adsorbed gases. The most prevalent invokes a subsidiary flow of matter in the adsorbed phase, by means of molecular migration along the surface. This point of view is developed in the papers of Barrer, Carman, Haul, and others[87-92].

Tomlinson and Flood[31] consider that the greater permeability to adsorbed gases is a manifestation of the importance of slip, since the density of these gases is considerably increased near the pore walls. In more recent publications[93-99] Flood has developed the idea of a flow of matter in the adsorbed phase. The overall flow of gas in the porous medium is increased by this auxiliary transport mechanism.

Diffusion Along the Sorbent Surface

Molecules adsorbed on the surface of solids are in a state of continuous thermal motion, and are able to migrate along the surface under the influence of a concentration gradient. The first demonstration of this phenomenon is due to Vollmer and Esterman[100] who studied the growth of mercury crystals at -63° from the vapour of mercury at -10°. They observed an extremely rapid growth of thin hexagonal crystals in the direction of the hexahedral plane. The linear crystallisation velocity was about 1000 times greater than could be accounted for by the molecular-kinetic theory. Later work by Vollmer, and also by other authors, considers surface migration in different systems[101-107]. Various methods have been applied to the study of the mobility of adsorbed molecules[108-114], notably the adsorption method, which is based on the evaluation of the adsorption entropy.

Clausing[115] and Damköhler[43] were the first to attempt an appraisal of the surface-migration effect in relation to the velocity of transport of adsorbed gases in capillaries. These workers expressed the diffusion current P in the direction of the concentration gradient as the sum of two parallel flows: one in the gas phase (P_g) and one along the surface (P_a). In the steady state the rate of mass transport is proportional to the concentration gradient, i.e.:

$$P = P_g + P_a = -\left(D_g\frac{\partial c}{\partial x} + D_a\frac{\partial a}{\partial x}\right), \qquad (24)$$

where D_g and D_a are the diffusion coefficients appropriate to the gaseous and to the adsorbed phases respectively; $\frac{\partial c}{\partial x}$ is the concentration gradient in the gas phase; $\frac{\partial a}{\partial x}$ is the concentration gradient in the adsorbed phase.

Assuming a linear adsorption isotherm $a = Hc$ (where H is Henry's constant) we can writen Eqn. (24) as

$$P = -\left(D_g\frac{\partial c}{\partial x} + D_a H\frac{\partial c}{\partial x}\right) \qquad (25)$$

or

$$P = -D_g\left(1 + \frac{D_a H}{D_g}\right)\frac{\partial c}{\partial x}. \qquad (26)$$

For non-stationary one-dimensional diffusion we have the analogous equation

$$\frac{\partial c}{\partial t} + \frac{\partial a}{\partial t} = D_g\frac{\partial^2 c}{\partial x^2} + D_a\frac{\partial^2 a}{\partial x^2}, \qquad (27)$$

which in the case of a linear adsorption isotherm takes the form

$$\frac{\partial c}{\partial t} = \frac{D_g + D_a H}{1 + H}\frac{\partial^2 c}{\partial x^2}. \qquad (28)$$

In the majority of cases $H \gg 1$, so that

$$\frac{\partial c}{\partial t} = D_e\frac{\partial^2 c}{\partial x^2}, \qquad (29)$$

TABLE 4. Diffusion coefficients D_a and D_g in carbon cylinders.

Gas	ε=0.37		ε=0.64	
	$D_a \times 10^5$	$D_g \times 10^5$	$D_a \times 10^5$	$D_g \times 10^5$
He	1.74	5.7	2.7	15.4
Ne	1.05	2.6	1.6	6.7
H_2	2.8	8.3	4.2	20.9
A	0.16	1.9	0.54	4.7
N_2	0.21	2.2	0.61	5.6
Kr	0.05	1.2	0.13	3.1

TABLE 5. Values of D_a and D_g on porous glass.

Gas	$D_a \times 10^5$	$D_g \times 10^5$
O_2	2.05	8.8
N_2	2.26	9.4
A	1.91	7.9
Kr	0.78	5.4
CH_4	0.73	12.4
C_3H_6	0.60	9.0

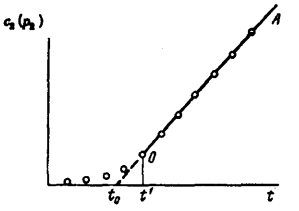


Fig. 6. Determination of the 'time-lag'.

