University Of Jordan
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Transport Phenomena II

Lec 4: Diffusion in Solids

Content
Diffusion following Fick's law, Diffusion that is Dependent on the Nature of the Solid

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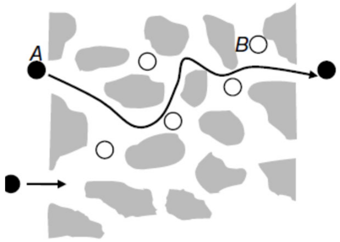
Content

- Introduction
- Diffusion following Fick's law
  - Steady state diffusion
- Diffusion that is Dependent on the Nature of the Solid
- The Relationship between the Fluxes at the Diffusion of Gases in Solids

Introduction

- Transfer of gas, liquid and solid by molecular diffusion in solids play important roles in some engineering applications.
- As example leaching, adsorption, drying of solids, separation of solutions by solid membranes and chemical reactions taking place in the pores of solid catalysts can be cited.
- Diffusion in solids occur in two different ways:
  i. Diffusion following Fick's law (does not depend on the structure of the solid)
  ii. Diffusion that is Dependent on the Nature of the Solid



Diffusion in Solids: Diffusion following Fick's law

i. Diffusion following Fick's law (does not depend on the structure of the solid)

- This situation is met, when the solute dissolves and forms a homogeneous solution with the solid.

Steady-State Diffusion in Solids Following Fick's Law

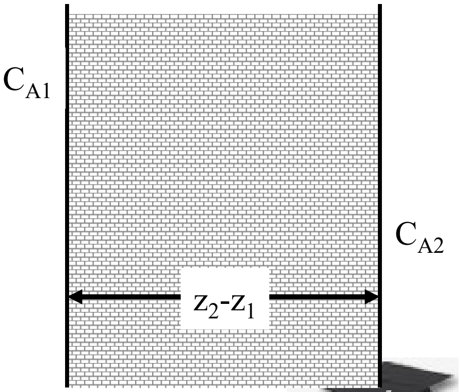
Steady-state diffusion through a solid slab (planner surface)

$$N_A = -D_{AB}\frac{dc_A}{dz} + \cancel{\frac{c_A}{c_T}(N_A + N_B)} \qquad (14)$$

Bulk term is set to zero in solids

Therefore, the following equation will be used to describe the process:

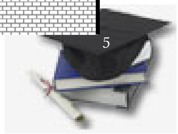
$$N_A = -D_{AB}\frac{dc_A}{dz}$$



- Applying the above equation for steady-state diffusion through a solid slab, we get

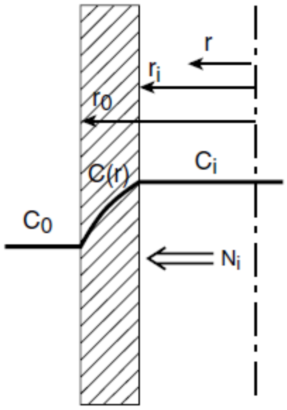
$$N_A = D_{AB}\frac{c_{A1} - c_{A2}}{z_2 - z_1} \qquad (33)$$

where N_A and D_{AB} are taken as constants.



Steady-State Diffusion in Solids Following Fick's Law

Steady-state diffusion through a hollow cylindrical surface



- Applying Fick's law for steady-state diffusion through a cylinder wall of inner radius r_i and outer radius r_o and length L in the radial direction outward, we get

$$\bar{N}_A = -2\pi r L D_A \frac{dc_A}{dr} \qquad (34)$$

where $\bar{N}_A$ constant since we assume steady operation

- Separating variables and formally integrating between the limits of internal and external concentrations c_{Ai} and c_{Ao} we obtain

$$\int_{C_{Ai}}^{C_{Ao}} d\,c_A = -\frac{\bar{N}_A}{D_A\,2\pi L}\int_{r_i}^{r_o}\frac{d\,r}{r} \qquad (35)$$

Mass transfer per time

$$N_A = \frac{\bar{N}_A}{\boxed{2\pi r L}}$$

Mass transfer per area per time

Area of mass transfer

Steady-State Diffusion in Solids Following Fick's Law

$$\Rightarrow \quad \bar{N}_A = 2\pi L D_A \frac{(c_{Ai}-c_{Ao})}{\ln\left(\frac{r_o}{r_i}\right)} \qquad (36)$$

- The Concentration profile can be obtained by integrating Eq.(35) again, but this time only up to an arbitrary radius *r* and the concentration *C* at that point

$$\int_{C_{Ai}}^{C_A} d\,c_A = -\frac{\bar{N}_A}{D_A\, 2\pi L}\int_{r_i}^{r}\frac{d\,r}{r}$$

