

Estimation of Surface Diffusion Through Porous Media

A mathematical model is developed to describe steady-state nonequilibrium surface diffusion of an adsorbing gas through an energetically homogeneous porous medium by assuming that the adsorption isotherm is linear and that the gas-surface mass transfer can be described by the linear driving force model. Analytical solutions for the model are reported. It is found that the conventional assumption of local thermodynamic equilibrium between the gas and surface phases within the porous medium can seriously underestimate the surface diffusivity when the mass transfer rate is finite. Also, the length of the porous medium becomes a critical variable in that case.

Meaningful estimation of surface diffusivity also requires that the gas phase diffusivity through the porous medium be accurately known. The estimated surface diffusivity is model dependent when local thermodynamic equilibrium is not established instantaneously. Modeling surface diffusion can be very complex when the surface is energetically heterogeneous.

S. Sircar
M. B. Rao

Air Products and Chemicals, Inc.
7201 Hamilton Boulevard
Allentown, PA 18195

Introduction

It is well known that the transport of an adsorbing gas across a porous medium under a concentration gradient is caused by simultaneous diffusion of gas molecules through the void space within the pores and diffusion of adsorbed molecules on the surface of the porous medium (Ash et al., 1967). The gas phase flow can be governed by molecular, Knudsen, or activated diffusion depending on the relative dimensions of the pores and the diffusing molecules. A combination of these mechanisms may also prevail. The mechanism of surface flow is usually activated diffusion and its magnitude depends on the extent of adsorption, the strength of adsorption, the surface mobility, and so on. The nature of the surface diffusion can be very complicated if the surface is energetically heterogeneous.

A quantitative knowledge of surface diffusion is very desirable for practical designs of adsorption columns, catalytic reactors, adsorbent membranes, etc. However, there are three major problems in achieving that goal: the morphology of porous media, measurement of surface diffusion, and the assumption of instantaneous thermodynamic equilibrium.

Morphology

The actual morphology of practical porous media such as microporous adsorbents or catalysts can be very complex, consisting of an intricate network of interconnecting micro- and mesopores of various sizes and shapes. A detailed pore structure for these materials cannot be measured with any certainty by today's technology. Only the total void fraction, ϵ , the density, ρ_M , the relative pore size distribution for pores larger than 30 Å in diameter, the BET surface area, and the equilibrium adsorption characteristics of the gas on the porous medium can be measured using standard techniques. This prevents any meaningful microscale modeling of the porous media for gas flow through them, and empirical tortuosity factors are often invoked to account for the complex passage of the diffusing molecules through both phases (Satterfield, 1970). Furthermore, porous media of the same chemical composition may have different physical structures and thus very different gas transport characteristics. This rules out data correlation based on chemical properties of the porous media.

Surface diffusion

There is no direct method to measure surface diffusion. The conventional method is to measure the total gas flow, N , through a slab of the porous medium (cross-sectional area A and

Correspondence concerning this paper should be addressed to S. Sircar.

thickness L) for a given gas phase concentration gradient, $C_g^0 - C_g^L$, across the slab under isothermal and steady-state conditions, and define an overall diffusivity, \bar{D} , a gas phase diffusivity, D_g , and a surface phase diffusivity, D_s , for the process as follows:

$$N = \frac{A\epsilon\bar{D}}{L} (C_g^0 - C_g^L) \quad (1)$$

$$N_g = \frac{A\epsilon D_g}{L} (C_g^0 - C_g^L) \quad (2)$$

$$N_s = \frac{AD_s}{L} (C_s^0 - C_s^L) \quad (3)$$

N_g and N_s are, respectively, the total flow through the gas and surface phases across the slab. C_g and C_s are concentrations of the diffusing gas in the gas and adsorbed phases, respectively. Superscripts 0 and L represent the two ends of the slab.

It is generally assumed that the gas and surface phases are in thermodynamic equilibrium at all points within the slab (local equilibrium model) so that C_s and C_g are related by the adsorption isotherm of the gas on the surface.

$$C_s = F(C_g) \quad \text{constant } T \quad (4)$$

F is the equilibrium adsorption isotherm at temperature T in a functional notation.

