Module 1 :

The equation of “continuity”

Lecture 5:

Conservation of Mass for each species

& Fick’s Law

Basic Definitions

In Mass Transfer, we usually deal with concentration in one form or other. For this we define some symbols which are discussed below.

Mass Concentration of i^th species: This is the **ratio of mass of species *i* per unit volume**. It is represented by the symbol ρ_i. Thus the ***total mass concentration*** is given by $\sum_{\text{all } i} \rho_i$.

Molar Concentration of i^th species: This is the **ratio of moles of species *i* per unit volume**. It is represented by the symbol c_i. Substituting for moles (i.e. Mass/molecular weight) we get

$$c_i = \frac{\rho_i}{M_i} \tag{3.1}$$

where

M_i – Molecular weight of the i^{th} component

Mass fraction of the i^th species: This is the **ratio of mass of species *i* to the total mass**. It is represented by the symbol w_i. Using definition of mass concentration, mass of species ***i*** equals volume times mass concentration of ***i*** th species. Therefore we can write

$$w_i = \frac{\rho_i}{\rho} \tag{3.2}$$

Mole fraction of the i^th species: This is the **ratio of moles of species *i* to the total moles**. It is represented by the symbol x_i. Using definition of molar concentration, we can write

$$x_i = \frac{c_i}{c} \tag{3.3}$$

Velocities For a mixture of n species

In mass transfer studies, we are interested in the number of moles of a particular species passing a certain point as well as the mass of molecules of a particular species passing a certain point in space. Accordingly we can define two velocities with respect to axes fixed in space as

Mass average velocity

Local Mass Average Velocity is defined as

$$\underline{U} = \frac{\sum_{i=1}^{n} \rho_i \underline{U}_i}{\sum_{i=1}^{n} \rho_i} \qquad (3.4.)$$

where ρ_i is the Mass Concentration of the i^{th} species and $\underline{U}_i$ is the velocity of the i^{th} species relative to stationary coordinate axes.

Molar average velocity

Local Molar Average Velocity is defined as

$$\underline{U}^* = \frac{\sum_{i=1}^{n} c_i \underline{U}_i}{\sum_{i=1}^{n} c_i} \quad (3.5)$$

Here it implies that

$$c\,\underline{U}^* = \underline{U}^* \sum_{i=1}^{n} c_i = \sum_{i=1}^{n} c_i\, \underline{U}_i \quad (3.6)$$

$\underline{U}_i$ is the velocity of the species i relative to stationary coordinate axes.

It is not the velocity of the individual molecules but rather the "average" velocity over a small volume element of the fluid.

Diffusion velocities

$\underline{U}_i - \underline{U}$: Diffusion velocity of species i with respect to $\underline{U}$

$\underline{U}_i - \underline{U}^*$: Diffusion velocity of species i with respect to U^*

Fluxes

The flux is defined as the product of a species "concentration", c_i or "density", ρ_i and its velocity $\underline{U}_i$. For fluxes relative to *stationary coordinates* we will use *n* (or *N*) while for fluxes referred to *moving coordinates* we will use *j* (or *J*). For moving coordinate, the speed at which the coordinate frame is moving for cases we will consider will be either **Mass average velocity** or **Molar average velocity**.

1. **Fluxes relative to Stationary Coordinates**

Mass $\underline{n}_i = \rho_i \underline{U}_i$ (3.7)

Molar $\underline{N}_i = c_i \underline{U}_i$ (3.8)

2. **Relative to the mass-average velocity** $\underline{U}$

Mass $\underline{j}_i = \rho_i \left(\underline{U}_i - \underline{U}\right)$ (3.9)

$\left(\underline{U}_i - \underline{U}\right)$ is the driving force for Mass flux

Molar $J_i = c_i \left(\underline{U}_i - \underline{U}\right)$ (3.10)

3. **Relative to the molar-average velocity** $\underline{U}^*$

Mass $\underline{j}_i^* = \rho_i \left(\underline{U}_i - \underline{U}^*\right)$ (3.11)

Molar $J_i^* = c_i \left(\underline{U}_i - \underline{U}^*\right)$ (3.12)

<u>Diffusion in a BINARY System (A and B)</u>

Fick's First Law

It relates the diffusive flux to the concentration field, by postulating that the flux moves from region of higher concentration to the region of lower concentration with a magnitude i.e. proportional to the concentration gradient (spatial derivative). The proportionality constant is known as diffusion coefficient or diffusivity, D_{AB} (m^2/s).

$$\boxed{\underline{j}_{\mathrm{A}} = -\rho D_{AB} \nabla w_{\mathrm{A}}} \qquad (3.13)$$

where

$\underline{j}_{\mathrm{A}}$ is **Mass Flux** of component A referred to axes moving at the Mass average velocity

