

**Polymer Process Engineering**  
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**Lecture – 21**



**Mass transfer phenomenon in polymers: Introduction**

Hello friends, welcome to the mass transfer phenomena in the polymeric systems. So, dear friends in this particular segment, we are going to discuss about the mass transfer operation. Then we will discuss about the mechanism of mass transfer, then the molecular diffusion, we will discuss about the Fick's law of molecular diffusion, then diffusion velocity is unsteady state diffusion, the steady state diffusion through the constant area. Then we will discuss about the Fick's second law of diffusion for polymers.

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- **Fick's second law of diffusion for polymers**



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Now, there are three most you can say the central topic in chemical engineering and they are equally applicable in the polymeric system. Like one is the synthesis of material for any raw material, we need to process them and to make the finished product for our commodity use or day to day use or for the different industrial or specialized use.



is much less quantity in a lower concentration. So, to purify and to produce a pure product it involves a huge separation cost, whereas the production of the sulfuric acid is much cheaper.

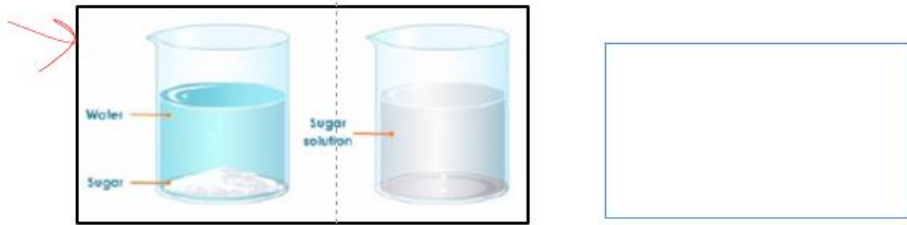
Now, there are various separation protocols, which are based on either entirely the separation of different particles, grids or different particle sizes, usually maybe by the screening, maybe by other separation protocols or the filtration of the solid from the suspension of the liquid. Now, let us talk about the mass transfer. The mass transfer is net movement of component in a mixture from one location to another location in the presence of a difference in the concentration or a partial pressure because some driving force must be there. One example is that lump of a sugar added to a cup of water, which dissolves and then diffuses throughout the cup uniformly. Another example is to deliberate the use of agarbathi.

## Mass transfer

- **The mass transfer** is **the net movement of a component** in a mixture from **one location to the another location** in presence of a **difference in concentration or partial pressure**.

Examples:

a) **Lump of sugar added to a cup of water** which dissolves and then diffuses throughout the tea cup uniformly.



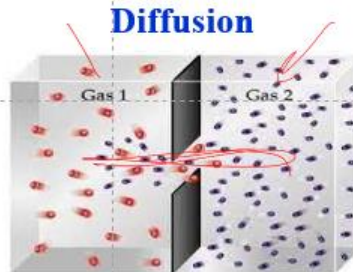
The fragments generally spread uniformly and when we put agarbathi at home. So, if you light the agarbathi at one corner over the period of time, the perfume or a fragrance it approaches to the all corners and you may say that all these fragrances distributed throughout the area in question. And drying of cloths under the sun, the drying occurs because the moisture diffuses into the air. So, these are the some of the driving forces. Then let us classify the mass transfer operation.

## Classification of mass transfer operations

- As we know there are three states of matter the gas, liquid and solids.
- So, the combination of these three states can form three different phases of possibilities of phases of contacts.

### a) Gas-Gas system:

- Two different gas and if we keep them in two container and allow them to mix they will **uniformly mix by the process of diffusion.**



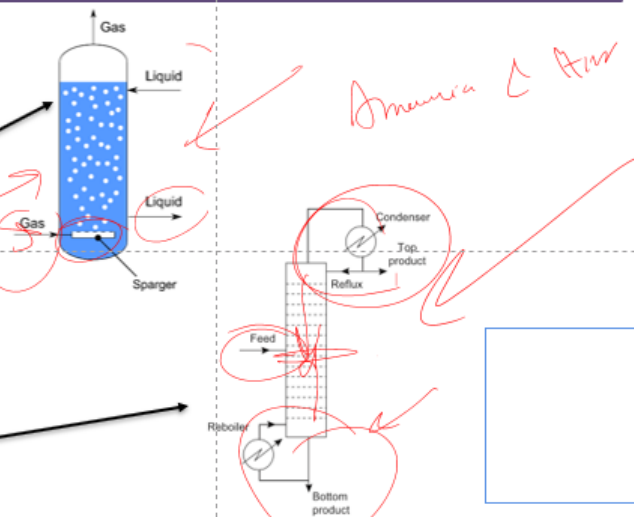
As we know that the three stages of matter gas, liquid and solid. So, the combination of these three states can form three different phases of possibilities of phase of contact. One is the gas-gas system, the two different gases, gas 1 and gas 2. Two different gases if we keep them in two container and allow them to mix, they will uniformly mix by the process of diffusion. Then the gas liquid type of a system, absorption.

## Classification of mass transfer operations

### b) Gas-Liquid system:

#### 1) Absorption:

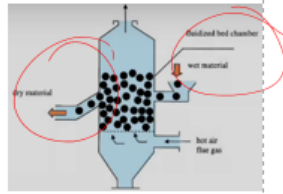
#### 2) Distillation:



## Classification of mass transfer operations

c) Gas-Solid system:

1) **Drying:**

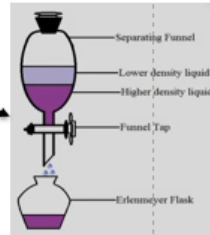


2) **Adsorption:**



d) Liquid-Liquid system

1) **Extraction:**



Usually, it is one of the such examples like here you are having the gas, liquid and sparger, when the sparger is there. So, one of such example of a gas-liquid system, is suppose a solute is changing from a gas phase to the liquid phase and two mixtures of ammonia and air. Let us say that ammonia and air. We have water in the liquid phase. So, ammonia will dissolve, this is ammonia, ammonia will dissolve in water and form the ammonium hydroxide and air does not dissolve in the liquid.

