FDE 307 Mass Transfer and Unit Operations



Diffusion through a varying crosssectional area

In many mass-transfer operations, the area where the diffusion occurs may vary with time. If the diffusion occurs through a varying cross sectional area, a specified form of equation for diffusion through a stagnant gas may be used. When this condition exists for the diffusion from a sphere; the general equation may be simplified as discussed:



Let's consider diffusion to or from a sphere in a gas. This may be observed in the evaporation of a drop of liquid or in the diffusion of nutrients to a sphere-like microorganism in a liquid. Figure illustrates a sphere of fixed radius r_1 in an infinite gas medium. Component (A) at partial pressure P_{A1} at the surface is diffusing into the surrounding stagnant medium (B), where $P_{A2}=0$ at some large distance away. At steady state the flux can be determined as:



PA2

$$N_A = \frac{\overline{N}_A}{A}$$

where is kg moles of A diffusing per second or kg mol/s. is constant but A is not at steady state conditions.

Inserting the area of sphere as $4\pi r^2$

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

Since it is a special case of diffusion through stagnant gas

$$N_A = \frac{\overline{N}_A}{4\pi r^2} = -\frac{D_{AB}}{RT} \frac{dP_A}{(1 - P_A / P)dr}$$

 $\frac{N_A}{4\pi} \int_{r}^{r_2} \frac{dr}{r^2} = -\frac{D_{AB}}{RT} \int_{P_{AB}}^{r_{A2}} \frac{dP_A}{(1 - P_A / P)}$





 Another case that can be discussed as one of the important cases for varying cross – sectional area is the diffusion through a conical vessel as shown in Figure 21.5.
Component A diffuses at steady state through a conical vessel. At point 1 the radius is r₁ and at point 2 it is r₂. A is diffusing through stagnant B in z direction.



$$N_{A} = \frac{N_{A}}{\pi r^{2}} = -\frac{D_{AB}}{RT} \frac{dP_{A}}{(1 - P_{A} / P)dz}$$

 By using the theorem of similar triangles, the variable radius r can be related to position z as the following;

$$r = \left(\frac{r_2 - r_1}{z_2 - z_1}\right)z + r_1$$

$$\frac{\overline{N}_{A}}{\pi} \int_{z_{1}}^{z_{2}} \frac{dz}{\left[\left(\frac{r_{2}-r_{1}}{z_{2}-z_{1}}\right)z+r_{1}\right]^{2}} = -\frac{D_{AB}}{RT} \int_{P_{A1}}^{P_{A2}} \frac{dP_{A}}{(1-P_{A}/P)}$$

Molecular diffusion in solids

- The rate of diffusion in solids is not as fast as diffusion in fluids. On the other hand, diffusion in solids is quite important for some food engineering processes such as leaching of foods, drying of foods, membrane separation of fluids, diffusion of gases through polymer films used in packaging, etc.
- This type of diffusion can be classified as diffusion in solids following Fick's Law and diffusion in porous solids that depends on structure.



Diffusion in solids following Fick's Law

 In this type of diffusion, the system is under steady state conditions and the diffusivity is not a function of concentration and pressure of solids and there is no bulk flow in the system.
With these considerations the general equation is simplified into;

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

• One should notice that D_{AB} is not equal to D_{BA} for solids.

For the diffusion through a flat slab of thickness (z_2-z_1) , the equation becomes;

$$N_{A} = D_{AB} \frac{C_{A1} - C_{A2}}{z_{2} - z_{1}}$$



Important definitions for diffusion in solids

- Solubility is important in diffusion in solids. It can be defined as amount of a solute that dissolves in a unit volume of a solvent to form a saturated solution under specified conditions of temperature and pressure. It is usually denoted by S.
- In case of gas diffusion through a solid, it can be declared that the solubility of gas in the solid is directly proportional to partial pressure of solute.

