Adsorption by Nonhomogeneous Porous Solids—Effect of Adsorption Energy Gradient on Surface Flow

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Surface diffusion often plays an important role in processes involving interactions between a fluid and a solid, such as adsorption, permeation, compound formation, catalysis, and others. The contribution of surface diffusion to the penetration of gases in macroporous solids is appreciable when adsorption is strong and the pores contain a significant amount of adsorbate of low vapor pressure. In microporous solids with pore widths of the order of the size of the sorbate molecules, surface diffusion is the only possible mode of diffusion as the pore space is incapable of accommodating a gas phase as well as an adsorbate phase and all the molecules occluded in a pore are sorbed molecules. Surface diffusion may be of importance also in chemisorption on nonporous surfaces. The kinetics of chemisorption have been explained (Birnholtz et al., 1984) by assuming that the adsorbate is taken up from the fluid phase at patches with low activation energy for adsorption and that it subsequently migrates onto patches with higher activation energy for adsorption.

The laws governing the kinetics of surface diffusion are well established for simple systems: diffusion taking place on a homogeneous surface and no interactions between the adsorbed molecules undergoing diffusion (Riekert 1970). In this case an expression equivalent to Fick's equation is applicable:

$$J = -D(\partial c/\partial x) \qquad (1)$$

D is independent of c; its variation with temperature is exponential and determined by the activation energy for diffusion:

$$D = D_o \exp(-E_a/RT) \qquad (2)$$

More complex expressions equivalent to Fick's equation, but with D varying with c, were derived for cases in which interactions between admolecules are important (Reed and Ehrlich, 1981; Ruthven, 1984) and for multilayer adsorption (Okazaki et al., 1981).

The equations for surface diffusion that have been derived are generally based on the implicit assumption that the adsorption energy of the diffusing adsorbate does not vary along the diffusion path. Heterogeneous surfaces containing sites with various adsorption energies were considered by Okazaki et al. They smoothed the variation of the adsorption energy along the diffusion path by averaging the heat of adsorption. Their treatment is valid for systems in which the energy varies over microscopic distances, whereas the diffusion path extends over a macroscopic distance. The equation obtained corresponds to Eq. 1, with D varying with c.

There are, however, surface diffusion processes of practical importance involving adsorbents in which the adsorption energy varies over a macroscopic distance. Various authors (e.g., Samusenko et al., 1984) have shown that pellets prepared by extruding and pressing have nonuniform porosity—i.e., the pore volume, the mean pore radius, and the specific area vary along the pellet radius as a result of nonuniform distribution of the pressure during the pelletization process. Pellets with nonuniform porosity are often used as catalyst supports, and at some stage of the preparation of the catalyst active components are introduced by impregnation. The penetration of the impregnating solute and the resulting distribution in the pellet is affected by the variation of the adsorption energy along the diffusion path, which should be taken into account in the derivation of kinetic models. There are also cases in which variation of the energy of adsorption should be taken into account even when it varies over microscopic distances. This is true if the diffusion path is also microscopic, e.g., in applications of the model of Birnholtz et al. to diffusion on a heterogeneous surface.

Surface Flux in a Medium in which Energy of Adsorption Varies

When a transport process is determined by the concentration gradient as well as other driving forces, Eq. 1 is not applicable and one must use a more fundamental form of the diffusion equation. The driving force for transport, in the general case, is the gradient of the chemical potential, and the flux is given by

$$J = -uc(d\mu/dx) \quad (3)$$

This fundamental equation has been used for deriving diffusion equations applicable to various situations: diffusion of atoms in solid crystals (Jost, 1960; Manning, 1968), and surface diffusion on a uniform surface with lateral interactions between admolecules (Reed and Ehrlich, 1981).

Rewriting Eq. 3 in terms of the fugacities, using the equation

$$\mu - \mu_{eq} = RT \ln (f/f_{eq}) \quad (4)$$

gives

$$J = -ucRT(f/f_{eq})^{-1}[\partial(f/f_{eq})/\partial x] \quad (5)$$

For a dilute sorbate the fugacity at any location is proportional to the concentration at that location (Henry's law)

$$f_x(c, x) = h_x(x)c(x) \quad (6)$$

where h_x is constant for a given location but varies with x. If this relation persists until equilibrium is attained we also have

$$f_{eq} = h_x(x)c_{eq}(x) \quad (7)$$

Equations 6 and 7 give

$$(f/f_{eq})_x = (c/c_{eq})_x \quad (8)$$

and introducing this in Eq. 5, one obtains

$$J = -Dc_{eq}[\partial(c/c_{eq})/\partial x] \quad (9)$$

where

$$D = uRT \quad (10)$$

Expressions for $\partial c/\partial t$

An expression for $\partial c/\partial t$ is obtained by applying to Eq. 9 the continuity equation

$$\partial c/\partial t = -\partial J/\partial x \quad (11)$$

The resulting equation is

$$\partial c/\partial t = D\partial\{c_{eq}[\partial(c/c_{eq})/\partial x]\}/\partial x + c_{eq}[\partial(c/c_{eq})/dx](\partial D/\partial x) \quad (12)$$

where c is a function of x, and t, c_{eq}, and D are functions of x.

