MOLECULAR DIFFUSION IN SOLIDS

Important Applications

- Leaching of foods (e.g. soyabeans)
- Leaching of metal ores
- Drying of timber, slats, and foods
- Diffusion and catalytic reaction in solid catalysts
- Separation of fluids by membranes
- Diffusion of gases through polymer films using in packaging
- Treatment of metals at high temperatures by gases

Types of diffusional transport in solids

1. Diffusion following Fick's law (valid for homogeneous solid with uniform structure)
2. Diffusion in porous solids depends on the actual structure and void channels

Diffusion in Solids Following Fick's Law

General equations:

$$N_A = -cD_{AB}\frac{d(x_A)}{dz} + \frac{c_A}{c}(N_A + N_B)$$

But,

$$\frac{c_A}{c}(N_A + N_B) \cong 0$$

Therefore,

$$N_A = -D_{AB}\frac{dc_A}{dz}$$

Note $D_{AB} \neq D_{BA}$. Integrating (for solid slab),

$$N_A = \frac{D_{AB}(c_{A1} - c_{A2})}{(z_2 - z_1)}$$

For cylinder with radii r_1 and r_2 and length L,

$$\frac{\overline{N_A}}{2\pi rL} = -D_{AB}\frac{dc_A}{dr}$$

$$\overline{N_A} = D_{AB}(c_{A1} - c_{A2})\frac{2\pi L}{\ln(r_2/r_1)}$$

Outside pressure of solute (liquid/gas) does not affect its diffusion coefficient (D_{AB}) inside the solid. For example, if CO_2 gas is outside a slab of rubber and is diffusing through the rubber, D_{AB} would be independent of the partial pressure of CO_2 at the surface. This means,

$$D_{AB} \neq f(p_A)$$

Note: Solubility of CO_2 in the solid is directly proportional to p_A. This is similar to the case of the solubility of O_2 in water being directly proportional to the partial pressure of O_2 in the air by Henry's law. The solubility of a solute gas (A) in a solid is usually expressed as S in m^3 solute (at STP of 0 °C and 1 atm) per m^3 solid per atm partial pressure of (A).

$$c_A = \frac{S\dfrac{m^3(STP)}{m^3 solid \cdot atm}}{22.4\dfrac{m^3(STP)}{kg\ mol\ A}} p_A atm = \frac{Sp_A}{22.4}\frac{kg\ mol\ A}{m^3 solid}$$

EXAMPLE 6.5-1. Diffusion of H_2 Through Neoprene Membrane

The gas hydrogen at 17°C and 0.010 atm partial pressure is diffusing through a membrane of vulcanized neoprene rubber 0.5 mm thick. The pressure of H_2 on the other side of the neoprene is zero. Calculate the steady-state flux, assuming that the only resistance to diffusion is in the membrane. The solubility S of H_2 gas in neoprene at 17°C is 0.051 m^3 (at STP of 0°C and 1 atm)/m^3 solid · atm and the diffusivity D_{AB} is 1.03×10^{-10} m^2/s at 17°C.

Solution: A sketch showing the concentration is shown in Fig. 6.5-1. The equilibrium concentration c_{A1} at the inside surface of the rubber is, from Eq. (6.5-5),

$$c_{A1} = \frac{S}{22.414} p_{A1} = \frac{0.051(0.010)}{22.414} = 2.28 \times 10^{-5} \text{ kg mol } H_2/m^3 \text{ solid}$$

Since p_{A2} at the other side is 0, $c_{A2} = 0$. Substituting into Eq. (6.5-2) and solving,

$$N_A = \frac{D_{AB}(c_{A1} - c_{A2})}{z_2 - z_1} = \frac{(1.03 \times 10^{-10})(2.28 \times 10^{-5} - 0)}{(0.5 - 0)/1000}$$

$$= 4.69 \times 10^{-12} \text{ kg mol } H_2/s \cdot m^2$$

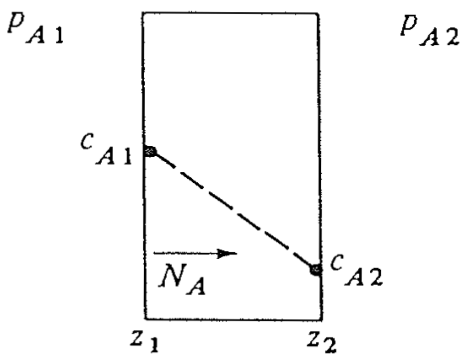


FIGURE 6.5-1. *Concentrations for Example 6.5-1.*

Permeability equations for diffusion in solids

$$c_{A1} = \frac{S p_{A1}}{22.4} \frac{kg\ mol\ A}{m^3 solid}; \quad c_{A2} = \frac{S p_{A2}}{22.4} \frac{kg\ mol\ A}{m^3 solid}$$