Equations 1–4 can be combined to get:

$$\bar{D} = \frac{N \cdot L}{A\epsilon (C_g^0 - C_g^L)} = D_g + D_s \left[\frac{F(C_g^0) - F(C_g^L)}{\epsilon(C_g^0 - C_g^L)} \right] \quad (5)$$

Equation 5 shows that D_s for an adsorbing gas can be estimated from the experimentally measured N value if D_g can be estimated independently.

The commonly used technique to estimate D_g , pioneered by Barrer and Strachan (1955), is to measure the flow of a nonadsorbing gas, N^* , such as helium at moderate to high temperature, through the slab at different temperatures and obtain a temperature coefficient of the gas phase diffusivity ($D_g^* = \bar{D}$) for helium using Eq. 5. If helium flow experiments establish that the transport through the gas phase is controlled by Knudsen diffusion ($D_g^* \propto \sqrt{T}$), then D_g for an adsorbing gas of molecular weight M can be calculated by $D_g = D_g^*(4/M)^{0.5}$ at any given T . This method has been extensively used by many authors (Gilliland et al., 1974; Ash et al., 1976), who found that Knudsen diffusion predominated in the gas phase flow in the porous media of their work.

Once D_g for an adsorbing gas is estimated with confidence, D_s , its temperature coefficient, and its concentration dependence [$D_s(C_g)$] can be evaluated by measuring N at different temperatures and by using a differential diffusion test [$C_g^0 \sim C_g^L = C_g$] with varying C_g .

The above method for estimating D_g is acceptable when the pore diameter is much larger than the diameter of the adsorbing molecule. Otherwise, a confirmed Knudsen mechanism for helium flow does not guarantee Knudsen diffusion for the adsorbing gas. It may indeed be activated diffusion. Activated diffusion of the adsorbing gas through the void space of the

porous medium is certain when the helium diffusion itself is activated ($\ln D_g^* \propto 1/T$). In these cases, D_g cannot be estimated independently and therefore D_s cannot be evaluated. In fact, it may not even be possible to physically distinguish between the gas and surface phase flows when both are controlled by activated diffusion and \bar{D} will be the only meaningful diffusion parameter. Such a situation is expected to develop when the pores have molecular dimensions (≤ 10 Å dia.).

Another complication can be caused by the adsorbed molecules blocking or hindering the gas phase flow. This has been experimentally observed during flow of binary gas mixtures through porous media (Ash et al., 1973, 1976). In that case, measurement of helium diffusivity in the presence of the adsorbing gas can be used to estimate the degree of pore blockage.

It may be concluded that a meaningful estimation of D_s can only be made when the gas phase flow for helium is Knudsen and the effective Knudsen pore diameter ($d^* = 4.12 \times 10^3 D_g^* / \sqrt{T}$, nm) for the porous medium is much larger than the diameter of the adsorbing molecule so that the possibility of activated or hindered diffusion is remote. The estimated D_s is an effective surface diffusivity for a specific porous medium and it should be treated as a macroscopic property of that porous medium.

Thermodynamic equilibrium

The heart of the method for estimating D_s described above is based on the assumption of instantaneous thermodynamic equilibrium between the gas and surface phases within the porous medium. Recently Aris (1983) and Riekert (1985) independently argued that the rate of mass transfer of the adsorbing gas from the gas to surface phase can be finite and that introduces an additional unknown variable in the analysis of the gas transport data. Both authors correctly postulated that the diffusing gas enters and exits the porous medium through the gas phase while there are both gas and surface phase flows within the porous medium, as shown by Figure 1. This requires that the surface diffusion vanish at the two ends of the porous medium.

Using this model, Aris (1983) reported an analytical solution relating \bar{D} and D_s for a differential ($C_g^0 \sim C_g^L$) diffusion test when the adsorption equilibria and kinetics can be described by the Langmuir site-filling model. Riekert (1985) discussed the effect of a finite mass transfer rate from gas to surface on D_s by using a qualitative argument. Both authors demonstrated that a priori assumption of local adsorption equilibrium within the porous medium could be misleading.