D_{AB} = **diffusivity** of component A through B

w_{A} = mass fraction of component A

ρ = Total mass concentration of mixture

Also Molar flux of component A referred to axes moving at the Molar average velocity is given by

$$\boxed{\underline{J}_A^{*} = -\, c\, D_{AB} \nabla x_A} \qquad (3.14)$$

where

x_{A} = mole fraction of component A c = Molar density of mixture

The mass diffusivity $D_{AB} = D_{BA}$ for a **binary system**

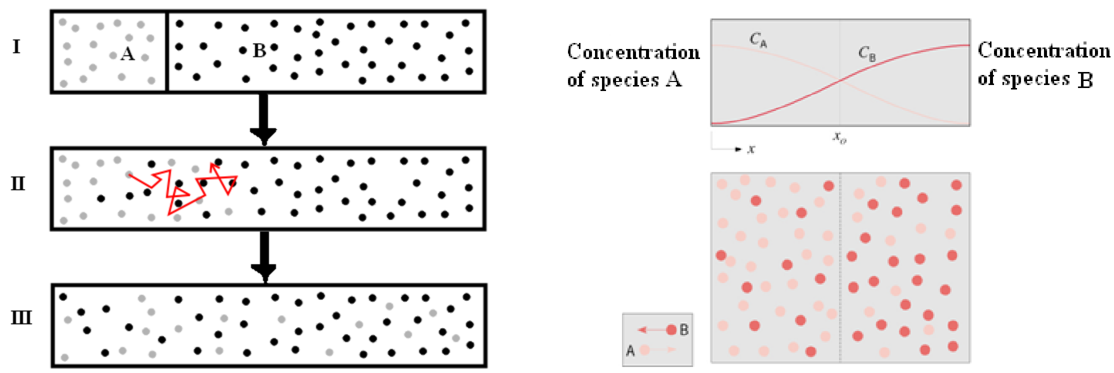

Fig.3.1 Mixing of two Gases (A and B) by Binary Diffusion

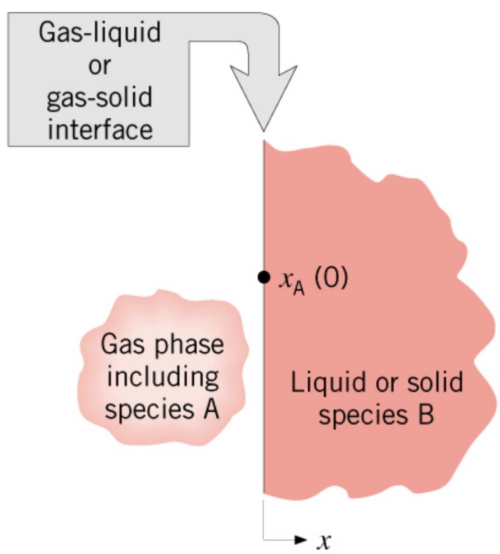

Fig.3.2 Diffusion of Gas (A) into Liquid or Solid (B) at Gas-Liquid (Solid) interface

Equivalent forms of Fick's first law

The mass flux relative to **stationary coordinates** is

$$\underline{n}_A = w_A(\underline{n}_A + \underline{n}_B) - \rho D_{AB} \nabla w_A \tag{3.15}$$

The molar flux of A relative to stationary coordinates is,

$$\underset{}{\underline{N}_A} = \underset{(\text{"Bulk" Fluid motion})}{x_A(\underline{N}_A + \underline{N}_B)} - \underset{\left(\begin{array}{l}\text{Diffusion superimposed} \\ \text{on bulk flow}\end{array}\right)}{c D_{AB} \nabla x_A} \tag{3.16a}$$

According to equation (3.6) we can write

$$\underline{N}_A = x_A c\, \underline{U}^* - c D_{AB} \nabla x_A \tag{3.16b}$$

Dilute Solutions

For dilute solution of component 'A' in a solvent 'B' e.g. a low concentration of NaCl (A) in H_2O (B), $\boxed{\underline{U}^* \approx \underline{U}}$ and equation (3.16b) becomes

$$\underset{(\text{Total Flux})}{\underline{N}_A} = \underset{(\text{Convection})}{c_A \underline{U}} - \underset{(\text{Diffusion})}{c D_{AB} \nabla x_A} \tag{3.17}$$

<u>Recapitulation of equations for the fluxes</u> in one dimension, e.g. y

Fick's law is an empirical law, as is the Fourier's law of heat conduction. Similarly Newton's law of viscosity establishes a relationship between shear stress and velocity gradient. So all these laws having analogy in between them and are discussed below.

Fick's law for ρ = constant

$$j_{Ay} = -D_{AB}\frac{d}{dy}\left(\rho_A\right) \tag{3.18}$$

Newton's law for ρ = constant

$$\tau_{yx} = -\nu\frac{d}{dy}\left(\rho U_x\right) \tag{3.19}$$

Fourier's law for ρ = constant

$$q_y = -\alpha\frac{d}{dy}\left(\rho \hat{c}_p T\right) \tag{3.20}$$

Thus we can draw a conclusion from the above three relationships that

(Flux)= - (Transport Coefficient) (gradient of "concentration" field)

With "concentration" field = mass, momentum, or energy, "concentration".

The analogy does not apply to two or three dimensions, because $\underline{\underline{\tau}}$ is tensor, while $\underline{j}$ and $\underline{q}$ are vectors.