Therefore,

$$N_A = \frac{D_{AB}}{(z_2 - z_1)}(c_{A1} - c_{A2}) = \frac{D_{AB}}{(z_2 - z_1)}\left(\frac{S p_{A1}}{22.4} - \frac{S p_{A2}}{22.4}\right) = \frac{D_{AB} S (p_{A1} - p_{A2})}{22.4(z_2 - z_1)}$$
$$= \frac{P_M (p_{A1} - p_{A2})}{22.4(z_2 - z_1)} = \frac{P_M}{L} \frac{(p_{A1} - p_{A2})}{22.4} = \frac{(p_{A1} - p_{A2})}{22.4\left(\frac{L}{P_M}\right)}$$

$$P_M = D_{AB}\left(\frac{m^2}{s}\right) S \left(\frac{m^3(STP)}{m^3 solid \cdot atm}\right) = \left(\frac{m^3(STP)}{s \cdot m^2 solid \cdot atm/m}\right)$$

For the case of a tube,

$$\overline{N_A} = D_{AB}(c_{A1} - c_{A2}) \frac{2\pi L}{\ln(r_2/r_1)} = \frac{D_{AB} S}{22.4}(p_{A1} - p_{A2}) \frac{2\pi L}{\ln(r_2/r_1)}$$
$$= \frac{P_M}{22.4}(p_{A1} - p_{A2}) \frac{2\pi L}{\ln(r_2/r_1)}$$

For several solids of different thickness in series,

$$N_A = \frac{(p_{A1} - p_{A2})}{22.4} \frac{1}{\left(\frac{L_1}{P_{M1}} + \frac{L_2}{P_{M2}} + \cdot\cdot\right)}$$

For several tubes of different radii in series, the resistance will be added. For the case of two different tubes of different material, for example, one can write

$$\overline{N_A} = \frac{(p_{A1} - p_{A2})}{22.4} \frac{2\pi L}{\left[\frac{\ln(r_o/r_i)}{P_M}\right]} = \frac{(p_{A1} - p_{A2})}{22.4} \frac{2\pi L}{\left[\left\{\frac{\ln(r_o/r_i)}{P_M}\right\}_{Material\_1} + \left\{\frac{\ln(r_o/r_i)}{P_M}\right\}_{Material\_2}\right]}$$

EXAMPLE 6.5-2. Diffusion Through a Packaging Film Using Permeability

A polyethylene film 0.00015 m (0.15 mm) thick is being considered for use in packaging a pharmaceutical product at 30 °C. If the partial pressure of O_2 outside is 0.21 atm and inside the package it is 0.01 atm, calculate the diffusion flux of O_2 at steady state. Use permeability data from Table 6.5-1. Assume that the resistances to diffusion outside the film and inside are negligible compared to the resistance of the film.

Solution: From Table 6.5-1 $P_M = 4.17(10^{-12})$ m^3 solute(STP)/(s · m^2 · atm/m). Substituting into Eq. (6.5-8),

$$N_A = \frac{P_M(p_{A1} - p_{A2})}{22.414(z_2 - z_1)} = \frac{4.17(10^{-12})(0.21 - 0.01)}{22.414(0.00015 - 0)}$$

$$= 2.480 \times 10^{-10} \text{ kg mol/s} \cdot \text{m}^2$$

Note that a film made of nylon has a much smaller value of permeability P_M for O_2 and would make a more suitable barrier.