Nonequilibrium Surface Diffusion Model

The purpose of this paper is to further investigate the effect of nonequilibrium gas adsorption on the estimation of steady-state

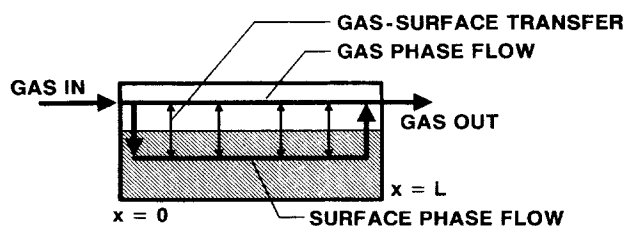


Figure 1. Flow through a porous medium.

surface diffusivity of a single gas flowing through an energetically homogeneous porous medium. This implies that the surface and gas phase diffusivities of the adsorbate, the gas-surface adsorbate mass transfer coefficient, and the equilibrium adsorption characteristics of the adsorbate do not vary across the length of the porous medium. We consider an integral diffusion test ($C_g^0 > C_g^L$), which is most commonly used. The transport mechanism through the porous medium is the same as that described by Figure 1.

We assume that the adsorption equilibrium is linear ($\bar{C}_s = KC_g$) and that the adsorbate mass transfer from gas to surface phase can be described by the linear driving force (LDF) model so that the local rate of adsorption, r , within the porous medium is given by $r = k(\bar{C}_s - C_s)$. \bar{C}_s is the local adsorbate surface concentration in equilibrium with the local gas phase concentration, C_g . K and k are, respectively, the dimensionless equilibrium constant and the adsorbate mass transfer coefficient. It follows that the isothermal steady-state adsorbate mass balance equations for the gas and surface phase diffusion may be written as:

Gas phase

$$\epsilon D_g \frac{d^2 C_g}{dx^2} = k(\bar{C}_s - C_s) \quad (6)$$

Surface phase

$$D_s \frac{d^2 C_s}{dx^2} = -k(\bar{C}_s - C_s) \quad (7)$$

x is the distance within the porous slab ($0 \leq x \leq L$) and C_g and C_s are, respectively, steady state gas and surface phase adsorbate concentrations at distance x . The boundary conditions are:

$$C_g(x=0) = C_g^0, C_g(x=L) = C_g^L \quad (8)$$

$$\left(\frac{dC_s}{dx}\right) = 0 \text{ at } x = 0 \text{ and } L \quad (9)$$

$$N = -A\epsilon D_g \left(\frac{dC_g}{dx}\right)_{x=0,L} \quad (10)$$

N is the total gas flow through the porous medium. In the absence of surface diffusion, which can be caused by no adsorption ($K = 0$), infinitely slow adsorbate mass transfer rate ($k \rightarrow 0$), and no surface mobility ($D_s \rightarrow 0$), N is equal to N_g^* , given by:

$$N_g^* = \frac{A\epsilon D_g}{L} [C_g^0 - C_g^L] \quad (11)$$

Equations 6–11 can be solved simultaneously to get:

$$E = \frac{(1+a)}{(1+a) - \psi(\theta)} \quad (12)$$

$$\psi(\theta) = 1 - \frac{2(\cosh \theta - 1)}{\theta \sinh \theta} \quad (13)$$

$$\theta^2 = \left(\frac{1+a}{b}\right) \quad (14)$$

$$\frac{C_g^0 - C_g}{C_g^0 - C_g^L} = 1 - \frac{a(1-z) - f(\theta, z)}{(1+a) - \psi(\theta)} \quad (15)$$

$$\frac{\bar{C}_s^0 - C_s}{\bar{C}_s^0 - \bar{C}_s^L} = 1 - \frac{(1-z) + f(\theta, z)}{\psi(\theta)} \quad (16)$$

$$f(\theta, z) = \frac{\cosh \theta z - \cosh \theta(1-z) - \cosh \theta + 1}{\theta \sinh \theta} \quad (17)$$

The variable E in Eq. 12 is the ratio of N to N_g^* . Thus, there is extra flow through the porous medium due to surface diffusion when $E > 1$. $E = 1$ in the absence of surface diffusion. Equations 15 and 16 respectively give steady state gas and surface phase adsorbate concentration profiles within the porous medium as functions of dimensionless distance $z (=x/L)$. $a [= \epsilon D_g / KD_s]$ and $b [= \epsilon D_g / (kL^2)K]$ are two independent dimensionless variables for this model. The variable a is the relative measure of gas and surface phase diffusivities through the porous medium, while the variable b is that for gas phase diffusivity and the adsorbate mass transfer rate.

