THAPAR INSTITUTE
OF ENGINEERING & TECHNOLOGY
(Deemed to be University)

Mass Transfer-I

Molecular Diffusion in Solids

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Molecular Diffusion in Solids

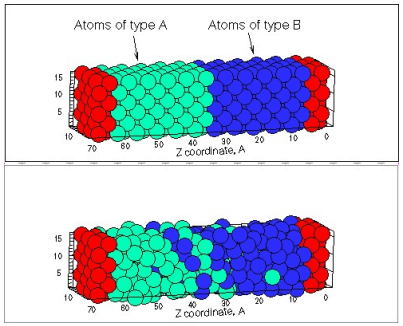
Diffusion phenomena in solids

- **Fick's law:** linear relation between the rate of diffusion of chemical species and the concentration gradient of that species.
- **Thermal diffusion:** Diffusion due to a temperature gradient. Usually negligible unless the temperature gradient is very large.
- **Pressure diffusion:** Diffusion due to a pressure gradient. Usually negligible unless the pressure gradient is very large.
- ***Forced diffusion*:** Diffusion due to external force field acting on a molecule. Forced diffusion occurs when an electrical field is imposed on an electrolyte (for example, in charging an automobile battery)
- ***Knudsen diffusion*:** Diffusion phenomena occur in porous solids.

How atoms move in solids

- Diffusion mechanisms
  - Vacancy diffusion
  - Interstitial diffusion
  - Impurities
- Mathematics of diffusion
  - Steady-state diffusion (Fick's first law)
  - *Unsteady-State Diffusion (Fick's second law)*
- Factors that influence diffusion
  - Diffusing species
  - Host solid
  - Temperature
  - Microstructure

Diffusion → transport by atomic motion

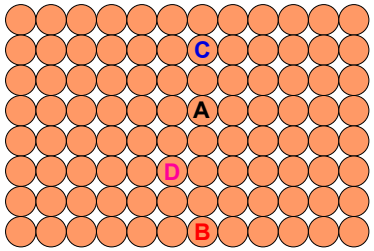


- Inhomogeneous material can become homogeneous by diffusion.
- Temperature should be high enough to overcome energy barrier.

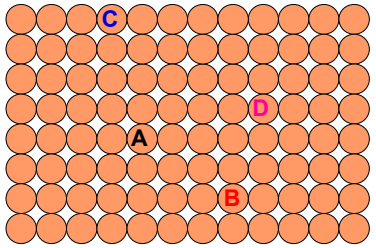
Self-diffusion

In an elemental solid, atoms also migrate

Label some atoms



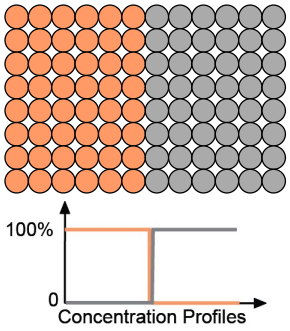
After some time



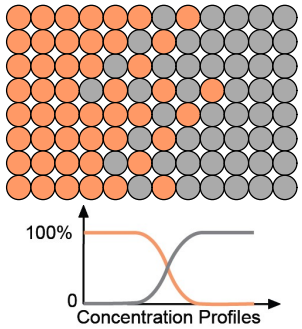
Interdiffusion

In an alloy, atoms tend to migrate from regions of high concentration to regions of low concentration

Initially



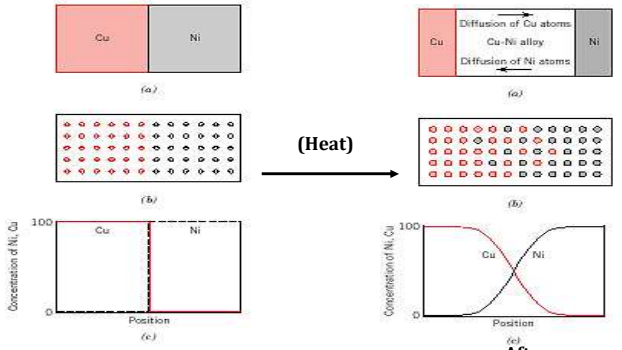
After some time



Adapted from Figs. 5.1 and 5.2, *Callister & Rethwisch 8e*.