$$S = \frac{m^3(STP)of A}{m^3 \ solid.atm}$$

$$C_A = \frac{Sp_A}{22.414} \frac{kgmol A}{m^3 \ solid}$$

The experimental data for diffusion of gases in solid can be given as *permeability* (P_M) in cm³ of solute gas (A) at STP (0°C, and 1 atm) diffusing per second per cm² cross-sectional area through of solid of 1 cm thick under a pressure difference of 1 atm

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

$$C_{A1} = \frac{SP_{A1}}{22.414} \qquad C_{A2} = \frac{SP_{A2}}{22.414}$$

$$N_{A} = \frac{D_{AB}S(P_{A1} - P_{A2})}{22.414(z_{2} - z_{1})} = \frac{P_{M}(P_{A1} - P_{A2})}{22.414(z_{2} - z_{1})}$$

$$P_{M} = D_{AB}S \frac{m^{3}(STP)}{s.m^{2}C.S.atm/m}$$



 If a system is composed of several solids in series and the thickness values of these solids are represented by L₁, L₂, L₃, ... the Equation for permeability can be rewritten as;

$$N_{A} = \frac{(P_{A1} - P_{A2})}{22.414} \frac{1}{L_{1}/P_{M1} + L_{2}/P_{M2} + \dots}$$



Example

The thickness of a polyethylene film, which is used for packaging a food product at 298 K, is given as 0.0002 m. If the partial pressure of oxygen inside and outside of package is 0.21 atm and 0.01 atm, respectively, what is the diffusion flux of oxygen at steady state conditions?

Note: The inside and outside resistances to diffusion can be assumed as negligible with respect to resistance of the film.



Solution

 $P_{\rm M}$ = The permeability of oxygen through polyethylene =4.17 10⁻¹² m³ solute(STP)/(s.m².atm/m)

T =temperature of system = 298 K

 $(z_2-z_1) =$ thickness of the film= 0.0002 m $P_{AI} =$ the partial pressure of oxygen outside the film = 0.21 atm

 P_{A2} = the partial pressure of oxygen inside the film = 0.01 atm

$$N_{A} = \frac{P_{M}(P_{A1} - P_{A2})}{22.414(z_{2} - z_{1})} = \frac{4.17 \times 10^{-12}(0.21 - 0.01)}{22.414(0.0002)} = 1.88 \times 10^{-10} \, kgmol \, / \, s.m^{2}$$

Diffusion in porous solids that depends on structure

In order to define the diffusion flux through a porous solid, new terms such as void fraction and tortuosity should be explained. When we consider porous solids, the effect of the pores or voids inside on diffusion is inevitable. This can be better understood by looking over the Figure. In this figure, the sketch of a typical porous solid is given.





Consider a solid block which is filled with salty water. For the situation where the voids are filled completely with liquid water, the concentration of salt in water at boundary 1 is C_{A_1} and at point 2 it is C_{A_2} . The salt diffusing through the water in the void volume takes a tortuous path which is unknown and greater than $(x_2 - x_1)$ by a factor τ, called tortuosity. Diffusion does not take place in the inert solid. The diffusion flux for this case can be abbreviated by;

$$N_{A} = \frac{\mathcal{E}D_{AB}(C_{A1} - C_{A2})}{\tau(z_{2} - z_{1})}$$

where ϵ is the open void fraction, D_{AB} is the diffusivity of salt in water, and τ is the tortuosity which is the factor which corrects for the path longer than (z_2-z_1) . The value of tortuosity varies between 1.5 to 5 for inert type solids. As a practical usage, the terms are combined into an effective diffusivity.

$$D_{AB\,eff} = \frac{\mathcal{E}D_{AB}}{\tau} \qquad N_A = \frac{D_{AB\,eff} \left(C_{A1} - C_{A2}\right)}{\left(z_2 - z_1\right)}$$
$$N_A = \frac{\mathcal{E}D_{AB}\left(P_{A1} - P_{A2}\right)}{RT\tau(z_2 - z_1)} \longleftarrow \frac{\text{For gases}}{\text{gases}}$$

It should be noted that the diffusion is assumed to occur only through the voids or pores not through the actual solid particles.