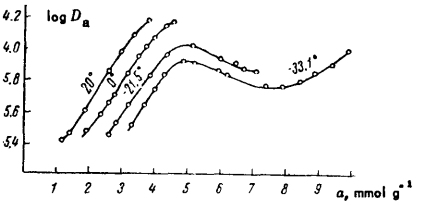


Fig. 7. Variation of the coefficient of surface diffusion with amount adsorbed, after Carman and Raal[84] (freon on compacted soot). The ordinates should be read with a minus sign.

where $D_e = \frac{D_g}{H}\left(1 + \frac{D_a H}{D_g}\right)$ is the effective diffusion coefficient.

In both cases (26) and (28) the migrational effect is estimated from the value of the expression $\frac{D_a H}{D_g}$.

If $\frac{D_a H}{D_g} \ll 1$, the fraction transported in the adsorbed phase is small and the contribution of surface diffusion to the rate of transport can be ignored. If, on the other hand, $\frac{D_a H}{D_g} \gg 1$, surface diffusion dominates the process of matter transport. Many other authors have also adopted a similar method for evaluating the part played by surface diffusion in the transport process.

Damköhler computed the expression $\frac{D_a H}{D_g}$ as follows. We know, from the molecular-kinetic theory, that $D_g = 1/3\, u\Lambda$. Assuming a mean pore radius $r = 10^{-6}$ cm for active carbon, and an average molecular velocity $u = 3 \times 10^4$ cm sec^{-1}, he obtained a diffusion coefficient for the gas phase of $D_g = \frac{2ru}{3} = 2 \times 10^{-2}$ cm^2 sec^{-1}. By treating the adsorbate as a two-dimensional gas, for which $D_a = 1/2\, u_a \Lambda_a$ (where u_a and Λ_a are the mean velocity and the mean free path of the molecules in the adsorbed layer), and assuming that $u_a = 3 \times 10^4$ cm sec^{-1} and $\Lambda_a = 4 \times 10^{-8}$ cm, Damköhler obtained $D_a = 6 \times 10^{-4}$ cm^2 sec^{-1} for the coefficient of surface diffusion. For readily adsorbed materials Henry's constant is of the order of 10^3, whence the expression $\frac{D_a H}{D_g} \cong 30$, i.e. is considerably in excess of unity. On the strength of these considerations Damköhler concludes that the transport of readily adsorbed substances is dominated by surface diffusion. Clausing's evaluation[115,116] of the migrational effect led him to similar conclusions. He showed that surface diffusion could be ignored for the case of argon on glass. Taking $\Lambda_a = 30 \times 10^{-8}$ and a capillary radius $r = 0.005$ cm, he finds $\frac{D_a H}{D_g} \ll 1$.

Later publications attempt more direct assessments of the role of surface diffusion. They follow three distinct approaches: (1) determination of the coefficient of surface diffusion from the experimental values of the overall ($D_0 = D_g + D_a H$) or of the effective (D_e) diffusion coefficient, and of the gas-phase diffusion coefficient (D_g); (2) comparison of the activation energy of the inner diffusion process with the heat of adsorption; and (3) total or partial elimination of the volume-diffusion component of the transport process.

The overall diffusion coefficient is most frequently determined by permeability measurements under steady-state conditions.

The method is essentially the following. Gas concentrations c_1 and c_2 (or pressures p_1 and p_2), constant with time, are maintained on the two sides of a porous slab of thickness L. After a time, a steady-state flow is set up, and its speed is determined by the equation

$$P = KF\frac{p_1 - p_2}{L}. \qquad (30)$$

In the absence of viscous flow, i.e. if the flow is molecular, or if a carrier gas is present, the constant K is related to the overall diffusion coefficient by the expression

$$K = D_0 \varepsilon. \qquad (31)$$

Making use of Eqn. (26), the overall diffusion coefficient becomes

$$D_0 = D_g\left(1 + \frac{D_a H}{D_g}\right). \quad (32)$$

For non-adsorbed gases

$$\frac{D_a H}{D_g} = 0 \text{ and } K = D_g\varepsilon. \quad (33)$$

Experiments with adsorbed and non-adsorbed gases yield K, whence D_0 and D_g are calculated by means of Eqns. (31) and (33). D_a is then derived from Eqn. (32). It remains understood that this calculation can only be meaningful if the assumption of a linear adsorption isotherm, upon which Eqn. (32) is based, is justifiable.