Experimental diffusivities, solubilities, and permeabilities

TABLE 6.5-1. *Diffusivities and Permeabilities in Solids*

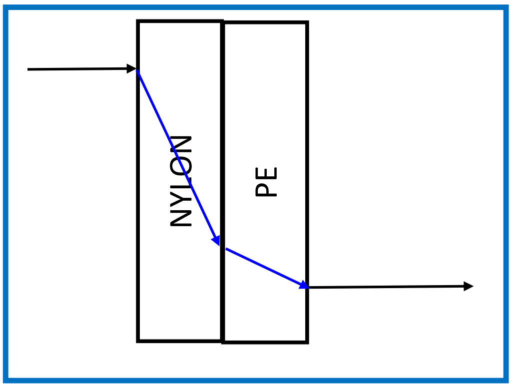
Solute (A)	Solid (B)	T (K)	D_{AB}, Diffusion Coefficient $[m^2/s]$	Solubility, S $\left[\frac{m^3 \text{ solute}(STP)}{m^3 \text{ solid} \cdot atm}\right]$	Permeability, P_M $\left[\frac{m^3 \text{ solute}(STP)}{s \cdot m^2 \cdot atm/m}\right]$	Ref.
H_2	Vulcanized rubber	298	$0.85(10^{-9})$	0.040	$0.342(10^{-10})$	(B5)
O_2		298	$0.21(10^{-9})$	0.070	$0.152(10^{-10})$	(B5)
N_2		298	$0.15(10^{-9})$	0.035	$0.054(10^{-10})$	(B5)
CO_2		298	$0.11(10^{-9})$	0.90	$1.01(10^{-10})$	(B5)
H_2	Vulcanized neoprene	290	$0.103(10^{-9})$	0.051		(B5)
		300	$0.180(10^{-9})$	0.053		(B5)
H_2	Polyethylene	298			$6.53(10^{-12})$	(R3)
O_2		303			$4.17(10^{-12})$	(R3)
N_2		303			$1.52(10^{-12})$	(R3)
O_2	Nylon	303			$0.029(10^{-12})$	(R3)
N_2		303			$0.0152(10^{-12})$	(R3)
Air	English leather	298			$0.15–0.68 \times 10^{-4}$	(B5)
H_2O	Wax	306			$0.16(10^{-10})$	(B5)
H_2O	Cellophane	311			$0.91–1.82(10^{-10})$	(B5)
He	Pyrex glass	293			$4.86(10^{-15})$	(B5)
		373			$20.1(10^{-15})$	(B5)
He	SiO_2	293	$2.4–5.5(10^{-14})$	0.01		(B5)
H_2	Fe	293	$2.59(10^{-13})$			(B5)
Al	Cu	293	$1.3(10^{-34})$			(B5)

Question:

i. Nitrogen gas at 5 atm and 30 ºC is diffusing through a membrane of nylon 0.5 mm thick and polyethylene 0.5 mm thick in series. The partial pressure at the other side of the two films is 1 atm. Assuming no other resistances, calculate the flux NA at steady-state.

ii. In the above case, draw a rough sketch of the profile of the partial pressure in the nylon and the polyethylene membrane.

Solution:



For several solids of different thickness in series,

$$N_A = \frac{(p_{A1} - p_{A2})}{22.4} \frac{1}{\left(\frac{L_1}{P_{M1}} + \frac{L_2}{P_{M2}} + \cdot\cdot\right)}$$

$$N_A = \frac{(5-1)}{22.4} \frac{1}{\left(\frac{0.5 \times 10^{-3}}{0.152 \times 10^{-12}} + \frac{0.5 \times 10^{-3}}{1.52 \times 10^{-12}}\right)} = 5.4 \times 10^{-12} \mathrm{kg\ mol/s \cdot m^2}$$

Question:

(Case I) A nylon film 0.15 mm thick is being considered for use in packaging a pharmaceutical product at 30°C. If the partial pressure of O_2 outside is 0.21 atm and inside the package it is 0.01 atm, calculate the diffusion flux of O_2 at steady state. Use permeability data from Table 6.5 -1. Assume that the resistances to diffusion outside the film and inside are negligible compared to the resistance of the film.

(Case II) A composite with two films in series is being considered for use in packaging a pharmaceutical product at 30°C. If the partial pressure of O_2 outside is 0.21 atm and inside the package it is 0.01 atm, calculate the diffusion flux of O_2 at steady state. Use permeability data from Table 6.5-1. Assume that the resistances to diffusion outside the film and inside are negligible compared to the resistance of the composite.

- Film 1: nylon film, thickness = 0.15 mm
- Film 2: polyethylene film, thickness = 0.15 mm

How much is the % reduction in the diffusion flux for Case II when compared with Case I.