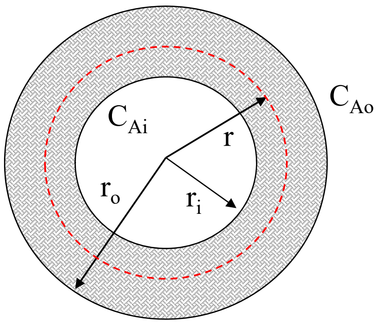
since $\bar{N}_A$ is a constant given by Eq.(36)

$$\Rightarrow \quad c_A(r) = c_{Ai} - \frac{(c_{Ai}-c_{Ao})}{\ln\left(\frac{r_o}{r_i}\right)}\ln\left(\frac{r}{r_i}\right) \qquad (37)$$

Steady-State Diffusion in Solids Following Fick's Law

Steady-state diffusion through a spherical cavity

Applying Fick's law for steady-state diffusion through a spherical shell of inner radius r_i and outer radius r_o in the radial direction outward, we get



$$\bar{N}_A = -4\pi\, r^2 D_A \frac{dc_A}{dr} \qquad (38)$$

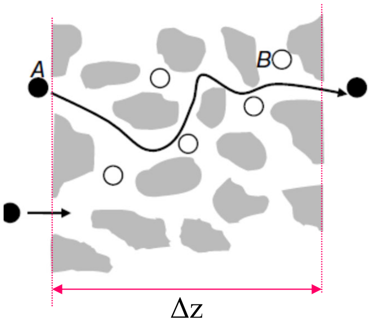
$$\Rightarrow \quad \bar{N}_A = 4\pi r_i r_o D_A \frac{(c_{Ai}-c_{Ao})}{r_o - r_i} \qquad (39)$$

$$N_A = \frac{\bar{N}_A}{4\pi r^2}$$

Diffusion in Solids: Diffusion that is Dependent on the Nature of the Solid

- Diffusion in porous solids where the actual structure and void channels are important
- Hence, the mass transfer is strongly influenced from the type and the size of the pores in the solid,

Diffusion of Liquids in Solids



- The transfer path is greater than Δz and
- The mass transfer area is smaller total area of each face of the solid

$$D_{Aef}=(\varepsilon/k_t^2)\,D_{AB}$$

where
ε is the volume void fraction of the porous volume within the porous material
k_t is the tortuousity factor

$$N_A=\frac{\varepsilon}{k_t^2}D_{AB}\frac{c_{A1}-c_{A2}}{z_2-z_1}$$

Diffusion in Solids: Diffusion that is Dependent on the Nature of the Solid

Diffusion of Gases in Solids

- Depending upon the relationship between the diameter of the pores in the solid and the mean free path of the gas molecules, transfer of gases in the porous solids take place at different mechanisms.
- The mean free path of the gas molecules is given by;

$$\lambda_A=\frac{3.2\,\mu_A}{P}\left(\frac{RT}{2\pi M_A}\right)^{0.5}$$

where λ_A(m) is mean free path of the gas molecules, which is defined as the distance the molecule travels before colliding with another molecule on its way, μ_A is the viscosity of the gas(kg/m s), P (N/m^2) is total pressure, T(K) is absolute temperature, and R is the general gas constant, which is 8314 J/k-mol K. The mechanisms that

- Define Knudsen number as

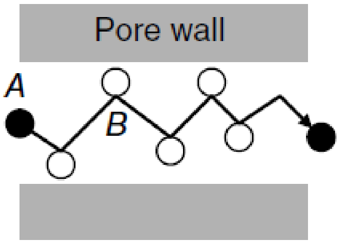
$$Kn=\frac{\lambda}{d_{\text{pore}}}=\frac{\text{mean-free path length of the diffusing species}}{\text{pore diameter}}$$

Diffusion in Solids: Diffusion that is Dependent on the Nature of the Solid

- For Knudsen number < 0.01.
  - If the diameter of the pore is much greater than the mean free path of the molecules, molecule-molecule collision rather than molecule-wall collision dominates throughout the pores,
  - As a result of this, pores do not have any effects on the transfer of solute A in a gas mixture of A+B through the pores of a solid.

$$N_A = -\frac{D_{AB}P}{RT}\frac{dy_A}{dz} + y_A(N_A + N_B)$$

Pure molecular diffusion



The diffusion is independent of the nature of the solid

Diffusion in Solids: Diffusion that is Dependent on the Nature of the Solid

if $Kn > 10$, Knudsen diffusion

- The mean free path of the molecules is much greater than the diameter of the pores, hence, the molecules collide with the wall of the pores rather than colliding with each other.
- The diffusion coefficient for Knudsen diffusion is