So, in this case, there is an interface between the gas and liquid, and one component of the gas phase is preferentially dissolved in the liquid phase from the solution, this is known as the absorption process. Another thing is the distillation. Now here, the salient feature like you are introducing the feed over here, this is the refluxes and this is the reboiler section. And so, we have a reboiler here, where we heat the liquid and it forms a vapor phase, and its liquid is fed from the top as a reflux and it comes down like this and there is an intimate contact of between the gas and liquid. So, when there is a difference in their boiling point among the mixture or the component and we can create two phases, the vapor phase and another liquid phase, and vapour phase will be mostly on the lighter component and the liquid phase will be on the heavier component.

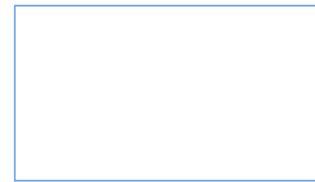
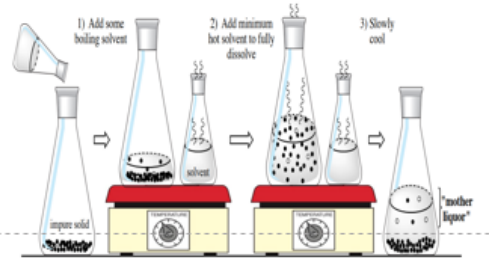
Therefore, we can separate the two different components or multiple component and this process is known as distillation. Another segment is called a drying. This is a type of a gas solid system. Now, here this is a typical dryer and you see the dry material, this is a fluidized by stich chamber. So, some sort of a drying force is there, then adsorption is a very common phenomena over the surface.

## Classification of mass transfer operations

e) Liquid-Solid system

- 1) **Crystallization:** the process of **formation of solids from a liquid solution** based on difference in **solute concentration** and its solubility at a certain temperature.
- 2) **Leaching:** **selective dissolution of a component from a solid particle** by a liquid solvent is known as **the leaching process**.

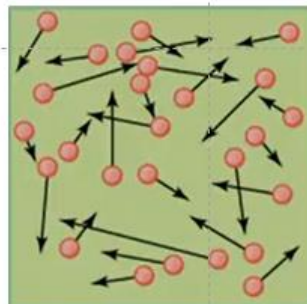
**Example:** formation of some medicinal components from the plants.



This is a sample surface over this, the adsorbate is being accumulated over the period of time. Then the liquid-liquid system, the prominent segment is the extraction. So, when we talk about the liquid-liquid system, the crystallization, the process of formation of the solid from the liquid solution based on the difference in the solute concentration and its solubility at a certain temperature. Then the leaching, this is a selective dissolution of a component from a solid particle by a liquid solvent, this is known as leaching. The example is the formation of some medicinal component from the plants.

## Mechanism of mass transfer operations

- Mass transfer occurs by two basic mechanisms.
- 1. **Molecular mass transfer:** The molecular diffusion by random and spontaneous microscopic movement of individual molecules in a gas, liquid or solid as a result of thermal motion is known as the molecular mass transfer.



Now, usually when we talk about the mechanism of mass transfer operation, so usually it occurs by two basic mechanisms. One is the molecular mass transfer, the molecular diffusion by random and spontaneous microscopic movement of individual molecule in a gas, liquid or a solid as a result of a thermal motion which is known as the molecular mass transfer. Then the convective mass transfer, in this case the ED diffusion by the random macroscopic fluid motion is the responsible function for the



convective mass transfer. Here you see that. What are the driving force for mass transfer operation? You see when we, the agarbati at one corner and it goes to the other part, then there must be some driving force.

## Mechanism of mass transfer operations

- Mass transfer occurs by two basic mechanisms.

**2. The convective mass transfer:** In this case eddy diffusion by random macroscopic fluid motion is the responsible for the convective mass transfer.

Time →

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 Treybal R.E., "Mass Transfer Operations", 3rd Ed., 1980, McGraw Hill.

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So, let us talk about those driving force for this mass transfer operation. One is the two-phase system, the spontaneous alteration through the molecular diffusion occurs in air ammonia mixture. The ammonia diffuses to the liquid and spontaneous alteration of the molecular diffusion occurs and ultimately the system comes into a state of equilibrium where the alteration stops. Another is the multi-phase system. It deals with diffusion process in each phase separately and the mass transfer in one phase, the concentration is the driving force where there is a multiple phase, the two-driving force for the mass transfer is the chemical potential.

## Driving forces of mass transfer operations

**a) Two phase system:**

- Spontaneous alterations** through molecular diffusions occurs.
- In air ammonia mixtures **the ammonia diffuses to the liquid** and spontaneous alterations of the molecular diffusions occurs and ultimately the systems comes into **a state of equilibrium** where the alteration stops.

**b) Multi phase system:**

- It deal with diffusion process in each phase separately.
- The mass transfer in one phase, **concentration is the driving force** when there is a multiple phases, **the true driving force** for mass transfer is **the chemical potential**.