In the absence of surface diffusion ($K \rightarrow 0$, $a \rightarrow \infty$, $b \rightarrow \infty$, $\theta \rightarrow \text{finite}$, $\psi \rightarrow \text{finite}$), ($D_s \rightarrow 0$, $a \rightarrow \infty$, $\theta \rightarrow \infty$, $\psi \rightarrow 1$), or ($k \rightarrow 0$, $b \rightarrow \infty$, $\theta \rightarrow 0$, $\psi \rightarrow 0$), Eq. 12 shows that E approaches unity. On the other hand, for local equilibrium conditions ($k \rightarrow \infty$, $b \rightarrow 0$, $\theta \rightarrow \infty$, $\psi \rightarrow 1$), Eq. 12 shows that E approaches \bar{E} , given by:

$$\bar{E} = \left(\frac{a+1}{a}\right) = 1 + \frac{KD_s}{\epsilon D_g} \quad (18)$$

\bar{E} is the maximum value of E , achieved under local equilibrium conditions. A comparison between Eqs. 12 and 18 shows that *a priori* assumption of local equilibrium in analyzing transport data of an adsorbing gas through a porous medium will yield a D_s value lower than the true surface diffusivity if k is finite.

It can be shown that Eq. 18 is equivalent to Eq. 5 for a linear adsorption isotherm. This is a very interesting result. Equation 5 was derived without invoking the Aris-Rieckert boundary condition of vanishing surface diffusion at the two ends of the porous medium, Eq. 9. Thus, that boundary condition has no effect on the form of the steady-state mathematical solution of the mass balance equations and, therefore, on the estimation of D_s under local equilibrium conditions even though it has a profound physical significance in terms of the actual mechanism of gas transport across the porous medium. This behavior will not be valid when the adsorption isotherm is nonlinear.

We estimated the possible error in evaluating D_s by assuming local equilibrium using the transport data for argon and sulfur hexafluoride across a porous plug of energetically homogeneous graphon at 304 K (Ash et al., 1967). The plug was 0.032 m long and had a void fraction of 0.42. The helium diffusivities at different temperatures through the graphon plug followed a \sqrt{T} dependence, indicating Knudsen diffusion. Its value at 304 K was $3.61 \times 10^{-6} \text{ m}^2/\text{s}$, which corresponded to an effective Knudsen pore diameter of 8.5 nm for the plug. Since this diameter was much larger than the molecular sizes of Ar and SF₆, it was safe to assume that the gas phase flow for those gases

through the plug was also Knudsen diffusion. The adsorption isotherms for these gases on graphon were linear with K values of, respectively, 0.52 and 8.30 for Ar and SF₆ (Ash et al., 1967). The respective isosteric heats of adsorption for Ar and SF₆ on graphon were calculated to be 9.28 and 18.14 kJ/mol. Thus, Ar was a much more weakly adsorbed gas than SF₆ on graphon. The D_s values for these gases were calculated from the experimental N data using the above nonequilibrium surface diffusion model in conjunction with different values of k . Table 1 summarizes the results.

It may be seen from Table 1 that the more weakly adsorbed Ar exhibits a much larger surface diffusivity than SF₆ as expected. But the effect of k on D_s for Ar is astounding. A sevenfold increase in D_s occurs when k decreases from 1.0 to 0.01 s⁻¹ for the same value of \bar{D} . That effect is much less pronounced for SF₆, which is fairly strongly adsorbed.

This analysis demonstrates that k must be independently known before a reliable value of D_s can be estimated. The assumption of local equilibrium can severely underestimate the surface diffusivity, in particular for less strongly adsorbed gases. The effect of nonisothermal adsorption must be taken into account during the measurement of k (Sircar, 1983).

Parametric Studies

The following parametric studies were carried out using the above simplified model to demonstrate the effects of nonequilibrium adsorption on the transport characteristics of a gas through a porous medium.