Question

$T = 303\ K;\ P_M = 2.9\times 10^{-14}\ m^3(STP)/s\cdot m^2\cdot atm;$

$$N_{A1} = \frac{P_M}{L}\frac{(p_{A1}-p_{A2})}{22.4} = \frac{2.9\times 10^{-14}}{0.15/1000}\frac{(0.21-0.01)}{22.4} = 1.725\times 10^{-10}\ \frac{\boldsymbol{kg\ mol}}{\boldsymbol{m^2\cdot s}}$$

$T = 303\ K;\ P_M = 2.9\times 10^{-10}\ m^3(STP)/s\cdot m^2\cdot atm;$

For several solids of different thickness in series,

$$N_{A2} = \frac{(p_{A1}-p_{A2})}{22.4}\frac{1}{\left(\frac{L_1}{P_{M1}}+\frac{L_2}{P_{M2}}+\cdots\right)}$$

$$= \frac{(0.21-0.01)}{22.4}\frac{1}{\left(\frac{0.00015}{2.9\times 10^{-14}}+\frac{0.00015}{417\times 10^{-14}}\right)}$$

$$= 1.7132\times 10^{-10}\ \frac{\boldsymbol{kg\ mol}}{\boldsymbol{m^2\cdot s}}$$

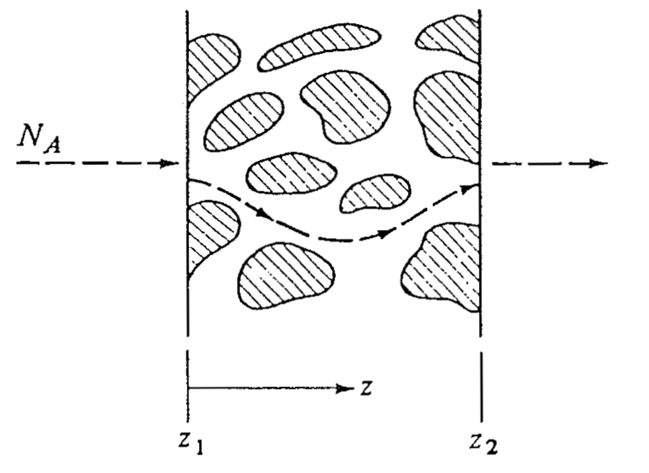
$$\%\ \text{Reduction} = \frac{|N_{A1}-N_{A2}|}{N_{A1}}\times 100$$

Explain:

- Why do the Pepsi plastic bottle after long time in shelf loose its fizziness?
- Compare flux of carbon dioxide for different plastics at ambient conditions.

Diffusion in Porous Solids with Structural Dependence

Diffusion of liquids in porous solids



The solid is porous containing pores or inter-connected voids as shown in the figure. For cases, where pores of solids are completely filled with liquid The solute diffusing through the pores or voids of the solid filled with liquid takes a longer tortuous path. No transport from the solid structure. Instead of $(z_2 - z_1)$, it travels $\tau(z_2 - z_1)$. Here, τ is known as tortuosity, which is a correction in the range of 1.5 to 5. Therefore,

$$N_A = \frac{D_{AB}(c_{A1} - c_{A2})}{(z_2 - z_1)}$$

can be written as,

$$N_A = \frac{\varepsilon D_{AB}(c_{A1} - c_{A2})}{\tau(z_2 - z_1)} = \frac{\varepsilon D_{AB}}{\tau}\frac{(c_{A1} - c_{A2})}{(z_2 - z_1)} = D_{A\,eff}\frac{(c_{A1} - c_{A2})}{(z_2 - z_1)}$$

where ε is the porosity or the bed void fraction.

EXAMPLE 6.5-3. ***Diffusion of KCl in Porous Silica***
A sintered solid of silica 2.0 mm thick is porous with a void fraction ε of 0.30 and a tortuosity τ of 4.0. The pores are filled with water at 298 K. At one face the concentration of KCl is held at 0.10 g mol/liter, and fresh water flows rapidly by the other face. Neglecting any other resistances but that in the porous solid, calculate the diffusion of KCl at steady state.