Equation 12 acquires a simple form at an interval $0 < x < \ell$ if the variation of E_{ads} with x during that interval is linear, and if D is constant. The condition $E_{ads}(x)$ linear can be written as

$$E_{ads} = E_{adso} + (\alpha RT/\ell)x \quad (13)$$

Assuming that the equilibrium concentration is related to the adsorption energy by

$$c_{eq} = K_{eq} \exp (E_{ads}/RT) \quad (14)$$

one obtains

$$c_{eq} = K_{eq} \exp (E_{adso}/RT) \exp (\alpha x/\ell) \quad (15)$$

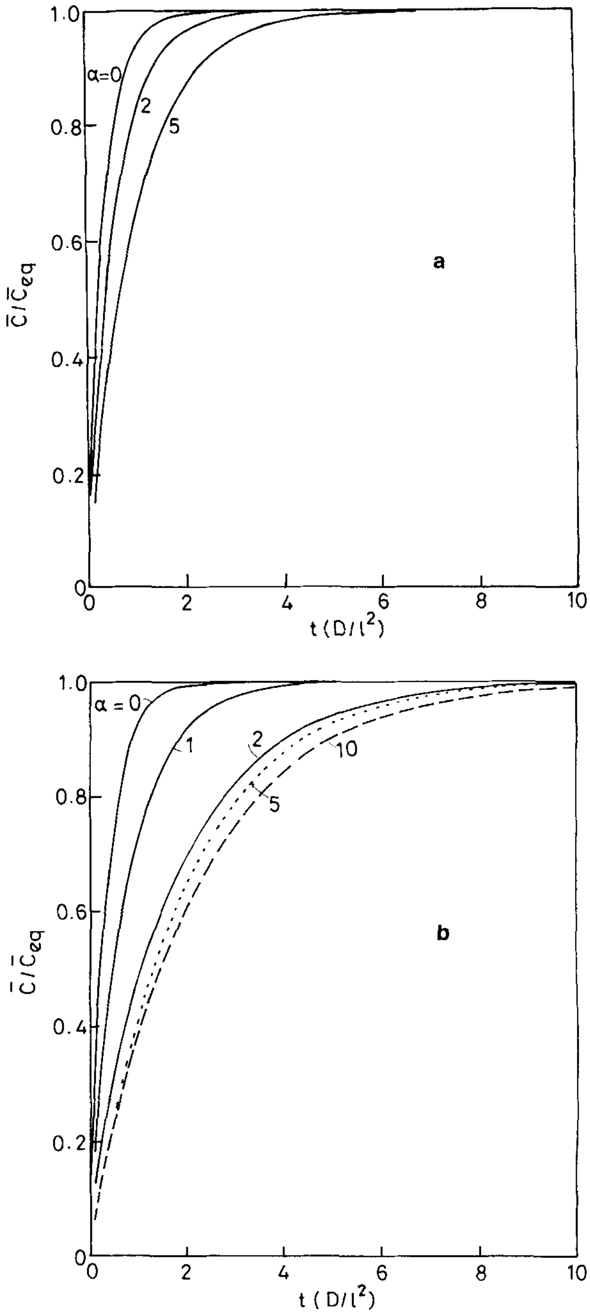

Figure 1. Rate of uptake. Plots of $\bar{c}/\bar{c}_{eq}$ against $t(D/\ell^2)$ for various α.

(a) Calculated according to Eq. 16.

(b) Calculated according to Eq. 19. For $\alpha = 5$ multiply abcissa figures × 10; for $\alpha = 10$ × 1,000.