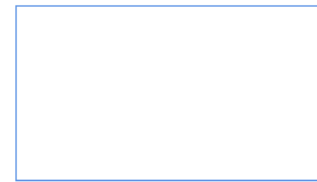
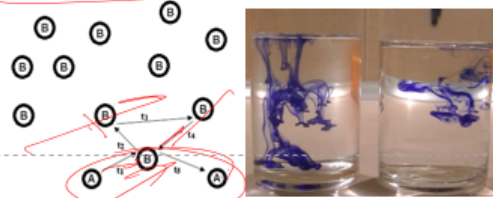
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## Molecular Diffusion

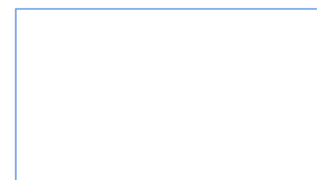
- **The molecular diffusion** is defined by **the movement of individual molecules** through a substance by virtue of **their thermal energy**.
- This can be explained **by simplified kinetic theory**.
- Consider two different types of molecules: molecule A and molecule B.
- **A molecule is imagined to travel in a straight path** at a uniform velocity until it **collides** with another molecule, whereupon **its velocity changes** both in their direction as well as magnitudes.



Let us talk about the molecular diffusion. The molecular diffusion is defined by the movement of individual molecules through the substance by virtue of their thermal energy. Now this can be explained by the simple kinetic theory. Now consider the two different type of molecules, molecule A and molecule B. A molecule is imagined to travel in a straight path at a uniform velocity until it collides with another molecule where upon its velocity change and both the directions as well as the magnitude.

## Mean free-path

- **The net distance** or the average distance **the molecules travels** between the two collisions is known as **the mean free path**.
- The molecules travels through a **highly zigzag path**.
- **The net distance travel in one direction** in a given time is defines as **the rate of diffusion**.
- The rate of molecular diffusions is **very slow**.
- The rate of diffusion can be:
  - a) **Increased by reducing the pressure:** reduces the number of collisions.
  - b) **Increased by increasing temperature:** increase the molecular velocity.



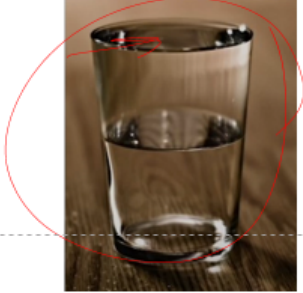
So, this is A and it collides with B. Now the net distance of or the average distance of the molecule travel between the two collision is known as the mean free path here. The molecule travels through a highly zigzag path. The net distance travel in one direction in a given time is defined as the rate of a





diffusion. So, the rate of molecular diffusion is very slow and this the rate of diffusion can be increased by reducing the pressure.

### Effect of barrier on molecular diffusion

- Lets, take a system where we have a **water and kept on a reservoir and it is vacuum above heat.**
- The rate of evaporation of water at 25°C into a complete vacuum **is quit high which is around 3.3 kg/s. m<sup>2</sup> of water surface.**
- However, if **we place a small layer on top** of this water surface of thickness ~0.1 mm.
- **The rate of diffusion will reduce by a factor of about 600.**
- This shows **the barrier has immense importance** on the molecular diffusions.







Binay G. G. and Associates, "Unit Operations", 1995, CBS Publishers. 18

When we reduce the pressure, then this reduces the number of collision and increasing by this can be increased by the increasing temperature. When this increases the molecular velocity. Now let us talk about the effect of barrier on the molecular diffusion. Let us take a system where we have a water and, on a reservoir, and it is vacuum above heat. So, the rate of evaporation of water at say 25 degree Celsius into the complete vacuum is quite high which is around 3. 3 kilograms per centimeter per square meter of water surface. Now if we place a small layer on top of this water surface of thickness say 0.1 mm, the rate of diffusion will reduce by a factor of say about 600. This shows the barrier has an immense importance on the molecular diffusion. Let us talk about the mass concentration.

### Mass concentrations

- **Mass concentration of component i:** →  $\rho_i = \frac{m_i}{V}$
- **Sum of mass fractions:**  $\sum_{i=1}^n W_i = \sum_{i=1}^n \frac{\rho_i}{\rho} = 1$
- **Total mass concentration:** →  $\rho = \sum_{i=1}^n \rho_i$
- **Mass fraction:** →  $W_i = \frac{\rho_i}{\sum_{i=1}^n \rho_i}$



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$$\rho_i = \frac{m_i}{V}$$

$$\sum_{i=1}^n W_i = \sum_{i=1}^n \frac{\rho_i}{\rho} = 1$$

$$\rho = \sum_{i=1}^n \rho_i$$

$$W_i = \frac{\rho_i}{\sum_{i=1}^n \rho_i}$$

**Molar concentrations**

- **Molar concentration of component i:**  $C_i = \frac{p_i}{RT}$
- **Total molar concentration:**  $C = \sum_{i=1}^n C_i$
- **Total molar concentration of ideal gas mixture:**  $C = \frac{1}{RT} \sum_{i=1}^n p_i = \frac{p_t}{RT}$
- **Mole fraction of component i (liquid or solid):**  $x_i = \frac{C_i}{C}$

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$$C_i = \frac{p_i}{RT}$$

$$C = \sum_{i=1}^n C_i$$

$$C = \frac{1}{RT} \sum_{i=1}^n p_i = \frac{p_t}{RT}$$

$$x_i = \frac{C_i}{C}$$

Mole fraction component I (in ideal gas mixture)

$$y_i = \frac{p_i}{p_t}$$

Mole fraction of component I (in gasses)

$$y_i = \frac{C_i}{C}$$

Sum of mole fractions

$$\sum_i x_i = 1 \quad \sum_i y_i = 1$$

### Molar concentrations

- Mole fraction component  $i$  (ideal gas mixture):

$y_i = \frac{p_i}{p_t}$
- Mole fraction of component  $i$  (gasses):

