

Surface diffusion

Surface diffusion is the transport of adsorbed molecules on a surface in the presence of a concentration gradient.

Molecules adsorbed on a surface remain anchored to the active sites. If the fractional surface coverage (it is the ratio of the actual amount adsorbed to that required to form a monolayer) is less than unity, some of the active sites remain vacant.

An adsorbed molecule tends to migrate to an adjacent empty site if it has sufficient energy to jump the energy barrier. Since the active sites are discrete, the migration or surface diffusion is visualized to occur by a 'hopping' or 'leap frog' mechanism.

The flux due to surface diffusion is given by equation similar to Fick's Law

$$J_s = -D_s \frac{dC_s}{dz} \quad \text{The experimental values of } D_s \text{ normally range between } 10^{-4} \text{ and } 10^{-5} \text{ cm}^2/\text{s}.$$

where

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

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

J_s is the number of moles transported across unit distance on the surface normal to the direction of transport ($\text{mol}/\text{m}\cdot\text{s}$).

Self-diffusion

The molecules of a gas or a liquid continuously move from one position to another. As a result of this continual motion, the molecules in a mixture of uniform composition also diffuse but the net rate of transport across any plane over a macroscopic time scale is zero.

Self diffusion refers to the diffusion of the molecules in a pure substance; the corresponding diffusion coefficient is called the 'self-diffusion coefficient' or 'self diffusivity'.

An approximate value of the self diffusivity, D_{AA} , can be obtained by measuring the diffusivity of molecules of A having an atom substituted by its isotope in an otherwise pure A.

Expectedly, the self-diffusion coefficient of a molecule is close to that in a mixture with similar molecules. For example, the self diffusivity of liquid benzene is $2.2 \times 10^{-9} \text{ m}^2/\text{s}$ at 25°C .

Diffusion in solids

Fick's law of diffusion can be applied to the system which is under steady state condition. It is applicable when diffusivity is independent of concentration and when there is no bulk flow.

So, the rate of diffusion of substance A per unit cross section of solid is proportional to the concentration gradient in the direction of diffusion.

$$N_A = -D_A \left(\frac{dC_A}{dZ} \right)$$

Where D_A is the diffusivity of A through the solid. When the diffusion is taking place through a flat slab of thickness Z , then equation becomes

$$N_A = \frac{D_A (C_{A1} - C_{A2})}{Z}$$

Here C_{A1} and C_{A2} are concentration at opposite sides of the slab. For solids of varying transfer area, the diffusional rate is given by,

$$W = N_A S_{av} = \frac{D_A S_{av} (C_{A1} - C_{A2})}{Z}$$

S_{av} is average mass transfer area of respective solid surfaces. Hence for radial diffusion through a solid cylinder of inner and outer radii r_1 and r_2 respectively and its length l

$$S_{av} = 2\pi rl$$

$$W = -D_A 2\pi rl \left(\frac{dC}{dr} \right)$$

On integrating

$$W \int_{r_1}^{r_2} \frac{dr}{r} = -D_A 2\pi l \int_{C_{A1}}^{C_{A2}} dC$$

or

$$W \ln \left(\frac{r_2}{r_1} \right) = -D_A 2\pi l (C_{A2} - C_{A1})$$

or

$$W = \frac{[D_A 2\pi l (C_{A1} - C_{A2})] \left(\frac{r_2 - r_1}{r_2 - r_1} \right)}{\ln \left(\frac{r_2}{r_1} \right)}$$

or

$$W = \frac{D_A S_{av} (C_{A1} - C_{A2})}{Z}$$

$$\text{where } S_{av} = \frac{2\pi l (r_2 - r_1)}{\ln \left(\frac{r_2}{r_1} \right)} \text{ and } Z = (r_2 - r_1).$$

Similarly for radial diffusion through a spherical shell of inner and outer radii r_1 and r_2 the surface is

$$S_{av} = 4\pi r_1 r_2 \text{ and } Z = (r_2 - r_1)$$

Types of solid diffusion

The nature of solids and its interaction with the diffusing substance influence the rate of mass transfer. Different types of solid diffusion are as follows.

1. Diffusion through polymers

Diffusion through polymeric membranes, e.g. gaseous separation through a membrane, mainly depends on the pressure gradient as the driving force.