Concentration profiles within the porous medium

The dimensionless gas and surface phase concentration profiles within the porous medium are given by Eqs. 15 and 16, respectively. They were used to generate these profiles for transport of Ar through the graphon slab for the values of k , D_g , and D_s listed in Table 1. The results for two cases are shown in Figure 2 ($k = 0.01$) and Figure 3 ($k = 0.1$). For slow adsorbate uptake, Figure 2 shows that the gas and surface phase concentration profiles across the slab are very nonlinear (S-shaped). As k increases, they become more linear, Figure 3. Ultimately, for local equilibrium conditions, the dimensionless C_g profile becomes a linear function of z as required while the dimensionless C_s profile approaches linearity over a large value of z except at the two ends, where the slopes of the C_s profiles are zero due to the Aris-Rieckert boundary conditions. The zero slopes of the C_s profiles at $z = 0$ and $z = 1$ can be clearly seen from Figures 2 and 3. These figures also show the ratios of the steady state surface to total flow, F_s , through the porous medium as functions of z . F_s is equal to zero at the two ends of the slab and it goes through a maximum at $z = 0.5$. F_s remains constant over a large

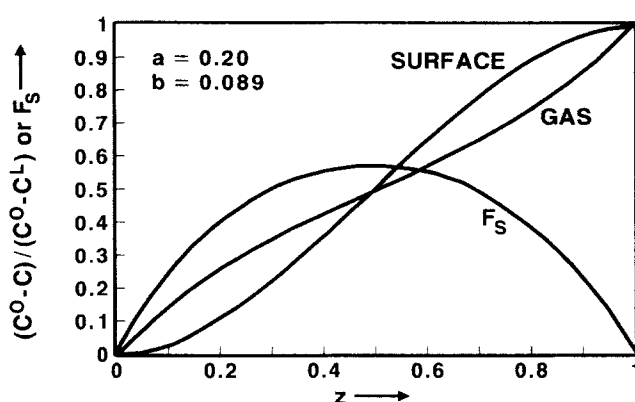


Figure 2. Profiles of dimensionless gas and surface phase concentrations and F_s within porous medium, $a = 0.20$, $b = 0.089$.

range of z when k is large and eventually F_s becomes practically constant throughout the entire length of the porous medium except at the two ends when $k \rightarrow \infty$. The maximum value of F_s decreases as k increases. The limiting value of F_s for the system of Figures 2 and 3 is 0.39 under local equilibrium conditions. Earlier, Rieckert (1985) had conceptualized these forms of concentration profiles using qualitative arguments.

Magnitude of extra flow due to surface diffusion

The variable E ($1 \leq E \leq \bar{E}$) given by Eq. 12 gives the magnitude of extra flow due to surface diffusion. We studied the effect of the independent variables a and b on E by defining a new dimensionless variable η as follows:

$$\eta = b/a = \frac{D_s}{(kL^2)} \quad (19)$$

Thus, η is a measure of the relative ratio of surface diffusion and adsorbate mass transfer rate from gas to surface phase. It is sort of a reciprocal of the Thiele modulus. η is zero for the local equilibrium case.

Figure 4 shows a family of plots of E as functions of η for different values of a . It may be seen that E approaches \bar{E} when

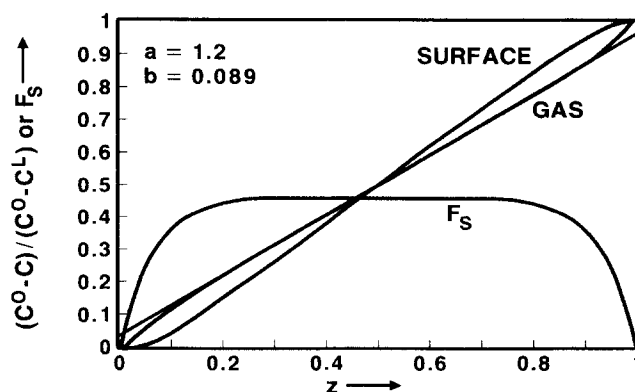


Figure 3. Profiles of dimensionless gas and surface phase concentrations and F_s within porous medium, $a = 1.20$, $b = 0.0089$.