$y_i = \frac{C_i}{C}$
- Sum of mole fractions:

$$\sum_i x_i = 1$$

$$\sum_i y_i = 1$$

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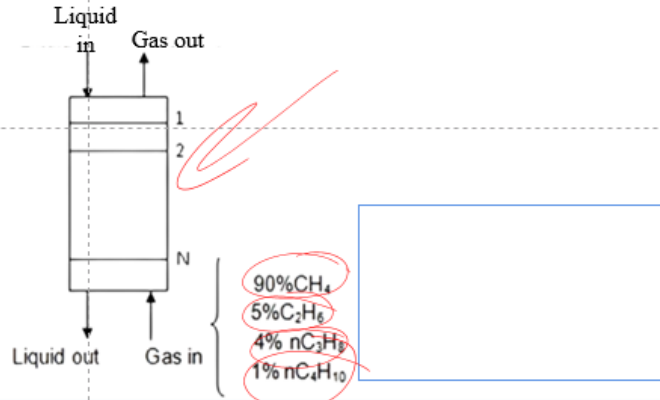
The mass concentration of the component is given by the  $\rho_i$  is equal to  $m_i$  over  $v$  and some of the mass fractions can be given as summation of  $i$  is equal to 1 to  $n$   $w_i$ . This can be the summation of  $i$  to  $n$   $\rho_i$  over  $\rho$  that must be equal to 1 and the total mass concentration can be given as  $\rho$  is equal to summation of  $i$  to  $n$   $\rho_i$  and the mass fraction is  $w_i$  is equal to  $\rho_i$  over summation of  $i$  to  $n$   $\rho_i$ . Another component in question is that molar concentration of component  $i$  that is  $c_i$  is equal to  $p_i$  over  $r t$  and the total molar concentration can be given represented as  $c$  is equal to summation of  $i$  to  $n$   $c_i$  and the total molar concentration of ideal gas mixture can be given or can be mathematically represented by this particular formula  $c$  is equal to  $1$  over  $r t$  summation of  $i$  to  $n$   $p_i$  is equal to  $p_t$  over  $r t$  and the mole fraction of component  $i$  that is very common in the liquid or solid that can be given as  $x_i$  is equal to  $c_i$  over  $c$  and the mole fraction of component  $i$  in the ideal gas mixture this can be given as  $y_i$  is equal to  $p_i$  over  $p_t$  that is the total pressure and the mole fraction of the component  $i$  in gases can be given in terms of the concentration and that is  $y_i$  is equal to  $c_i$  over  $c$ . So, if we talk about the sum of the mole fraction that is the summation  $i$  is equal to  $x_i$  is equal to 1 and  $y_i$  summation  $y_i$  is equal to 1.

## Question-1

**Question:** The feed gas to an absorber has the following composition at 313 K and 200 kPa as given in the figure:

**Calculate:**

- a) the composition of the feed gas in terms of the mass fraction.
- b) total concentration in the feed gas.



Now, let us take up one question that is the feed to an absorber has the following composition at 313 Kelvin and 200 kilopascal that is per the given the figure like 90 percent of methane then 5 percent c 2 h 6 4 percent of n c 3 h 8 and 1 percent of n c 4 h 10 and you need to calculate the composition of the feed gas in terms of the mass fraction and the total concentration in the feed gas.

*Assume 100 kmol of feed gas composition*  
*total molar concentration c*  

$$C = \frac{P_i}{RT} = \frac{200}{8.314 \times 313}$$

$$= 0.077 \text{ kmol/m}^3$$

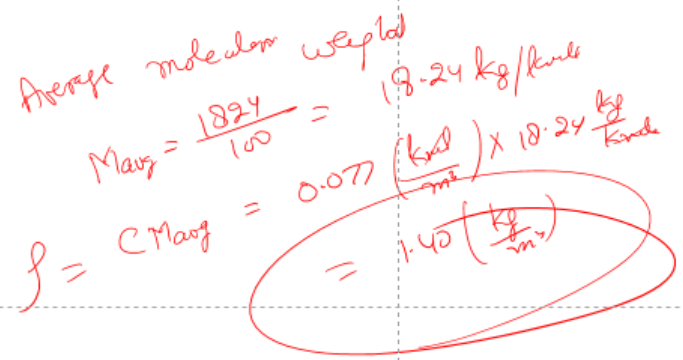
Components	kmol	Mol. Wt.	Mass (kg) = kmol x Mol wt.	Mass fractions
CH <sub>4</sub>	90	16	1440	0.80
C <sub>2</sub> H <sub>6</sub>	5	30	150	0.08
nC <sub>3</sub> H <sub>8</sub>	4	44	176	0.09
nC <sub>4</sub> H <sub>10</sub>	1	58	58	0.03
<b>Total</b>	<b>100</b>		<b>1824</b>	<b>1.0</b>





Average molecular weight

$$M_{avg} = \frac{1824}{100} = 18.24 \text{ kg/kmole}$$

$$f = c_{M_{avg}} = 0.077 \left( \frac{\text{kmol}}{\text{m}^3} \right) \times 18.24 \frac{\text{kg}}{\text{kmole}}$$

$$= 1.40 \left( \frac{\text{kg}}{\text{m}^3} \right)$$




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Now, for this we need to take the basis 100 kilo mole of feed gas mixture. Now, here we have given the components  $C_1$ ,  $C_2$ ,  $C_3$  and  $C_4$  butane and which is total 100 and the mole molecular weight and the mass in kilogram or kilo mole the molecular weight and the mass fraction is given like this because we have calculated the total one. So, the molar concentration total molar concentration  $c$  is equal to  $p_i$  over  $R T$  and this 200 is given 8.314 into 313 and that comes out to be 0.