The "time-lag" method is widely used for determining the effective diffusion coefficient $D_e = D_0/H$. It consists of the following. On one side of the porous slab we maintain a constant gas concentration c_1, and on the other side $c_2 \cong 0$. Under these conditions the flow through the slab will be as shown in Fig. 6. If the diffusion is allowed to take place into a closed volume we find that from a time t' onwards the concentration c_2 in this volume increases linearly with time provided that c_2 remains, throughout, much smaller than c_1. Diffusion is now proceeding under stationary conditions. The intercept obtained on the t axis by producing the line OA gives the time t_0, corresponding to $c_2 = 0$, and related to the effective diffusion coefficient by the expression

$$t_0 = \frac{k_1^2 L^2}{6D_e}, \quad (34)$$

where L is the thickness of the porous slab and k_1 is a coefficient which allows for the sinuosity of the channels (see Fig. 2*b*).

Eqn. (34) is an approximate solution of the differential equation for diffusion, obtained[88] for the boundary and the initial conditions stated above. Deryagin[117] gives a statistical derivation of Eqn. (34).

Some doubt exists as to the value of k_1 for porous bodies. For granular layers[47,57,118] $k_1 = 1.4 - 2.0$, but anomalously high values have been obtained in the case of porous substances[119] by electrical conductivity and other methods. Fortunately, k_1 can be eliminated from relative calculations involving adsorbed and non-adsorbed gases.

The possible use of the time-lag method of determining the effective diffusion coefficient in cases where the diffusion "constant" is a function of concentration has been examined[120]. Methods for deriving D_e from measurements of the rates of adsorption from a constant volume but under different gas concentrations are discussed by Carman and Haul[121].

Barrer and Strachan's[92] values for D_a and D_g, obtained by the time-lag method, are listed in Table 4. In this interesting investigation the authors studied the permeability of cylinders of soot, compacted under various pressures. The porosity ϵ of these carbon cylinders varied from 0.37 to 0.79. The mean pore sizes, estimated by the authors for specimens of porosity 0.37 and 0.64, were 6.5 and 18.8 Å respectively.

The same authors, assessing the migrational effect from the value of $\frac{D_a H}{D_g}$, came to the conclusion that the more readily adsorbed gases, such as nitrogen and krypton, are transferred mainly by surface diffusion.

Barrer and Barrie[44] have determined isotherms and sorption rates for a number of gases on porous glass. The Kelvin radius of the pores, estimated by formula (20) from measurements with different gases, was approximately 30 Å. Values of D_a and D_g, derived from experiments at 70°, are given in Table 5. Henry's constant varied from 2 to 8, and the value of the expression $\frac{D_a H}{D_g}$ was considerably less than one. These data led the authors to the conclusion that volume diffusion is the more important if the pore radius $r \geq 30$ Å.

Wicke and Kallenbach[87] investigated the permeability of carbon membranes to carbon dioxide, over the temperature range 0°–300°, by the stationary diffusion method. They found that the rate of penetration of carbon dioxide is considerably more dependent on temperature than should be the case for volume diffusion. Hence, they estimate that the contribution of surface diffusion to the transport process varies from 0 to 50% according to the conditions of their experiments.

The value of $\frac{D_a H}{D_g}$ increases with H if D_a is not a function of concentration. In the case of convex adsorption isotherms we can evaluate the contribution of surface diffusion over different regions of the isotherm by applying, for example, Carman's "differential method"[121]. The result is that in the region of low coverage this contribution is much smaller than that calculated on the assumption that the value of D_a, found at higher adsorptions, applies. It follows that the surface-diffusion coefficient decreases as the extent of adsorption decreases.

The variation of the surface-diffusion coefficient with extent of adsorption has been studied by a number of workers[83,84].

Fig. 7 shows the dependence of D_a on coverage, after Carman and Raal[84].

From a study of the permeability of paper to water vapour at various relative pressures, Vollmer[85] derived a linear relationship between the surface-diffusion flow and the product of the amount of adsorption, a, and the slope, $\Delta a/\Delta p$:

$$P_a = 2\pi r D_a a \frac{\Delta a}{\Delta p}. \quad (35)$$

Babbit[122] obtained a similar expression. Kammermeyer[123] gives a more precise form of Eqn. (35) by assuming that the diffusion current along the surface is described by

$$P_a = 2\pi r D_a\left[a_1\left(\frac{\Delta a}{\Delta p}\right)_1 - a_2\left(\frac{\Delta a}{\Delta p}\right)_2\right], \quad (36)$$

where a_1 and a_2 are the amounts of adsorption corresponding to pressures p_1 and p_2.