Inter-diffusion *vs* Self-diffusion

Concentration Gradient → Inter-diffusion (or Impurity Diffusion)



Self-diffusion: one-component material, atoms are of same type.

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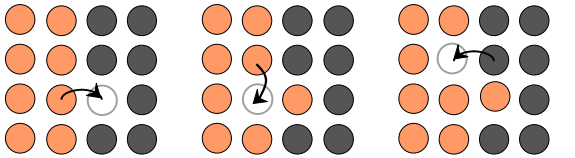
Vacancy Diffusion

- Atoms exchange with vacancies
- Applies to substitutional impurities atoms
- Rate depends on:
  - Number of vacancies
  - Activation energy to exchange



Increasing elapsed time

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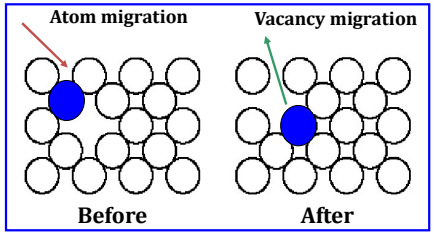

- To jump from lattice site to lattice site, atoms need energy to break bonds with neighbors, and to cause the necessary lattice distortions during jump.
- Therefore, there is an energy barrier.
- Energy comes from thermal energy of atomic vibrations (E_{av} ~ kT)
- Atom flow is opposite to vacancy flow direction.

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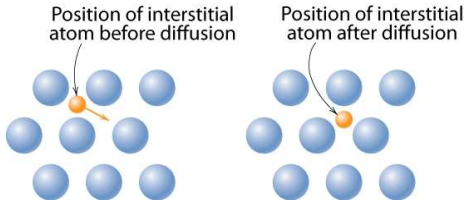
Interstitial diffusion

Smaller atoms can diffuse between atoms



It is more rapid than vacancy diffusion

Adapted from Fig. 5.3(b), *Callister & Rethwisch 8e.*

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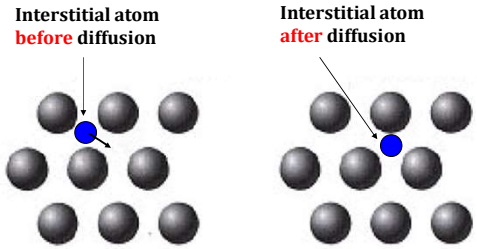
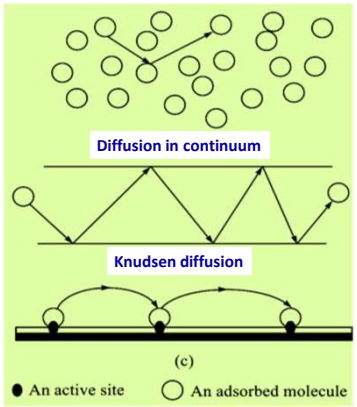
- Generally faster than vacancy diffusion because bonding of interstitials to surrounding atoms is normally weaker and there are more interstitial sites than vacancy sites to jump to Smaller energy barrier .
- Only small impurity atoms (e.g. C, H, O) fit into interstitial sites.