0.77 kilo mole per meter cube. So, average molecular weight  $M_{avg}$  is equal to 1824 over 100 and that comes out to be 18.24 kilogram per kilo mole. So, the total mass concentration  $\rho$  is given by  $c M_{avg}$  which is 0.77 kilo mole per meter cube into 18.24 kilogram per kilo mole. This comes out to be 1.40 in per meter cube and this is our answer. Now, let us talk about the diffusion and velocity.

## Diffusion velocity

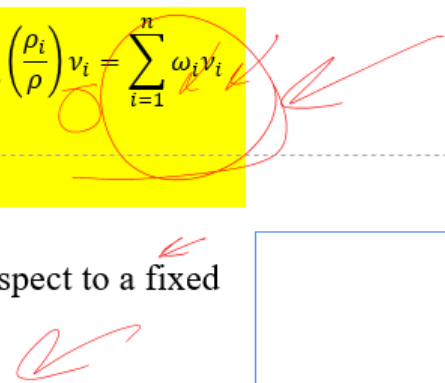
- Mass average velocity:



**The mass average velocity** is defined in terms of **the mass concentration**.

$$V_{mass-avg} = \frac{\sum_{i=1}^n \rho_i v_i}{\sum_{i=1}^n \rho_i} = \sum_{i=1}^n \left( \frac{\rho_i}{\rho} \right) v_i = \sum_{i=1}^n \omega_i v_i$$

Where,

- $v_i$  = **absolute velocity** of species  $i$  with respect to a fixed reference frame
- $\omega_i$  = **mass fraction** of species  $i$





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$$V_{mass-avg} = \frac{\sum_{i=1}^n \rho_i v_i}{\sum_{i=1}^n \rho_i} = \sum_{i=1}^n \left( \frac{\rho_i}{\rho} \right) v_i = \sum_{i=1}^n \omega_i v_i$$

Where,

$v_i$  = absolute velocity of species  $i$  with respect to a fixed reference frame



$\omega_i$  = mass fraction of species  $i$

### Diffusion velocity

- Molar average velocity:  
**The molar average velocity** is defined in terms of **the molar concentration**.

$$V_{mol-avg} = \frac{\sum_{i=1}^n C_i v_i}{\sum_{i=1}^n C_i} = \sum_{i=1}^n \left( \frac{C_i}{C} \right) v_i = \sum_{i=1}^n x_i v_i$$

Where,  
 $x_i$  = **mole fraction** of species  $i$



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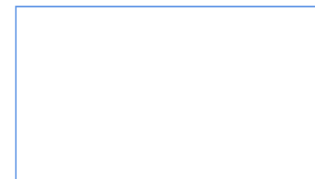
The molar average velocity is defined in terms of the molar concentration;

$$V_{mol-avg} = \frac{\sum_{i=1}^n C_i v_i}{\sum_{i=1}^n C_i} = \sum_{i=1}^n \left( \frac{C_i}{C} \right) v_i = \sum_{i=1}^n x_i v_i$$

The mass average velocity is defined as the mass concentration which can be represented as this particular mathematical relationship where  $v$  is equal to absolute velocity of a species  $i$  with respect to a fixed reference frame and  $\omega_1$  to  $\omega_i$  is equal to mass fraction of a species  $i$ . So, this is the mass average is summation of  $\rho_i v_i$  over summation  $\rho$  and that is equal to summation  $\rho_i v_i$  over  $\rho$  into  $v_i$  and this is the summation  $\omega_i v_i$  is equal to  $1$  to  $n$   $\omega_i$  into  $v_i$ . If we talk about the diffusion velocity, then the molar average velocity is very important and it is sometimes defined as in terms of a molar concentration. So, which can be represented like this where  $x_i$  this is slightly different from the previous formula here  $x_i$  is the mole fraction of a species  $i$  rather here we use this  $\omega_i$  which is a mass fraction of a species  $i$ .

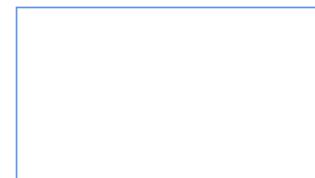
## Question-2

**Question:** A gas mixture containing  $H_2$ : 15 %, CO: 30 %,  $CO_2$ : 5 % and  $N_2$ : 50 % flows through a tube of 1 inch diameter, at 15 bar total pressure. If the velocities of the respective components are 0.05 m/s, 0.03 m/s, 0.02 m/s and 0.03 m/s. **Calculate the mass average and molar average velocities of the mixture?**



Now, let us take up another question that is a gas mixture this contains about 15 percent of hydrogen, 30 percent of carbon monoxide and 5 percent of  $CO_2$  and remaining is nitrogen. This flow through a tube of say 1 inch diameter and 15 bar with the total pressure. If the velocities of the respective component they are 0.

$$\begin{aligned}
 & H_2 \rightarrow 1 \quad CO \rightarrow 2 \quad CO_2 \rightarrow 3 \quad N_2 \rightarrow 4 \\
 V_{molar} &= \frac{1}{C} (C_1 v_1 + C_2 v_2 + C_3 v_3 + C_4 v_4) \\
 &= Y_1 v_1 + Y_2 v_2 + Y_3 v_3 + Y_4 v_4 \\
 V_{molar} &= (0.15)(0.05) + (0.3)(0.03) + (0.05)(0.02) \\
 &\quad + (0.5)(0.03) \\
 &= 0.0325 \text{ m/s}
 \end{aligned}$$



The mass average velocity is given by

$$V_{mass} = \frac{1}{\rho} (\rho_1 V_1 + \rho_2 V_2 + \rho_3 V_3 + \rho_4 V_4)$$