Combining Eq. 15 with Eq. 12 and putting $\partial D/\partial x = 0$ one obtains

$$\partial c/\partial t = D[(\partial^2 c/\partial x^2) - (\alpha/\ell)(\partial c/\partial x)] \tag{16}$$

Another simple expression can be derived if both E_{ads} and E_a increase linearly with x, and $E_{ads}(x)$ and $E_a(x)$ have the same slopes. The condition E_a proportional to x can be written as

$$E_a = E_{ao} + (\alpha RT/\ell)x \tag{17}$$

The corresponding expression for D is

$$D = D_k \exp(-\alpha x/\ell) \tag{18}$$

where D_k is a constant.
Combining Eqs. 15 and 18 with Eq. 12 one obtains

$$\partial c/\partial t = D_k \exp(-\alpha x/\ell)[(\partial^2 c/\partial x^2) - (2\alpha/\ell)(\partial c/\partial x) + (\alpha^2/\ell^2)c] \tag{19}$$

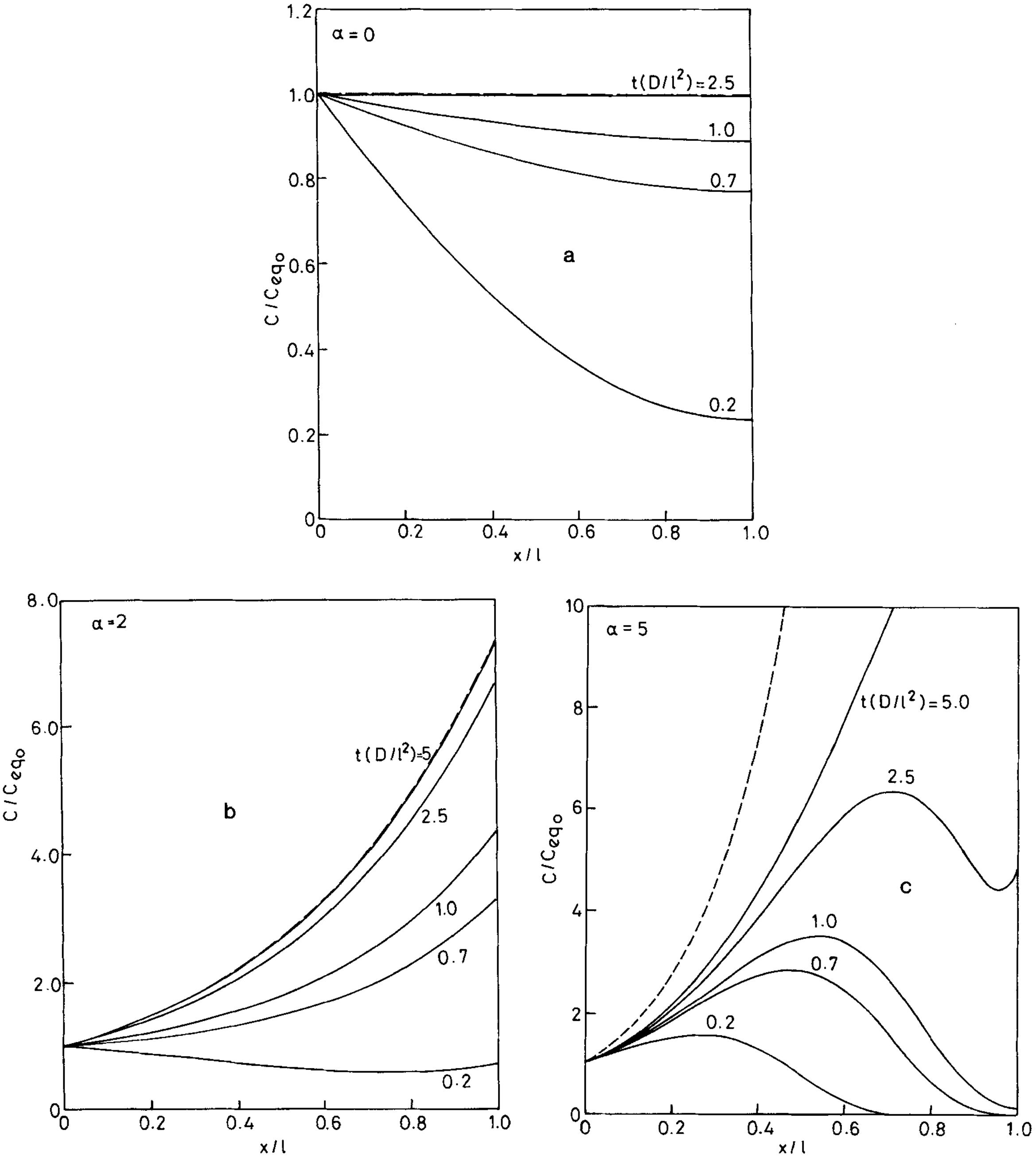

Figure 2. Concentration profiles at various times. Plots of c/c_{eqo} against x/ℓ for various values of $t(D/\ell^2)$.

(a) $\alpha = 0$.
(b) Calculated according to Eq. 16, $\alpha = 2$.
(c) Calculated according to Eq. 19, $\alpha = 5$.

