

A. Hines / R. Maddox

Mass Transfer

Fundamentals and Applications

Prentice-Hall (1985)

### Porous solids

This section is included to provide an introduction to the subject of diffusion in porous materials because of its importance in the study of catalysis and reaction in solids. Detailed discussions are presented by Satterfield (1970) and by Smith (1970).

Diffusion through porous materials is typically described as either ordinary, Knudsen, or surface diffusion and has been found to play an important role in catalyzed reactions. *Ordinary diffusion* occurs when the pore diameter of the material is large in comparison to the mean free path of the molecules of the gas. Molecular transport through pores which are small in comparison to the mean free path of the gas is described as *Knudsen-type diffusion*. Surface diffusion is the third type of mechanism for molecular transport in porous materials and has been found to be the most difficult to characterize. In *surface diffusion*, molecules are adsorbed on the surface of the material and are subsequently transported from one site to another in the direction of decreasing concentration. Since for

many cases surface diffusion has been assumed to contribute little to the overall transport, it will not be discussed here.

For Knudsen diffusion, molecules collide more often with the pore walls than with other molecules. Upon collision, the atoms are instantly adsorbed on the surface and then are desorbed in a diffuse manner. As a result of the frequent collisions with the wall of the pore, the transport of the molecule is impeded. The Knudsen diffusion coefficient can be predicted from kinetic theory by relating the diameter of the pore and the mean free path of the gas by the expression

$$D_{A,K} = \frac{\bar{U}d}{3} \quad (2-59)$$

where  $\bar{U}$  is the velocity of the gas molecule and  $d$  is the pore diameter. For straight, round pores the diffusivity becomes

$$D_{A,K} = 97.0r \left( \frac{T}{M_A} \right)^{1/2} \quad (2-60)$$

where  $r$  = pore radius, m,  
 $T$  = temperature, K,  
 $D_{A,K}$  = Knudsen diffusion coefficient, m<sup>2</sup>/s,  
 $M_A$  = molecular weight of component  $A$ .

The mean pore radius can be evaluated from the bulk density, the surface area of the porous solid, and the porosity by the expression

$$r = \frac{2\epsilon}{S\rho_B} = \frac{2V_p}{S} \quad (2-61)$$

where  $S$  = surface area of the porous solid, m<sup>2</sup>/kg,  
 $\rho_B$  = bulk density of the solid particle, kg/m<sup>3</sup>,  
 $V_p$  = specific pore volume of a solid particle, m<sup>3</sup>/kg,  
 $\epsilon$  = porosity of the solid.

In order to account for the tortuous path of the molecule and the porosity of the material, an effective Knudsen diffusivity may be expressed as

$$D_{A,K,\epsilon} = D_{A,K} \frac{\epsilon}{\tau} \quad (2-62)$$

where  $\tau$  is the tortuosity factor related to the path of the molecule. Bulk diffusion also contributes to the total molecular transport through the pores, but it also is decreased because of the porosity of the particle and the length of the path along which the molecule travels. The effective diffusivity can be described in terms of the ordinary diffusion coefficient by the equation

$$D_{AB,\epsilon} = D_{AB} \frac{\epsilon}{\tau} \quad (2-63)$$

Obvious cases exist where bulk and Knudsen diffusion both contribute to the effective diffusion coefficient. For self-diffusion or equimolar counter transfer, the effective diffusivity in a porous material can be written as

$$\frac{1}{D_{A,e}} = \frac{1}{D_{A,K,e}} + \frac{1}{D_{AB,e}} \quad (2-64)$$

In porous solids, in which transfer takes place primarily by Knudsen diffusion, the effective diffusivity can be used to estimate the tortuosity. A number of these systems have been studied experimentally and are shown in Table 2-11. An extensive list of values is presented by Satterfield (1970). Although ordinary diffusion coefficients for gases are influenced significantly by pressure, Knudsen diffusion coefficients are independent of pressure as shown by Eq. (2-60). The extent to which the effective diffusivity depends on pressure is a function of the relative magnitudes of the bulk and Knudsen diffusivities. Typical Knudsen diffusion coefficients may be an order of magnitude smaller than bulk coefficients for gases, particularly at low pressures.

TABLE 2-11. TRANSFER IN POROUS SOLIDS

<i>Material</i>	<i>Gases</i>	<i>T (K)</i>	<i>r × 10<sup>10</sup> (m)</i>	<i>τ</i>	<i>ε</i>
Alumina pellets: Henry et al. (1961)	N <sub>2</sub> , He, CO <sub>2</sub>	303	96	0.85	0.812
Silica gel: Schneider and Smith (1968)	C <sub>2</sub> H <sub>6</sub>	323–473	11	3.35	0.486
Silica-alumina cracking catalyst: Barrer and Gabor (1959)	He, Ne, Ar, N <sub>2</sub>	273–323	16	0.725	0.40
Vycor glass: Gilliland et al. (1958)	H <sub>2</sub> , He, Ar, N <sub>2</sub>	298	30.6	5.9	0.31