Types of solids diffusion

- Diffusion in porous solids
- Diffusion through polymers/ polymeric membrane
- Diffusion through crystalline solids



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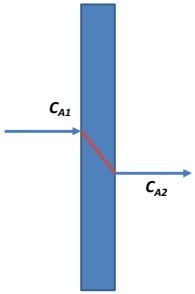
According to Fick's law of Diffusion $N_A = -D_{AB}\frac{dC_A}{dz}$

$$N_A = -\frac{D_{AB}(C_{A_1} - C_{A_2})}{z}$$



For other solid shape (variable area)

$$w = N_A S_{av} = \frac{D_{AB} S_{av}(C_{A_1} - C_{A_2})}{z}$$

For other radial diffusion through a solid cylinder with inner and outer radii a_1, a_2

$$S_{av} = \frac{2\pi l(a_2 - a_1)}{\ln(a_2/a_1)};\ z = a_2 - a_1$$

For other radial diffusion through a spherical shell with inner and outer radii a_1, a_2

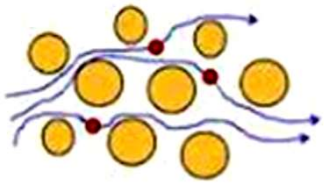
$$S_{av} = 4\pi a_1 a_2;\quad z = a_2 - a_1$$

Diffusion through polymers/ polymeric membrane

The diffusion of solutes through polymeric solids is more like diffusion in liquids

The polymeric chains are in a state of constant thermal motion and diffusing molecule move from one location to the adjacent location due to the potential barrier

An Arrhenius type equation may be applied for the temperature dependency of the diffusion coefficient in polymers.



$$D_A = D_0 e^{-H_D/RT}$$

Where:

H_D is the energy of activation,
D_0 is a constant and R and T
R is the universal gas constant
T is the temperature

Cont.…

Diffusivity is independent of concentration and there is no bulk flow, the steady state molar flux N_A in the *x*-direction is given by Fick's law as follows.

$$N_A = -D_{AB}\frac{dC_A}{dx}$$

D_{AB} is the diffusivity of A through the solid.

Solving the integration of this equation gives diffusion through a flat slab of thickness *l*.

$$N_A = \frac{D_{AB}(C_{A1} - C_{A2})}{l}$$

For other solid shapes general equation for rate of diffusion

$$w = N_A S_{av} = \frac{D_{AB} S_{av}(C_{A1} - C_{A2})}{l}$$

S is the average is the average cross sectional area for diffusion. *w* has a unit of mole or *kmol/s.*

Cont....

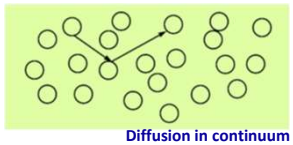
The diffusion coefficient in the solid is not dependent on pressure of the gas or liquid on the outside of the solid.

For example, if carbon dioxide gas is outside a slab of rubber and is diffusing through it, would be independent of pressure of carbon dioxide at the surface. The solubility of carbon dioxide in the solid; however, is directly proportional to the partial pressure of carbon dioxide.

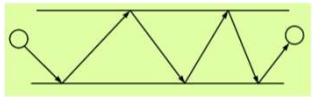
The solubility $\boldsymbol{S}$ = m^3 solute at STP /atm. m^3 solid.

Diffusion in porous solid (Knudsen diffusion)

- Collision of the diffusing molecules offers resistance to diffusion.
- If the gas diffusion occurs in a very fine pore when the diffusion occurs inside the fine pores particularly at low pressure, the mean free path of the molecules may be larger than the diameter of the passage.
- The collision with wall becomes important and diffusion arising from the collision is called known Knudsen diffusion

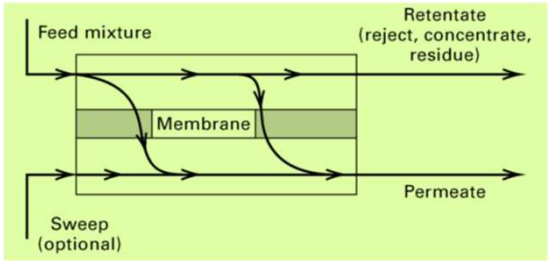


Diffusion in continuum



Knudsen diffusion

Separation by means of a semipermeable barrier (membrane) through which one or more species move faster than another or other species



Characteristics

- The two products are usually miscible
- The separating agent is a semipermeable barrier
- A sharp separation is often difficult to achieve

Cont....