Diffusion takes place from high pressure region to low pressure region. A particular activation energy is needed for diffusion to take place and the temperature dependency of diffusivity is given by Arrhenius type relation,

$$D_A = D_o \exp \left[\frac{-H_D}{RT} \right]$$

Where H_D is the energy of activation and D_o is a constant.

For simple gases, D_A is independent of concentration but for permanent gases, diffusivity is strongly dependent on solute concentration in the solid.

The diffusional flux is given by

$$V_A = \frac{D_A S_A (p_{A1} - p_{A2})}{Z}$$

where

V_A is the diffusional flux, $\text{cm}^3 \cdot \text{gas (STP)}/\text{cm}^2\text{s}$

D_A is the diffusivity of A, cm^2/s

p_A is the partial pressure of diffusing gas, cm Hg

S_A is the solubility coefficient, $\text{cm}^3 \cdot \text{gas (STP)}/\text{cm}^3 \text{ solid} \cdot \text{cm Hg}$

Z is the thickness of polymeric membrane, cm

Permeability can be defined as

$$P = D_A S_A$$

where P is the permeability, $\text{cm}^3 \text{ gas} \cdot (\text{STP})/\text{cm}^2 \cdot \text{s (cm Hg/cm)}$

The solubility is related to concentration in SI units as,

$$c_A (\text{kmol}/\text{m}^3 \text{ solid}) = S p_A = 22.414$$

and in CGS system as $c_A (\text{g mol}/\text{cm}^3 \text{ solid}) = S p_A = 22414$

2. Diffusion through crystalline solids

Solute nature and crystalline structure are the important parameters in the type of diffusion. Some of the mechanism followed for diffusion through crystal geometry are given below:

1. Interstitial Mechanism- Solute atoms diffuse from one interstitial site to the next in the crystal lattice.
2. Vacancy Mechanism- If lattice sites are vacant , an atom in an adjacent site may jump into the vacant site.
3. Interstitialcy Mechanism- A large atom occupying in an interstitial site pushes the neighboring lattice into an interstitial position and moves into the vacancy produced.
4. Crowded-ion Mechanism- An extra atom in a chain of close-packed atoms can displace several atoms in the line from their equilibrium position.
5. Diffusion along grain boundaries- Diffusion takes place in crystal interface and dislocations.

Diffusion in porous solids

The solid may be porous in nature such as adsorbents or membrane and the diffusion takes place either by virtue of concentration gradient or by hydrodynamic flow behavior because of pressure difference.

In steady state diffusion of gases, there are two types of diffusive movement, depending on the ratio of pore diameter d , to the mean free path of the gas molecule, λ .

If the ratio $d/\lambda > 20$, molecular diffusion predominates

$$N_A = \left(\frac{N_A}{N_A + N_B} \right) \left(\frac{D_{AB,eff} P_t}{RTZ} \right) \ln \left[\frac{\frac{N_A}{N_A + N_B} - y_{A2}}{\frac{N_A}{N_A + N_B} - y_{A1}} \right]$$

If $d/\lambda < 0.2$, the rate of diffusion is governed by the collision of gas molecules within the pore walls and follows Knudsen's law.

$$N_A = \frac{D_{K,A} (p_{A1} - p_{A2})}{RTl}$$

where

$D_{K,A}$ is the Knudsen diffusivity, cm^2/s l is the length of the pore, cm

p_A is the partial pressure of diffusing substance, cmHg

Knudsen diffusivity can be determined by using an empirical relation,

$$D_{K,A} = \left(\frac{d}{3}\right) \left(\frac{8 g_c RT}{\pi M_A}\right)^{1/2}$$

The mean free path λ can be estimated by

$$\lambda = \left(\frac{3.2\mu}{P_t}\right) \left(\frac{RT}{2\pi g_c M_A}\right)^{1/2}$$

If $0.2 < d/\lambda < 20$, both molecular and Knudsen diffusion take place

$$N_A = \left(\frac{N_A}{N_A + N_B}\right) \left(\frac{D_{AB,eff} P_t}{ZRT}\right) \ln \left[\frac{\left(\frac{N_A}{N_A + N_B}\right) \left(1 + \frac{D_{AB,eff}}{D_{KA,eff}}\right) - y_{A2}}{\left(\frac{N_A}{N_A + N_B}\right) \left(1 + \frac{D_{AB,eff}}{D_{KA,eff}}\right) - y_{A1}} \right]$$