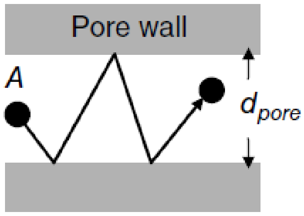
$$D_{KA} = 4850\, d_{\text{pore}} \sqrt{\frac{T}{M_A}}$$

d_{pore} – pore diameter in cm

M_A - molecular weight of species A

T - temperature in K

Pure Knudsen diffusion



$$N_A = -D_{kA}\frac{dc_A}{dz} = -\frac{D_{kA}}{RT}\frac{dp_A}{dz} = \frac{D_{kA}P}{RT\Delta z}(y_{A1} - y_{A2})$$

Diffusion in Solids: Diffusion that is Dependent on the Nature of the Solid

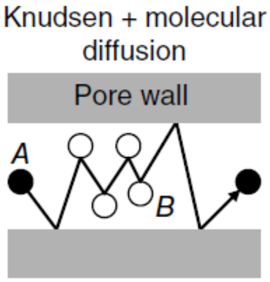
- Generally, the Knudsen diffusion process is significant only at low pressure and small pore diameter.

If $0.1 < Kn < 1$, Then Knudsen diffusion plays a measurable but moderate role in the overall diffusion process

If $Kn > 1$, Knudsen diffusion becomes important

- **0.01 < Knudsen number < 10**, then Knudsen diffusion and molecular diffusion compete with one another by a "resistances in series" approach (i.e. both molecule-molecule and molecule-wall collisions are important in the pores), then the effective diffusion coefficient of species *A* in a gaseous binary mixture of *A* and *B within the pore* is determined by

$$\frac{1}{D_{Ae}} = \frac{1}{D_{AB}} + \frac{1}{D_{KA}}$$



(Mixed diffusion)

Diffusion in Solids: Diffusion that is Dependent on the Nature of the Solid

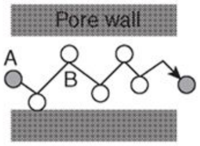
- However, in most porous materials, pores of various diameters are twisted and interconnected with one another, and the path for diffusion of the gas molecule within the pores is "tortuous, then the effective diffusion coefficient in random pores is

$$D'_{Ae} = \varepsilon^2 D_{Ae}$$

where ε is the volume void fraction of the porous volume within the porous material

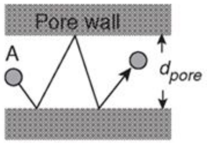
Summary

Pure molecular diffusion



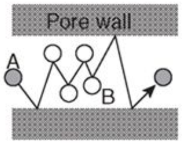
$$D_{AB} = \frac{0.001858\,T^{3/2}\left[\frac{1}{M_A} + \frac{1}{M_B}\right]^{1/2}}{P\,\sigma_{AB}^2\,\Omega_D}$$

Pure knudsen diffusion



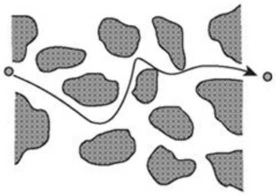
$$D_{KA} = 4850\, d_{\text{pore}} \sqrt{\frac{T}{M_A}}$$

Knudsen + molecular diffusion



$$\frac{1}{D_{Ae}} \cong \frac{1}{D_{AB}} + \frac{1}{D_{KA}}$$

Random porous material

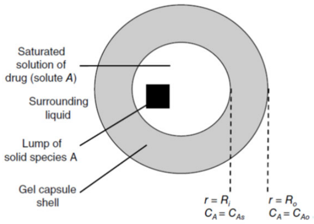


$$D'_{Ae} = \varepsilon^2 D_{Ae}$$

26.2 The spherical gel capsule shown in the figure at the top of the next column is used for long-term, sustained drug release. A saturated liquid solution containing the dissolved drug (solute *A*) is encapsulated within a rigid gel-like shell. The saturated solution contains a lump of solid *A*, which keeps the dissolved concentration of *A* saturated within the liquid core of the capsule. Solute *A* then diffuses through the gel-like shell (the gel phase) to the surroundings. Eventually, the source for *A* is depleted, and the amount of solute *A* within the liquid core goes down with time. However, as long as the lump of solid *A* exists within the core to keep the source solution saturated in *A*, the concentration of *A* within the core is constant. The diffusion coefficient of solute *A* in the gel phase (*B*) is $D_{AB} = 1.5 \times 10^{-5}$ cm^2/s. The maximum solubility of the drug in the gel capsule material is $c_A^* = 0.01$ gmole A/cm^3.

a. Starting from the appropriately simplified *differential forms* of Fick's flux equation and the general differential equation for mass transfer relevant to the physical system of interest, develop the final, analytical, integrated equation to determine the total rate of drug release (W_A) from the capsule under conditions where the saturated concentration of *A* within the liquid core of the capsule remains constant.

b. What is the maximum possible rate of drug release from the capsule, in units of gmole *A* per hour, when $c_{Ao} \approx 0$?