Activation Energy of the Diffusion Process in Porous Bodies

Dacey and Thomas[124-126] made a systematic attempt to evaluate the role of surface diffusion from the magnitude of the activation energy attending the inner-diffusion process. They proceeded from the hypothesis that diffusion must take place in the volume of the pores in those cases where the activation energy equals the heat of adsorption. Each jump of a molecule then results in its complete detachment from the surface. If, on the other hand, the observed activation energy is smaller than the heat of adsorption, the molecules

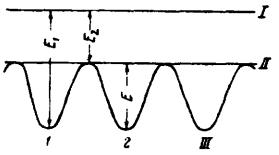


Fig. 8. Potential energy curve for a homogeneous adsorbent: I) energy of the gas molecules in the free volume; II) energy of the two-dimensional gas; III) energy of the adsorbed molecules.

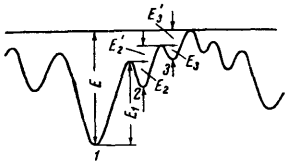


Fig. 9. Potential energy curve for an inhomogeneous adsorbent.

only slide about the surface. As we shall see below, this treatment is not entirely correct.

Molecular movements along the surface have activation requirements even in the case of homogeneous adsorbents with a regular crystal lattice. The heat of adsorption is the same for every site, but the transfer of adsorbate from position 1 to position 2 (see Fig. 8) nevertheless requires an activation energy given by

$$E = E_1 - E_2, \tag{37}$$

where E_1 is the energy of the adsorbed molecules and E_2 the energy of the two-dimensional gas.

The surface of real adsorbents is energetically even more heterogeneous. The potential energy curve for an inhomogeneous adsorbent is sketched in Fig. 9. The probability of a transition from position 1 to position 2 (Fig. 9) is given by $\nu e^{-E_1/kt}$, where ν is the vibration frequency of the adsorbed molecules. From position 2 the molecule can either revert to its original position 1 or go over to position 3. The probability of a transition from 2 to 3 is

$$\frac{1}{2}\exp\left[-\frac{E_2+E_2'}{kT}\right],$$

so that the combined probability for the complete transition from 1 to 3 will be

$$\frac{1}{2}\nu\exp\left[-\frac{E_1+E_2+E_2'}{kT}\right].$$

By carrying the argument further we can derive the probability of a transition in the presence of n energy barriers:

$$\left(\frac{1}{2}\right)^n \nu\exp\left[-\frac{E}{kT}\right]\exp\left[-\sum_{i=2}^{n}\frac{E_i}{kT}\right]. \tag{38}$$

If the quantity ΣE_i is sufficiently large, the probability that a molecule shall leave a given neighbourhood becomes small[127,128]. Hence it follows that (a) surface mobility, as inferred, for example, from the value of the adsorption entropy, does not necessarily imply free migration along the whole surface and ability to contribute to matter transport, and (b) the activation energy may be equal to the heat of adsorption even in cases of surface diffusion.

Frenkel'[129] relates the surface-diffusion coefficient to the mean time of residence in the adsorbed state:

$$D_a = \frac{\Delta}{4\tau}, \tag{39}$$

where Δ is the "jump length".

On the other hand, the time τ is related to the periodic time τ_0 of the atomic vibrations in the lattice of the adsorbent:

$$\tau = \tau_0 e^{\frac{E}{RT}}. \tag{40}$$

From Eqns. (39) and (40) it follows that

$$D_a = D_0 e^{\frac{E}{RT}}, \tag{41}$$

where

$$D_0 = \frac{\Delta^2}{4\tau_0}.$$

TABLE 6.

Adsorbent	$\tau_0 \cdot 10^{14}$ sec
Graphite (active charcoal)	5
Al_2O_3	7.5
SiO	9.5
MgO	6.7

The values of τ_0 for various adsorbents[130] are listed in Table 6.

The activation energy is measured by observing the diffusion coefficient D_a at two neighbouring temperatures. If it is found to have the values D_1 and D_2 at temperatures T_1 and T_2, it follows from Eqn. (41) that

$$E = 4.58\,\frac{T_1T_2}{T_1-T_2}\log\frac{D_1}{D_2}. \tag{42}$$

A method[125] for determining E at two temperatures in the course of a single experiment has been described.