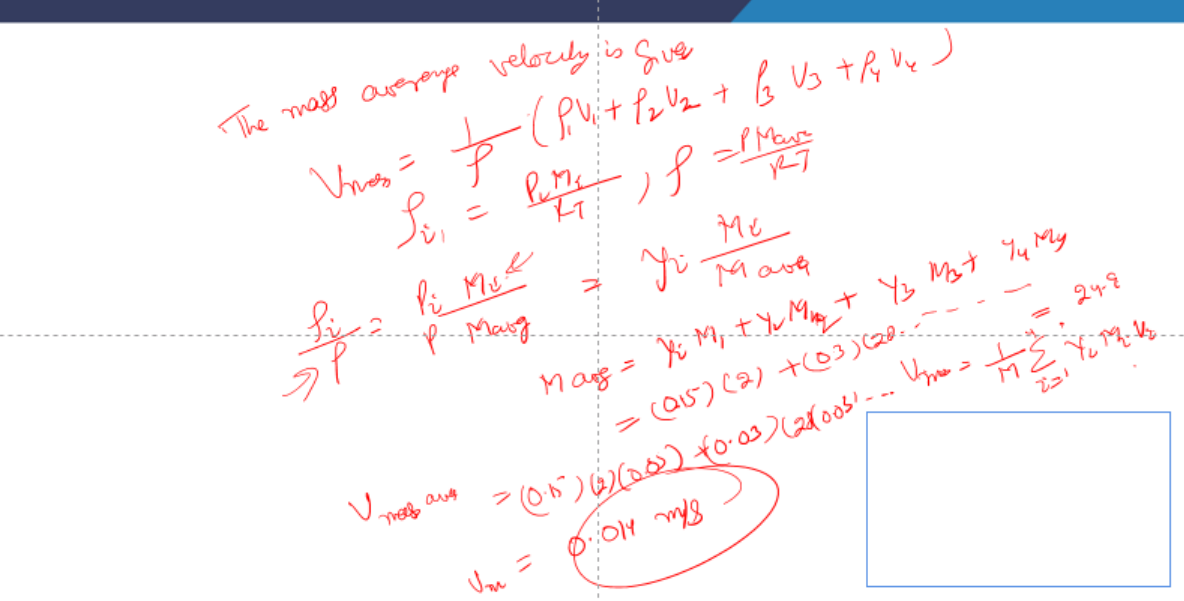
$$\rho_i = \frac{\rho_i M_i}{RT}, \quad \rho = \frac{\rho_{mass}}{RT}$$

$$\frac{\rho_i}{\rho} = \frac{\rho_i M_i}{\rho_{mass}} = Y_i \frac{M_i}{M_{avg}}$$

$$M_{avg} = Y_1 M_1 + Y_2 M_2 + Y_3 M_3 + Y_4 M_4$$

$$= (0.15)(2) + (0.3)(28) + \dots = 24.9$$

$$V_{mass\ avg} = (0.15)(2) + (0.3)(28) + \dots = 0.14 \text{ m/s}$$

$$V_m = 0.14 \text{ m/s}$$


05 meter per second and 0.03 meter per second and 0.02 meter per second respectively, you need to calculate the mass average and molar average velocities of the mixture. Now, let us rename the gas mixture as H<sub>2</sub> is equal to H<sub>2</sub>, CO<sub>2</sub>, CO, N<sub>2</sub> and N<sub>2</sub>. So, the molar average velocities can be given as per the formula  $\frac{1}{C} (C_1 V_1 + C_2 V_2 + C_3 V_3 + C_4 V_4)$  and thus that comes out to be  $Y_1 V_1 + Y_2 V_2 + Y_3 V_3 + Y_4 V_4$  where Y is the mole fraction of component i in the gas mixture. So, if we put the values then V can be given as 0.

15 into 0.05 plus 0.3 into 0.03 plus 0.05 into 0.02 plus 0.5 into 0.03 and this comes out to be the 0.

0.325 meter per second. So, the mass average velocity the mass average velocity is given by V mass average which is equal to  $\frac{\rho_1 V_1 + \rho_2 V_2 + \rho_3 V_3 + \rho_4 V_4}{\rho}$  and  $\rho_i$  is equal to  $\frac{P_i M_i}{RT}$  and  $\rho$  is equal to  $\frac{P M_{avg}}{RT}$ . So,  $\frac{\rho_i}{\rho}$  is equal to  $\frac{P_i M_i}{P M_{avg}}$  which is equal to  $Y_i \frac{M_i}{M_{avg}}$  where  $\rho_i$  is the mass density of ith component,  $\rho$  is the total mass density,  $M_i$  is the molecular weight of ith component and  $M_{avg}$  is the average molecular weight of the mixture. Now, if we put all the values, so,  $M_{avg}$  is equal to  $Y_1 m_1 + Y_2 m_2 + Y_3 m_3 + Y_4 m_4$  and if we substitute the value 0.15 into 2 plus 0.

3 into 28 and so on, this comes out to be 24.9. So, if we calculate V mass average that is  $\frac{1}{M_{avg}} \sum_{i=1}^n Y_i M_i V_i$ . So, if we substitute the value of V mass average which is comes out to be if we substitute all the values given, then it comes out to be 0.15 into 2, 0.305 plus 0.03 into 28 into 0.03 and so on. This comes out to be V mass average comes out to be 0.14 metre per second and that is our answer.