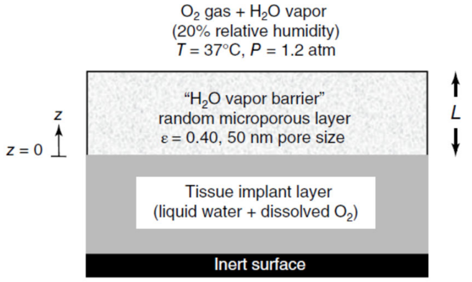


26.10 A porous "water vapor barrier" is placed over the tissue implant shown in the figure in the next column. The purpose of the porous "water vapor barrier" is to allow O_2 gas direct access to the tissue while minimizing the diffusion-limited rate of evaporation of water from the tissue. Both the vapor barrier and the tissue implant possess "slab" geometry. The process is slightly pressurized and operates at 37°C and 1.2 atm total system pressure (P). The O_2 gas stream contains water vapor at 20% relative humidity at 37°C. The vapor barrier material is a random microporous polymer with mean pore size of 50 nm (1×10^7 nm $= 1.0$ cm) and void fraction (ε) of 0.40. The tissue approximates the properties of liquid water. At 37°C, the vapor pressure of liquid water is 47 mm Hg (1.0 atm = 760 mm Hg), and the Henry's law constant (H) for the dissolution of O_2 gas in water is 800 L·atm/gmole. Let $A = H_2O$, $B = O_2$.

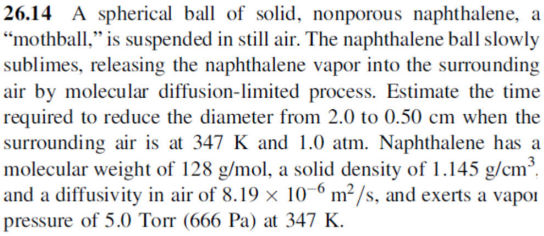
a. Making use of the Fuller–Schettler–Giddings correlation in the calculations, what is the effective diffusion coefficient (D_{Ae}) of H_2O vapor in the randomly microporous water vapor barrier?

b. What is the thickness of the vapor barrier (L) required to limit the rate of water evaporation from the tissue to 0.180 g $H_2O/cm^2 \cdot$day? State all assumptions for your analysis.

c. What is the concentration of dissolved oxygen *in the tissue* (C_{BL}^*, gmole O_2/L tissue) at the interface between the tissue and the porous vapor barrier ($z = 0$)?



A = H_2O vapor, B = O_2 gas



26.14 A spherical ball of solid, nonporous naphthalene, a "mothball," is suspended in still air. The naphthalene ball slowly sublimes, releasing the naphthalene vapor into the surrounding air by molecular diffusion-limited process. Estimate the time required to reduce the diameter from 2.0 to 0.50 cm when the surrounding air is at 347 K and 1.0 atm. Naphthalene has a molecular weight of 128 g/mol, a solid density of 1.145 g/cm^3, and a diffusivity in air of 8.19×10^{-6} m^2/s, and exerts a vapor pressure of 5.0 Torr (666 Pa) at 347 K.

The Relationship between the Fluxes at the Diffusion of Gases in Solids

- At the transfer of gases through the pores of a solid in a system which is **closed** to atmosphere and kept under constant pressure, it follows from this that mass transfer always takes place under "equimolar counter transfer conditions

$$N_A = - N_B.$$

- On the other hand in an open system there is always the following relationship between the fluxes, regardless of whether mass transfer takes place by Knudsen molecular diffusion or mixed diffusion

$$\Sigma N_i \sqrt{M_i} = 0$$

Hence, for binary system gives

$$N_A \sqrt{M_A} = - N_B \sqrt{M_B}.$$

Relating the Concentration and Solubility

- The solubility of a solute gas in a solid is usually expressed by the notation *S*.
- Unit used in general is the following:

$$\frac{\text{m}^3 \text{ solute at STP}}{\text{m}^3 \text{ solid . atm partial pressure of solute}}$$