Characteristics of Rate of Uptake and Concentration Profiles

The rate of uptake and the concentration profiles of the diffusing adsorbate can be calculated by introducing in Eq. 12 expressions for c_{eq} and D corresponding to the functions $E_{ads}(x)$ and $E_a(x)$, and integrating the resulting equation with appropriate boundary conditions.

An insight into the results expected from these calculations can be obtained by considering the simplified cases expressed by Eqs. 16 and 19, with the sorbate penetrating into a slab from a gas phase at constant concentration, and E_{ads} increasing with depth of penetration. The initial and boundary conditions are $c = 0$ at $t = 0$, $c = c_{eqo}$ at $x = 0$, and $d(c/c_{eq})/dx = 0$ at $x = \ell$. E_a is constant for case A (Eq. 16 valid), and it is porportional to E_{ads} for case B (Eq. 19 valid). Equations 16 and 19 were integrated numerically employing space discretizations by Galerkin's method (Schryer, 1977).

The time dependence of the amount taken up by the surface is depicted in Figure 1 as plots of $\bar{c}/\bar{c}_{eq}$ against $t(D/\ell^2)$ for various α, where $\bar{c}$ and $\bar{c}_{eq}$ are the average concentrations over the slab

$$\bar{c}(t) = \left(\frac{1}{\ell}\right)\int_0^{\ell} c(x, t)dx, \tag{20}$$

$$\bar{c}_{eq} = \left(\frac{1}{\ell}\right)\int_0^{\ell} c_{eq}(x)dx \tag{21}$$

The ratio $\bar{c}/\bar{c}_{eq}$ is equal to the ratio between the amounts taken up at t and at equilibrium. The concentration profiles are depicted in Figure 2 as plots of c/c_{eqo} against x/ℓ for various values of $t(D/\ell^2)$.

Figure 1 shows that the rate of uptake decreases with the time and vanishes at $\bar{c}/\bar{c}_{eq} = 1$ in nonuniform surfaces ($\alpha \neq 0$) as well as in uniform surfaces ($\alpha = 0$). However, the plots for nonuniform surfaces are determined by two parameters, α and D/ℓ^2, whereas the plot for a uniform surface is determined by the single parameter D/ℓ^2.

The concentration profiles for $\alpha \neq 0$ have features that distinguish them clearly from the profiles for $\alpha = 0$, Figure 2. There are ranges of t and x at which the concentration increases with x, i.e., ranges at which diffusion is uphill from a lower concentration to a higher one. Some of the profiles given by Eq. 19 have a maximum, as shown in Figure 2c. The position is at some point inside the slab at a distance from the external surface increasing with the time.

Concentration profiles with a maximum have been obtained in experiments in which porous pellets were impregnated by solutions of metallic ions (Vincent and Merrill, 1974; Hanika et al. 1982), and may indicate that the adsorbent pellets had nonuniform porosity. The energy of adsorption presumably varies along the radius, although the variation is not necessarily linear.

In conclusion, when one considers diffusion in pellets with nonuniform porosity, Fick's equation in its simple form can be inadequate and more realistic modeling can be achieved by taking into account heterogeneity.

Acknowledgment

Integrations and computation of data were performed by Dr. Farrow, Bell Laboratories, Murray Hill, NJ. The author is grateful for her contribution.

Notation

c = concentration of adsorbed molecules at t and x, mol · m^{-3}
c_{eq}, c_{eqo} = equilibrium concentration of adsorbed molecules at x and $x = 0$, mol · m^{-3}
$\bar{c}$ = average concentration of adsorbed molecules at t, Eq. 20, mol · m^{-3}
$\bar{c}_{eq}$ = average equilibrium concentration of adsorbed molecules, Eq. 21, mol · m^{-3}
D = diffusion coefficient, m^2 · s^{-1}
D_o, D_k = constants, Eqs. 2 and 18, m^2 · s^{-1}
E_a = energy of activation for diffusion, J
E_{ads} = adsorption energy at x, J
E_{adso}, E_{ao} = constants, Eqs. 13 and 17, J
f = fugacity of adsorbate at t and x, N · m^{-2}
f_{eq} = equilibrium fugacity at x, N · m^{-2}
h_x = constant, Eq. 6, J · mol^{-1}
J = surface flux, mol · m^{-2} · s^{-1}
ℓ = maximum values of x, m
R = gas constant, J · mol^{-1} · K^{-1}
T = temperature, K
t = time, s
u = constant, Eq. 3, m^2 · s^{-1} · J^{-1}
x = direction of diffusion path or distance from origin in this direction, m
α = constant dimensionless, Eq. 13
μ = chemical potential at t and x, J
μ_{eq} = equilibrium chemical potential, J

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Manuscript received Dec. 5, 1984, and revision received Feb. 25, 1986.