Dacey and Thomas investigated the rate of adsorption of a large number of substances on saran charcoal, and found that E = 1/2 to 1/3 ΔH. Hence they concluded that surface diffusion plays an essential role in the transfer of substances through charcoal. However, owing to the overlap of the adsorption fields of the opposite walls of fine micropores, molecular jumps from one wall to the other require an activation energy smaller than heat of desorption. It follows that the inequality $E < \Delta H$ may apply to matter transport through the gas phase. Measurements on other systems[44,91,131] indicate that the activation energy for the inner-diffusion process lies in the range $0.3-0.9\ \Delta H$.

Other Methods for Appraising the Role of the Migration Effect

Haul[89,90] and Timofeev and Voskresenskii[132] endeavoured to exclude volume diffusion. Haul studied the inner-diffusion rates of a number of organic vapours at low temperatures, at which the vapour pressure was low and the transport could be assumed to take place mainly in the adsorbed phase via surface migration. He determined, by means of a specially constructed balance, the centre of gravity of the adsorbate in a pellet of sorbent, and derived D_a from known equations. In his calculations Haul assumed that D_a was independent of the extent of adsorption. This, as Carman points out[133], is essentially incorrect, and casts doubts on the validity of the author's conclusions.

Timofeev and Voskresenskii[132] investigated the speed of diffusion of ethyl bromide vapour through charcoal cylinders, with and without a counter-current of a non-adsorbed gas (nitrogen). The position of the adsorption front of ethyl bromide was ascertained by X-radiography. The work was carried out at 20°, at a concentration of ethyl bromide of 20.7 to 75.9 mg litre^{-1} and under atmospheric pressure of nitrogen. Under these conditions nitrogen has practically no effect on the adsorption of ethyl bromide, and consequently the counter-current could only have affected the rate of transport of ethyl bromide in the gas phase, i.e. in pores of radius larger than the molecular mean free path. The experiments showed that the nitrogen counter-stream considerably inhibited the transport of ethyl bromide through active charcoal and thus underlined the importance of volume diffusion.

To recapitulate what has been said on the relative role of surface diffusion in transport processes at porous sorbents, it is established that this type of diffusion can contribute to the overall velocity of the process. The contribution can be a major or a minor one, according to the pore structure and the experimental conditions. With micro-porous, and fairly homogeneous sorbents, such as those described by Barrer, the flow of matter in the adsorbed phase may be comparable with that in the gas phase. With sorbents having a complex distribution of pore sizes surface diffusion may be ignored, in comparison with transport in the gas phase, when the sorption process is carried out at ordinary temperatures and, particularly, when coverage is low.

Flow of Liquid Adsorbates

Flood[93-98] considers that an increased speed of flow of adsorbed gases in porous media can result from the migration of the adsorbate in the liquid state. He bases his deduction on the following considerations.

If we assume that the thermodynamic properties of the adsorbate are the same as those which apply to the gas phase the condition for thermal equilibrium is expressed by the equation

$$v_1 dp_1 = v_2 dp_2, \tag{43}$$

where v_1 and v_2 are the volumes, and p_1 and p_2 the pressures in the gas and in the adsorbed phases respectively.

From (43) it follows that

$$p_2 = \int_0^{p_1} \frac{v_1}{v_2} dp_1 = \int_0^{p_1} \frac{\rho_2}{\rho_1} dp_1, \tag{44}$$

where ρ_1 and ρ_2 are the respective densities.

By taking the mean values of ρ_1 and ρ_2 for the pressure interval $0-p_1$, Flood obtained

$$p_2 = \left|\frac{\bar{\rho}_2}{\rho_1}\right| p_1 \quad . \tag{45}$$

Since $\rho_2/\rho_1 \gg 1$, it follows that considerable adsorbate pressures will correspond to relatively small pressure gradients in the gas phase, and give rise to a flow of adsorbate along the surface.

With the help of a number of simplifying assumptions Flood was able to derive a theoretical equation for the viscous flow in the adsorbed phase:

$$G = \frac{b}{\eta_2}\left|\frac{\bar{\rho}^2}{\rho_1}\right|\frac{\Delta p}{L}, \tag{46}$$

where η_2 is the viscosity of the liquid adsorbate, Δp the pressure drop in the gas phase, and b a constant.

Eqn. (46) leads to a more general expression for the permeability of porous media to adsorbed gases:

$$K = A\sqrt{\frac{T}{M}} + \frac{B}{\eta_1}\bar{p} + \frac{b}{\eta_2}\left|\frac{\rho_2^2}{\rho_1}\right|. \tag{47}$$

The third term on the right-hand side describes the flow of liquid adsorbate in the micropores.