Based on kinetic theory of gases, the Knudsen diffusivity is defined as

$$D_K = \left(\frac{2}{3}\right) r_p v_T$$

$$D_K = 9700\, r_p (T/M)^{1/2}$$

Flux equation (similar to Fick's law)

$$J_K = -D_K \frac{dC_A}{dz} = -\frac{D_K}{RT}\frac{dp_A}{dz}$$

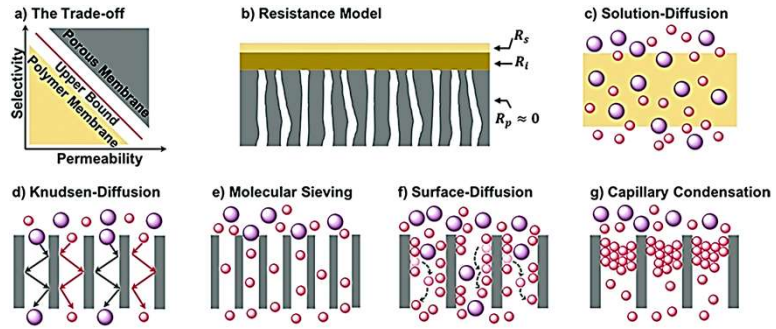
r_p = radius of the passage or capillary (cm)

$v_T = \left(\frac{8RT}{\pi M}\right)^{1/2}$ = average velocity of the molecules by virtue of their thermal energy

T = Temperature in K

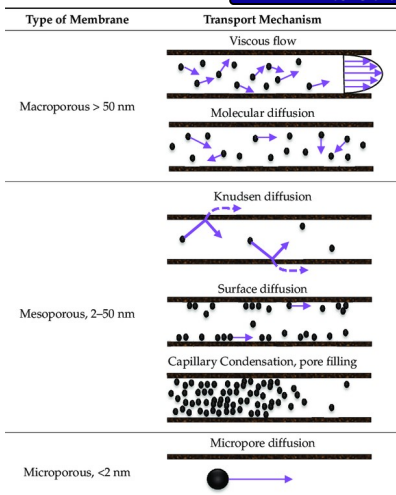
M = Molecular weight

Cont....



Source: ***J. Mater. Chem. A***, 2018,**6**, 23169-23196

Gas diffusion in membrane



Source: *Ghasemzadeh et al.*, Progress in Modeling of Silica-Based Membranes and Membrane Reactors for Hydrogen Production and Purification, ChemEngineering, 3 (2019) 11-17.

Surface diffusion

$$J_s = -D_s \frac{dC_s}{dz}$$

where

D_s = surface diffusion coefficient, in m^2/s

C_s = surface concentration of the adsorbed molecules, in $kmol/m^2$.

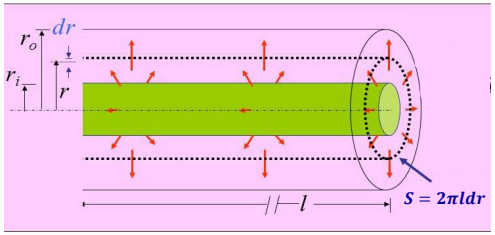
The surface diffusion flux J_s is the number of moles transported across unit distance on the surface normal to the direction of transport (mol/m·s). The experimental values of D_s normally range between 10^{-4} and 10^{-5} cm^2/s.

Diffusion through a Hollow Cylinder

The problem addressed here is the diffusional transport through a cylindrical wall of substantial thickness shown in Fig. Such processes can occur in case of fluids contained in a cylindrical enclosure under high pressure. The following situations can be arise:

- The **first**, the determination of the **diffusional flux** that results under these conditions.
- The **second** problem is the derivation of the **concentration profile**.

Both problems involve the solution of a simple ordinary differential equation by the technique of separation of variables.