Table 1. Estimation of D_s on Graphon at 304 K by Nonequilibrium Surface Diffusion Model

Gas	D_g $\text{m}^2/\text{s} \times 10^7$	K	$D_s, \text{m}^2/\text{s} \times 10^8$			
			$k = \infty$	$k = 1.0$	$k = 0.1$	$k = 0.01$
Argon	11.40	0.52	60.0	65.9	76.9	461.0
Sulfur hexafluoride	5.98	8.30	8.2	8.5	9.2	12.6

k values in s⁻¹.

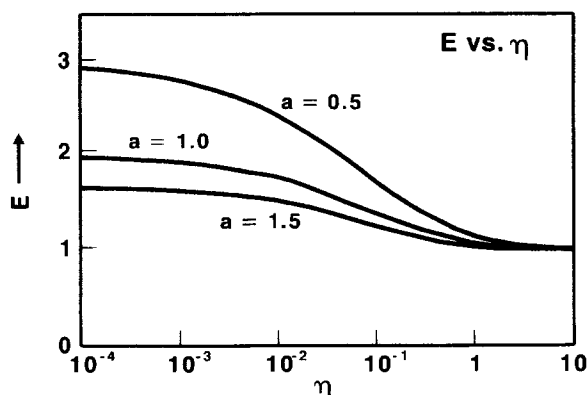


Figure 4. Extra flow, E , through a porous medium due to surface diffusion as a function of η .

$\eta \rightarrow 0$. E decreases with increasing η and finally E approaches unity when η is large. Also, E increases for a given η when the variable a decreases. These results have several very interesting consequences:

1. For a given η , E can be increased by increasing the product KD_s , which decreases the variable a . From adsorption thermodynamics, K may be expressed as (Sircar and Myers, 1988):

$$K = (K_0 \rho_M RT) \exp(q/RT) \quad (20)$$

where K_0 is a constant, R is the gas constant, and q is the isosteric heat of adsorption of the gas on the porous medium. K increases as q increases. D_s , on the other hand, is given by (Sladek et al., 1974):

$$D_s = D_{s0} \exp(-mq/RT) \quad (21)$$

where D_{s0} is the maximum value of D_s . D_s decreases as q is increased. m can vary between zero and unity depending on the size of the energy barrier to surface flow. It follows that:

$$KD_s = BT \exp[q(1-m)/RT] \quad (22)$$

where $B (=K_0 D_{s0} \rho_M R)$ is a constant.

Equation 22 shows that KD_s increases as q is increased when $m \neq 1$. Thus, the larger the value of q or the stronger the gas-solid interaction and the smaller the value of m or the lower the energy barrier for surface flow, the larger is the value of E .

2. For a given value of a , E increases as η decreases. This is facilitated by smaller D_s , larger k , and larger L . E approaches \bar{E} when $\psi(\theta)$ in Eq. 12 approaches unity. It can be shown that this limit is approximately reached when $\eta \leq 0.0004(a+1)/a$. On the other hand, E approaches unity when $\psi(\theta)$ in Eq. 12 approaches zero. This limit is approximately reached when $\eta \geq 4(a+1)/a$.

These results indicate that for given values of a , k , and D_s , there is a critical value of $L (=L^*)$ below which E approaches unity. In other words, the test medium must be longer than L^* to detect the extra flow due to surface diffusion. Conversely, one may measure surface diffusion by using a test slab of a certain length and then find that the surface diffusion has apparently vanished when a smaller slab is used.

A finite value of L^* exists only when k is finite. L^* approaches

zero when local equilibrium prevails. Thus, variation of E with varying L is a proof of a finite k . Otherwise, one may assume that local equilibrium prevails. We recommend that this test be carried out to check the validity of the local equilibrium assumption. The test, however, may be insensitive when L is very large, which makes η very small, and E approaches \bar{E} , giving the false appearance of the existence of local equilibrium.

Effect of L on E

Figure 5 shows a family of plots of E as functions of L for a given set of values of ϵ , D_g , D_s , and K , which have the same order of magnitudes as those for the Ar on graphon system. k is the variable parameter. The parameter a for this system has a value of 1.50 and \bar{E} is equal to 1.67. It may be seen that E is a very strong function of L , in particular when k is small. The values of L^* for the three curves shown in Figure 5 are 30 ($k = 100$), 300 ($k = 1$), and 3,000 ($k = 0.01$) μm . Thus, even for a large k of 100 s^{-1} , the extra flow due to surface diffusion may not be detectable unless the porous medium is at least 30 μm thick.