**Mass flux:**  $N_{i\_mass} = \rho_i V_i$

**Total mass flux:**  $N_{mass} = \rho V_{mass-avg}$

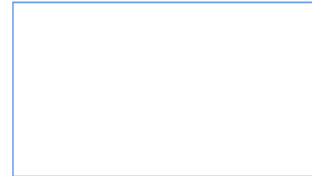
## Fluxes

- Flux is defined as **the rate of transport of species  $i$  through unit area normal to the transport.**
- The flux of a given species is a **vector quantity.**
- Flux may be calculated with respect to **coordinates fixed in space** or coordinates moving with **the mass or molar average velocity.**

### Mass Flux

Calculated with respect to **the coordinate fixed in space or relative to stationary observer**

- **Mass flux:**  $N_{i\_mass} = \rho_i v_i$
- **Total mass flux:**  $N_{mass} = \rho V_{mass-avg}$



Let us talk about the fluxes. Now, flux is defined as the rate of transport of a species  $i$  through the unit area normal to the transport. Now, the flux of a given species is a vector quantity. Flux may be calculated with respect to the coordinates fixed in space or coordinates moving with mass or molar average velocity. Now, mass flux, this is calculated with respect to the coordinate fixed in space or relative to the stationary observer.

**Mass flux:**  $J_{i\_mass} = \rho_i (v_i - V_{mass-avg})$

**Molar flux:**  $N_{i-mol} = C_i v_i$

**Total molar flux:**  $N_{mol} = C V_{mol-avg}$

**Molar flux:**  $J_{i\_mol} = C_i (v_i - V_{mol-avg})$

## Fluxes

Calculated with respect to mass average velocity or relative to an observer moving with the mass average velocity.

- **Mass flux:**  $J_{i \text{ mass}} = \rho_i (v_i - V_{\text{mass-avg}})$

### Molar Flux

Calculated with respect to the fixed phase or relative to stationary observer.

- **Molar flux:**  $N_{i \text{ mol}} = C_i v_i$
- **Total molar flux:**  $N_{\text{mol}} = C v_{\text{mol-avg}}$

So, this can be represented by this formula that is the mass flux  $N_{i \text{ mass}}$  is equal to  $\rho_i v_i$  the total mass flux and mass is equal to  $\rho V_{\text{mass average}}$ . Now, the calculated with respect to the mass average velocity or relative to an observer moving with the mass average velocity and thus can be the mass plus that is  $J_{i \text{ mass}}$  is equal to  $\rho_i (v_i - V_{\text{mass average}})$  and the molar flux, this is calculated with respect to the fixed phase or relative to stationary observer.

So, the molar flux is equal to  $N_{i \text{ mol}}$  that is  $C_i v_i$  then total molar flux that is  $N_{\text{mol}}$  is equal to  $C v_{\text{mol average}}$ . Now, this calculated with respect to the average velocity or the relative to an observer moving with the mass average velocity.

## Fluxes

Calculated with respect to the average velocity or relative to an observer moving with the mass average velocity

- **Molar flux:**  $J_{i \text{ mol}} = C_i (v_i - V_{\text{mol-avg}})$



So, the molar flux  $J_i$ , this can be represented as  $C_i V_i - V$  mole average. Now, let us talk about the relations between the fluxes. So, this can be  $J_i$  mass is equal to  $\rho_i V_i - V$  mass average and  $N_i$  mass is equal to  $\rho_i V_i$  and  $J_i$  mass is equal to  $\rho_i$  into  $N_i$  mass over  $\rho_i - \rho_i V$  mass average.

### Relation between fluxes

$$J_{i, \text{mass}} = \rho_i (v_i - V_{\text{mass ave}})$$

$$N_{i, \text{mass}} = \rho_i v_i$$

$$J_{i, \text{mass}} = \rho_i \times \frac{N_{i, \text{mass}}}{\rho_i} - \rho_i V_{\text{mass ave}}$$

$$N_{i, \text{mass}} = \frac{J_{i, \text{mass}} + \rho_i V_{\text{mass ave}}}{\rho_i}$$

$$N_{i, \text{mol}} = \frac{J_{i, \text{mol}} + C_i V_{\text{mole ave}}}{C_i}$$

So, the  $N_i$  mass is equal to  $J_i$  mass plus  $\rho_i V$  mass average and this comes out to be  $J_i$  mass plus  $\rho_i N_i$  mass over  $\rho_i$ . So, this is my first formula. Similarly, we can write  $N_i$  mole is equal to  $J_i$  mole plus  $C_i V$  mole average and this comes out to be  $J_i$  mole plus  $C_i N_i$  mole over  $C_i$ . So, this is our next one. Now, let us talk about the Fick's law of molecular diffusion.

For diffusion of component A in x direction is

$$J_{A,x} = -D_{AB} \frac{dC_A}{dx}$$

Where,

$J_{A,x}$  = molar flux of component A in x-direction

Unit: amount of material diffused/(l)<sup>2</sup>(t)

$D_{AB}$  = the diffusion coefficient

Unit: l<sup>2</sup>/t

$C_A$  = Concentration of A

## Fick's law of molecular diffusion

- **Adolf Eugen Fick** a German physiologist he has given a law for the diffusion of components.
- The Fick's first law defines **the diffusion flux of a component A** in an isothermal, isobaric binary system is **proportional to the concentration gradient** in a particular direction.