- Relationship between concentration and solubility:

$$\boxed{C_A = \frac{S \ x \, p_A}{22.414} \quad \text{kmol solute /m}^3 \text{ solid}}$$

where p_A is in atm

STP of 0°C and 1 atm

- Using this definition, Eq. (33) becomes

$$N_A = D_{AB} \frac{S(p_{A1} - p_{A2})}{22.414(z_2 - z_1)} \qquad (33b)$$

Relating the Concentration and Permeability

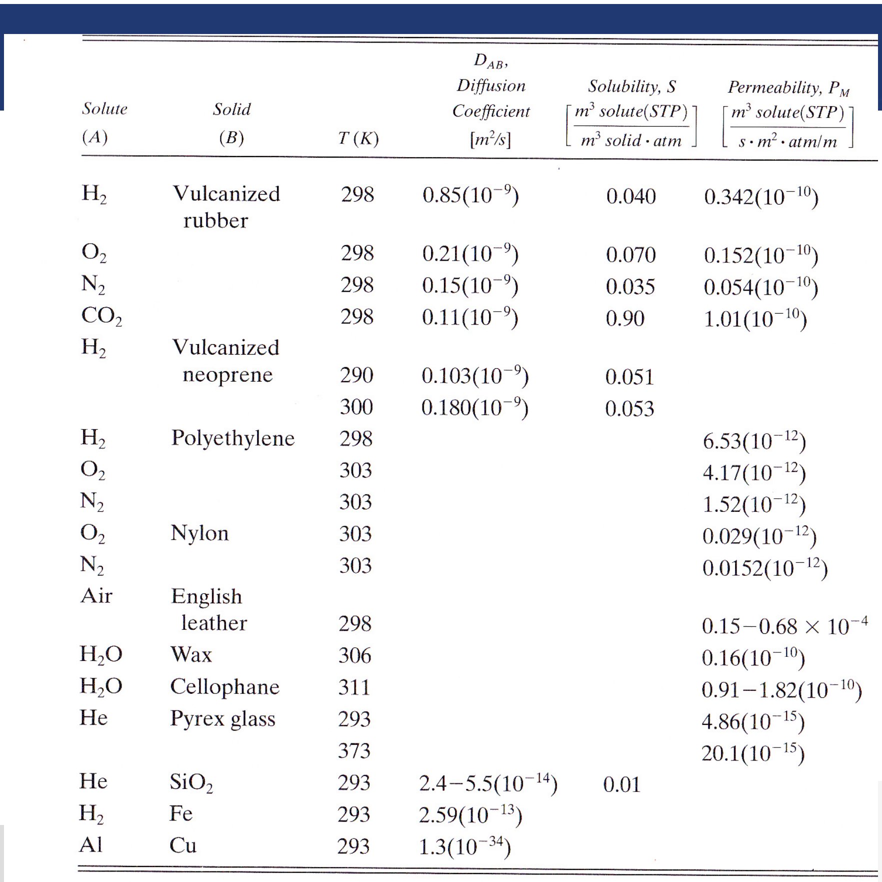
- The permeability of a solute gas (A) in a solid is usually expressed by the notation P_M. in m^3 solute at STP (0°C and 1 atm) diffusing per second per m^2 cross-sectional area through a solid 1 m thick under a pressure difference of 1 atm.
- Unit used in general is the following:

$$\frac{\text{m}^3 \text{ solute at STP . 1 m thick solid}}{\text{s . m}^2 \text{ cross-sectional area . atm pressure difference}}$$

- Relationship between concentration and permeability:

$$\boxed{P_M = D_{AB}\, S}$$

where D_{AB} is in m^2/s and S is in m^3/m^3.atm



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

Example

Diffusion of H_2 through Neoprene membrane:

The gas hydrogen at 17°C and 0.010 atm partial pressure is diffusing through a membrane on vulcanized neoprene rubber 0.5 mm thick. The pressure of H_2 on the other side of 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.

Answer: 4.69×10^{-12} kmol $H_2/m^2.s$

Example cont.

Example

Diffusion through a packging film using permeability:

A polythene 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 the package is 0.21 atm and inside it is 0.01 atm, calculate the diffusion flux of O_2 at steady state. Assume that the resistances to diffusion outside the film and inside are negligible compared to the resistance of the film. Permeability of O_2 in polythene at 303 K is 4.17×10^{-12} m^3 solute (STP)/(s.m^2.atm.m).

Answer: 2.480×10^{-12} kmol $O_2/m^2.s$

Would you prefer nylon to polythene? Permeability of O_2 in nylon at 303 K is 0.029×10^{-12} m^3 solute (STP)/(s.m^2.atm.m). Support your answer.

Example cont.