The figure also shows that even for a fairly thick porous medium, E can be substantially less than \bar{E} . For a very low k (0.01 s^{-1}), a length of 1.2 m of the porous medium will be needed for E to approach \bar{E} for this system.

The key conclusion reached from this parametric study is that the experimentally measured value of E , and hence the estimated value of D_s by the assumption of local equilibrium, can be a strong function of the length of the porous medium used in the test unless $k \rightarrow \infty$. Consequently, the conventional method of estimating D_s can give erroneous values depending on the length of the porous medium used in the test.

Model dependency of D_s

The equilibrium adsorption characteristics of a diffusing gas on the porous medium can be measured unequivocally without knowing the physicochemical structure of that medium, but a model is required to describe the gas to surface phase mass transfer rate, which is determined by the structure of the porous medium. Consequently, the estimation of D_s becomes model dependent when local equilibrium between the gas and surface phases is not instantaneously established. The present study uses the simplified LDF model of mass transfer and its validity must be checked before it can be used for reliable data interpretation.

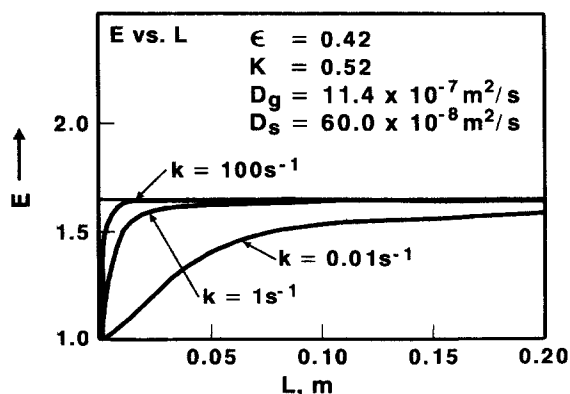


Figure 5. Extra flow, E , through a porous medium due to surface diffusion as a function of thickness L of the medium.

A more serious problem arises when the surface of the porous medium is energetically heterogeneous. In this case, the diffusing molecule passes over patches of different energy barriers and equilibrium adsorption characteristics, giving rise to a varying local surface diffusivity across the porous medium. Although models can be developed to describe integral equilibrium adsorption on such surfaces (Sircar and Myers, 1988), extraordinary assumptions must be made about the geometry and distribution of these surface energy patches in order to model the surface diffusion process.

Conclusions

Reliable estimation of surface diffusivity of adsorbing gases through porous media requires an accurate estimation of gas phase diffusivity through the pores, and a priori knowledge of gas to surface phase mass transfer coefficient.

The commonly used assumption of local thermodynamic equilibrium between the gas and surface phases within the porous medium can significantly underestimate the surface diffusivity when the adsorbate mass transfer rate is finite, particularly for less strongly adsorbed gases. Also, the thickness of the porous medium becomes an important variable in determining the surface diffusivity in that case. In fact, the variation in the measured extra flows through the porous medium due to varying thickness of the medium is evidence of a finite adsorbate mass transfer rate. There is a minimum thickness of the porous medium that is required to even detect the extra flow due to surface diffusion.

The commonly used relationship between D and D_s , Eq. 5, under local equilibrium conditions, Eq. 18, is equivalent to the solution of the mass balance equations for linear adsorption equilibrium when the Aris-Riekert boundary conditions, Eq. 9, are applied.

The estimation of surface diffusivity is model dependent when instantaneous thermodynamic equilibrium is not established between the gas and surface phases within the porous medium. Modeling the surface diffusion process for an energetically heterogeneous surface can be complicated due to lack of knowledge of the geometry and distribution of patches of different energies on the surface.