The empirical equation of Flood, Tomlinson, and Leger[93] offers much better agreement with experiments results:

$$K = A\sqrt{\frac{T}{M}} + \frac{B}{\eta_1}\bar{p} + \alpha\bar{a} + \beta\frac{a_1^n - a_2^n}{\Delta p}, \tag{48}$$

where $\bar{a}$ is the mean value of the adsorption in the pressure interval Δp, a_1 and a_2 are the adsorptions corresponding to the pressures p_1 and p_2, and α, β, and n are constants.

The authors showed that Eqn. (48) applies very well to the experimental data obtained in their study of the rate of flow of the following vapours on activated charcoal: benzene, ethyl chloride, ethyl ether, and methyl alcohol.

Capillary Flow

In the region of capillary condensation capillarity forces, arising from unequal meniscus curvatures, can give rise to the transport of adsorbate[133]. To illustrate the phenomenon an idealised sorbent pore is shown in Fig.10. The vapour exerts pressures p_1 and p_2 on its ends, and an adsorbate in the state of capillary condensation fills it. The well-known Kelvin equation relates the meniscus curvature to the relative pressure:

$$\ln\frac{p_s}{p_1} = \frac{\sigma}{r_{m_1}\rho_2}\frac{M}{RT}\cos\theta_1,$$

$$\ln\frac{p_s}{p_2} = \frac{\sigma}{r_{m_2}\rho_2}\frac{M}{RT}\cos\theta_2, \tag{49}$$

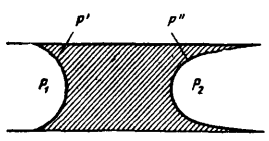


Fig.10. Liquid flow in a capillary.

where σ and ρ are the surface tension and density of the liquid adsorbate, θ the limiting contact angle, and ρ_s the saturated-vapour pressure. The inner pressure is related to the meniscus radius by Laplace's equation:

$$p' = \frac{\sigma \cos \theta_1}{r_{m_1}}; \quad p'' = \frac{\sigma \cos \theta_2}{r_{m_2}}. \tag{50}$$

Combining (49) and (50) we find

$$\Delta p = p'' - p' = \frac{\rho RT}{M} \ln \frac{p_1}{p_2}. \tag{51}$$

On account of this difference of pressure the adsorbate, in the state of capillary condensation, moves along the pores of the sorbent.

Special Features of the Transport of Water Vapour in Micro-Porous Adsorbents

Dacey and Thomas[124] measured the rates of adsorption of numerous substances on saran charcoal, and drew attention to the fact that water vapour adsorbs more slowly than other substances of similar molecular size. They carried out a special experiment on the rates of sorption and desorption of water vapour on three specimens of saran charcoal[134].

Up to the region of steep rise of the adsorption isotherm, water was found to behave like a gas of low molecular weight (extent of adsorption proportional to the square root of time). As the concentration and, consequently, the adsorption is increased, the effect of hydrogen bonding begins to be felt. At relatively high concentrations the rate of adsorption of water vapour becomes independent of time. The authors suggest that when the dry charcoal is exposed to a high relative pressure of water vapour the latter condenses on the outer surface and seals off the openings of the pores. As the water gradually penetrates into the very narrow pores, which can accommodate only a very few molecules, the hydrogen bonds begin to dissociate. This dissociation, according to the authors, is the rate-limiting stage of the penetration of water molecules into the depth of saran-charcoal particles. It follows that the rate of adsorption should be constant with time, as indeed is found to be the case.

CONCLUSION

A variety of methods have been applied to the study of the mechanism of transport in porous sorbents. A deeper understanding of the special features of the transport of adsorbed gases has been the result. A broad, qualitative picture of the process of transport of adsorbed gases in various regions of relative pressure, and at various coverages, can be established on the basis of existing knowledge. However, one deficiency in our understanding of the process must be pointed out. Great interest still attaches to a quantitative elucidation of the dependence of the several modes of transport on the structure of the sorbent. A few trends have been reported, but they are only the first steps in the required direction.

The structure of sorbents has received very little attention from the point of view of kinetics. Existing, quite delicate methods, e.g. those based on sorption, enable us to determine the effective dimensions of pores and their statistical distribution with sufficient precision. However, these methods are powerless to elucidate the interplay of adsorbing pores and transport pores, which is of fundamental importance to the kinetics of the process. A need exists for the development of kinetic methods of investigating the structure of porous substances. These problems are still awaiting solution.

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