Source: Basmadjian, D. Mass Transfer and Separation Processes, (2007), Boca Raton: CRC Press

Cont....

Fick's law of diffusion is applied to a cylindrical surface of radius r and length l

$$N_A = -D_{AB}\frac{dC}{dZ}$$

$$z = r_o - r_i$$

$$w = SN_A = -D_{AB}S\frac{dC}{dZ} = \text{Constant (Mass Conservation)}$$

$$S = 2\pi l dr$$

Where:
N_A = Diffusion flux
S = Surface area (In case of radial diffusion in cylinder the area is **variable**)

Source: Basmadjian, D. Mass Transfer and Separation Processes, (2007), Boca Raton: CRC Press

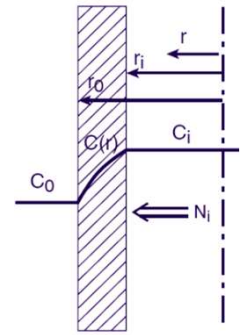
Cont....

Separating variables and formally integrating between the limits of internal and external concentrations C_i and C_o we obtain

$$\int_{C_i}^{C_0} dC = -\frac{N_A}{D_{AB}(2\pi l)}\int_{r_i}^{r_0}\frac{1}{r}dr$$

$$w = N_A S_{av} = \frac{D_{AB}S_{av}(C_i - C_o)}{z}$$

$$S_{av} = \frac{2\pi l(r_o - r_i)}{\ln(r_o/r_i)}$$



$$z = r_o - r_i$$

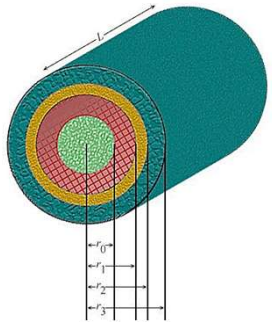
Source: Basmadjian, D. Mass Transfer and Separation Processes, (2007), Boca Raton: CRC Press

For Composite cylinder

The mass transfer resistance R is defined $R = \frac{r_o - r_i}{D_{AB}S_{av}}$

In the case of a composite cylinder made up of different materials, describe the system by simply adding resistances. This principle of adding resistances in series is routinely applied in electrical circuits. For a cylinder composed of three different materials, for example, one obtains

$$w = \frac{(C_0 - C_3)}{R_1 + R_2 + R_3}$$



where the resistances (R_1, R_2, R_3) can be expressed respectively as

$$R_1 = \frac{r_1 - r_0}{D_{AB_1}S_{av_1}} \qquad R_2 = \frac{r_2 - r_1}{D_{AB_2}S_{av_2}} \qquad R_3 = \frac{r_3 - r_2}{D_{AB_3}S_{av_3}}$$

$$S_{av} = \frac{2\pi L(r_{i+1} - r_i)}{\ln(r_{i+1}/r_i)}$$
$i = 0, 1, 2, 3$

Source: Basmadjian, D. Mass Transfer and Separation Processes, (2007), Boca Raton: CRC Press

Concentration profile $C = f(r)$

Fick's law integrate again, but this time only up to an arbitrary radius r and the concentration C at that point

$$\int_{C_i}^{C} dC = -\int_{r_i}^{r}\frac{N_A}{D_{AB}(2\pi l)}\frac{dr}{r}$$

or, since N_A is a constant given by

$$C(r) = C_i - \frac{C_i - C_o}{\ln(r_o/r_i)}\ln(r/r_i)$$

This equation expresses the concentration profile within the cylindrical wall.

Source: Basmadjian, D. Mass Transfer and Separation Processes, (2007), Boca Raton: CRC Press

References

ETH

Mass Transfer

Theories for Mass Transfer Coefficients

Lecture 9, 15.11.2017, Dr. K. Wegner

- Lecture notes/ppt of Dr. Yahya Banat (**ybanat@qu.edu.qa**)