Notation

A = cross-sectional area of porous medium, m^2
 a = dimensionless variable, $\epsilon D_g / K D_s$
 b = dimensionless variable, $\epsilon D_g / (k L^2) K$
 C_g = gas phase concentration, $kmol/m^3$
 C_s = surface phase concentration, $kmol/m^3$ of porous medium
 \bar{C}_s = surface phase concentration in equilibrium with C_g , $kmol/m^3$ of porous medium
 \bar{D} = overall diffusivity through porous medium, m^2/s
 D_g = gas phase diffusivity, m^2/s
 D_s = surface phase diffusivity, m^2/s
 D_{s0} = constant, Eq. 21
 D_s^* = helium diffusivity, m^2/s
 d^* = effective Knudsen pore diameter, nm
 E = extra flow through porous medium due to surface diffusion, Eq. 12
 \bar{E} = maximum value of E , Eq. 18

F = adsorption isotherm in functional notation, Eq. 4
 F_s = ratio of surface to total flow
 f = function, Eq. 17
 K = dimensionless adsorption equilibrium constant
 K_0 = constant, Eq. 20
 k = adsorbate mass transfer coefficient, s^{-1}
 L = thickness of porous medium, m
 L^* = minimum thickness of porous medium to detect surface flow, m
 M = molecular weight of adsorbing gas
 m = dimensionless constant, Eq. 21
 N = overall steady state flow through porous medium, $kmol/s$
 N_g^* = overall steady state flow through porous medium in the absence of surface diffusion, $kmol/s$
 q = isosteric heat of adsorption, kJ/mol
 R = gas constant
 r = adsorbate mass transfer rate, $kmol/s \cdot m^3$ of porous medium
 T = temperature, K
 x = distance, m
 z = dimensionless distance, x/L

Greek letters

ϵ = void fraction
 ρ_M = density of porous medium, kg/m^3
 θ = dimensionless variable, Eq. 14
 ψ = dimensionless variable, Eq. 13
 η = dimensionless variable, Eq. 19

Superscripts

0 = end of porous medium defined by $x = 0$
 L = end of porous medium defined by $x = L$

Literature Cited

- Aris, R., "Interpretation of Sorption and Diffusion Data in Porous Solids," *Ind. Eng. Chem. Fundam.*, **22**, 150 (1983).
 Ash, R., R. W. Baker, and R. M. Barrer, "Sorption and Surface Flow in Graphitized Carbon Membranes. I: The Steady State," *Proc. Roy. Soc.*, **A299**, 434 (1967).
 Ash, R., R. M. Barrer, and R. T. Lowson, "Transport of Single Gases and of Binary Gas Mixtures in a Microporous Carbon Membrane," *J. Chem. Soc. Faraday Trans. I*, **69**, 2166 (1973).
 Ash, R., R. M. Barrer, and P. Sharma, "Sorption and Flow of Carbon Dioxide and Some Hydrocarbons in a Microporous Carbon Membrane," *J. Mem. Sci.*, **1**, 17 (1976).
 Barrer, R. M., and E. Strachan, "Sorption and Surface Diffusion in Microporous Carbon Cylinders," *Proc. Roy. Soc.*, **A231**, 52 (1955).
 Gilliland, E. R., R. F. Baddour, G. P. Perkinson, and K. J. Sladek, "Diffusion on Surfaces. I: Effect of Concentration on the Diffusivity of Physically Adsorbed Gases," *Ind. Eng. Chem. Fundam.*, **13**, 95 (1974).
 Riekert, L., "The Relative Contributions of Pore Volume Diffusion and Surface Diffusion to Mass Transfer in Capillaries and Porous Media," *AIChE J.*, **31**, 863 (1985).
 Satterfield, C. N., *Mass Transfer in Heterogeneous Catalysis*, MIT Press, Cambridge, MA, 41 (1970).
 Sircar, S., "Linear Driving Force Model for Non-Isothermal Gas Adsorption Kinetics," *J. Chem. Soc. Faraday Trans. I*, **79**, 785 (1983).
 Sircar, S., and A. L. Myers, "Equilibrium Adsorption of Gases and Liquids on Heterogeneous Adsorbents—A Practical Viewpoint," *Surface Sci.*, **205**, 353 (1988).
 Sladek, K. J., E. R. Gilliland, and R. F. Baddour, "Diffusion on Surfaces: Correlation of Diffusivities of Physically and Chemically Adsorbed Species," *Ind. Eng. Chem. Fundam.*, **13**, 100 (1974).

Manuscript received Dec. 5, 1989, and revision received June 8, 1990.