Solution: The diffusivity of KCl in water from Table 6.3-1 is $D_{AB} = 1.87 \times 10^{-9}$ m²/s. Also, $c_{A1} = 0.10/1000 = 1.0 \times 10^{-4}$ g mol/cm³ $= 0.10$ kg mol/m³, and $c_{A2} = 0$. Substituting into Eq. (6.5-13),

$$N_A = \frac{\varepsilon D_{AB}(c_{A1} - c_{A2})}{\tau(z_2 - z_1)} = \frac{0.30(1.870 \times 10^{-9})(0.10 - 0)}{4.0(0.002 - 0)}$$

$$= 7.01 \times 10^{-9} \text{ kg mol KCl/s} \cdot \text{m}^2$$

Question 3 (25 pts):

A sintered solid of silica 2.0 mm thick is porous with a void fraction (ε) of 0.30 and a tortuosity (τ) of 4.0. The pores are filled with water at 50°C. At one face the concentration of acetic acid is held at 0.10 g mol/liter, and fresh water flows rapidly by the other face. Neglecting any other resistances but that in the porous solid, calculate the diffusion of acetic acid at steady state $\frac{kg\,mol}{m^2 \cdot s}$. Use data from table/appendix with appropriate corrections, when needed.

Question 3 Solution:

Data for acetic acid in water from Table 6.3-1:, $T = 298\ K;\ D_{AB} = 1.26\ \times 10^{-9}\ m^2/s\,;$

Data for viscosity:, $\mu\ at\ 25\ °C = 0.8937 \times 10^{-3} Pa \cdot s;\ \ \mu\ at\ 50\ °C = 0.5494 \times 10^{-3} Pa \cdot s$

$$c_{A1} = 0.1 \frac{kg\ mol}{m^3};\ \ c_{A2} = 0.0;\ \ \varepsilon = 0.3;\ \ \tau = 4.0$$

Required molecular diffusion coefficient of acetic acid in water at 50 °C

$$D_{AB2} = D_{AB1}\left(\frac{T_2}{T_1}\right)\left(\frac{\mu_1}{\mu_2}\right); D_{AB2} = 1.26\ \times 10^{-9}\left(\frac{323}{298}\right)\left(\frac{0.8937 \times 10^{-3}}{0.5494 \times 10^{-3}}\right)$$
$$= \mathbf{2.22 \times 10^{-9}\, m^2/s}$$

$$N_A = \frac{\varepsilon D_{AB}(c_{A1} - c_{A2})}{\tau(z_2 - z_1)} = \frac{0.3 \times \mathbf{2.22 \times 10^{-9}} \times (0.1 - 0)}{4(0.002 - 0)}$$
$$= \mathbf{8.325}\ \times \mathbf{10}^{-9} \frac{kg\ mol}{m^2 \cdot s}$$

Diffusion of gases in porous solids

The solute diffusing through the pores or voids of the solid filled with a gas takes a longer tortuous path. Instead of $(z_2 - z_1)$, it travels $\tau(z_2 - z_1)$. Often, τ depends upon the void fraction as shown in the table. Therefore,

ε	τ
0.2	2.0
0.4	1.75
0.6	1.65

$$N_A = \frac{\varepsilon D_{AB}(c_{A1} - c_{A2})}{\tau(z_2 - z_1)} = \frac{\varepsilon D_{AB}}{\tau}\frac{(c_{A1} - c_{A2})}{(z_2 - z_1)} = D_{A\,eff}\frac{(c_{A1} - c_{A2})}{(z_2 - z_1)}$$

Notes:

- Fickian diffusion due to large pores
- Diffusion through large pores, no diffusion through the solid structure
- Accurate prediction in solids in generally not possible, experimental values are needed
- For the simple gases, such as He, H_2, O_2, N_2, and CO_2, with gas pressures up to 1 or 2 atm, the solubility in solids such as polymers and glasses generally follows Henry's law and Eq. (6.5-5) holds. Also, for these gases the diffusivity and permeability are independent of concentration, and hence pressure. For the effect of temperature T in K, the ln(P_M) is approximately a linear function of 1/T. Also, the diffusion of one gas, say H_2, is approximately independent of the other gases present, such as O_2 and N_2.

6.5-4. *Loss from a Tube of Neoprene.* Hydrogen gas at 2.0 atm and 27°C is flowing in a neoprene tube 3.0 mm inside diameter and 11 mm outside diameter. Calculate the leakage of H_2 through a tube 1.0 m long in kg mol H_2/s at steady state.

6.5-5. *Diffusion Through Membranes in Series.* Nitrogen gas at 2.0 atm and 30°C is diffusing through a membrane of nylon 1.0 mm thick and polyethylene 8.0 mm thick in series. The partial pressure at the other side of the two films is 0 atm. Assuming no other resistances, calculate the flux N_A at steady state.