For diffusion of component A in x direction is

$$J_{A,x} = -D_{AB} \frac{dC_A}{dx}$$

Where,

$J_{A,x}$  = molar flux of component A in x-direction

Unit: amount of material diffused/(l)<sup>2</sup>(t)

$D_{AB}$  = the diffusion coefficient

Unit: l<sup>2</sup>/t

$C_A$  = Concentration of A



Now, Fick, the head of Eugene Fick's, a German physiologist, he has given a law for the diffusion of a component. The Fick's first law defines the diffusion flux of a component A in an isothermal, isobaric binary system and proportional to the concentration gradient in a particular direction. For diffusion of a component A in X direction is given by  $J_{Ax}$  is equal to minus  $D_{AB} dC_A$  over  $dx$  where  $J_{Ax}$ , this is the molar flux of component A in X direction, the unit is having the amount of material diffused over N square time and then this  $D_{AB}$  is the diffusion coefficient and  $C_A$  is the concentration of A. Now, the relationship between the mutual diffusivity of species A and B, this can be given by say  $N_A$  is equal to  $J_A$  plus  $C_A$  over  $C_N$ . This is equation number 1 and for gas mixture  $C_A$  over  $C$  is equal to  $Y_A$  and  $J_A$  can be represented as minus  $D_{AB} dC_A$  over  $dx$ .

## Relationship between mutual diffusivity of species A and B

$$N_A = J_A + \frac{C_A}{C} N$$

$$\frac{C_A}{C} = Y_A \quad \& \quad J_A = -D_{AB} \frac{dC_A}{dx}$$

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

$$\frac{dC_A}{dx} = C \frac{dY_A}{dx}$$

$$N_A = -CD_{AB} \frac{dY_A}{dx} + Y_A N$$

$$N_B = -CD_{BA} \frac{dY_B}{dx} + Y_B N$$



So, if we put the values in the equation 1, we get  $N_A$  is equal to minus  $D_{AB} \frac{dC_A}{dx}$  plus  $Y_A N$ . This is our equation 2. Also,  $\frac{dC_A}{dx}$  is equal to  $C \frac{dY_A}{dx}$ . So, therefore, the equation 2 becomes, this equation can become  $N_A$  is equal to minus  $C D_{AB} \frac{dY_A}{dx}$  plus  $Y_A N$ .

This is our equation number 3. Similarly,  $N_B$  is equal to minus  $C D_{BA} \frac{dY_B}{dx}$  plus  $Y_B N$ . This is equation number 4. Now, some if we sum these two, equation 3 and 4, we get  $N_A$  plus  $N_B$  that is comes out to be minus  $C D_{AB} \frac{dY_A}{dx}$  plus  $Y_A N$  minus  $C D_{BA} \frac{dY_B}{dx}$  plus  $Y_B N$  or minus  $C D_{AB} \frac{dY_A}{dx}$  minus  $C D_{BA} \frac{dY_B}{dx}$  plus  $Y_A N$  plus  $Y_B N$ . Now, since for two components,  $N_A$  plus  $N_B$  is equal to  $N$ ,  $Y_A$  plus  $Y_B$  is equal to 1. So,  $\frac{dY_A}{dx}$  plus  $\frac{dY_B}{dx}$  is equal to 0 and  $\frac{dY_A}{dx}$  is equal to minus  $\frac{dY_B}{dx}$ .


Handwritten derivation on a whiteboard:

$$\begin{aligned}
 N_A + N_B &= -C D_{AB} \frac{dY_A}{dx} + Y_A N - C D_{BA} \frac{dY_B}{dx} + Y_B N \\
 &= -C D_{AB} \frac{dY_A}{dx} - C D_{BA} \frac{dY_B}{dx} + (Y_A + Y_B) N \\
 N_A + N_B &= N \quad Y_A + Y_B = 1 \\
 \frac{dY_A}{dx} + \frac{dY_B}{dx} &= 0 \\
 \frac{dY_A}{dx} &= -\frac{dY_B}{dx}
 \end{aligned}$$

The whiteboard also features a blue rectangular box in the lower right quadrant.

$N = -CD_{AB} \frac{dy_A}{dx} + CD_{BA} \frac{dy_B}{dx} + 1 \times N$

$D_{AB} = D_{BA}$



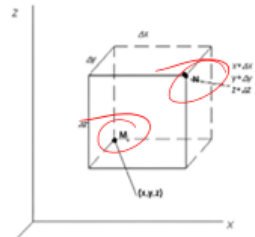
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Therefore, N is equal to minus C D AB dY A over dX plus C D B A dY B over dX plus 1 into N. Hence, d AB is equal to dBA. Now, let us talk about the unsteady state diffusion. So, let us consider unsteady state diffusion in this particular case.

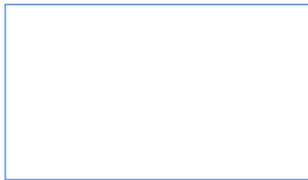
## Unsteady state diffusion

- Let us consider unsteady state diffusion in this case let us consider at point M and point N
- The change of concentration of a component of the diffusive constituents in a mixture over a time is unsteady state of diffusion.



**Balance equation:**

In + generation = out + accumulation



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Mass flow rate of component A in

$$M_A [N_{A,x}|_x \Delta y \Delta z + N_{A,y}|_x \Delta x \Delta z + N_{A,z}|_x \Delta x \Delta y]$$

Where,

$N_{A,x}$  = flux in the x direction

$[N_{A,x}]_x$  = value of flux at location x

$M_A$  = molecular weight of A

### Unsteady state diffusion

- Mass flow rate of component A In:
 

$$M_A [N_{A,x}|_x \Delta y \Delta z + N_{A,y}|_x \Delta x \Delta z + N_{A,z}|_x \Delta x \Delta y]$$

Where,

- $N_{A,x}$  = flux in the x direction →
- $[N_{A,x}]_x$  = value of flux at location x ↔
- $M_A$  = molecular weight of A ↪

- Generation of A by chemical reaction
  - a) Let **the rate of chemical reaction** be ↪
  - $R_A$  (mol/volume x time)

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Let us have a consider the point M here and a point N. The change in the concentration of a component of the diffusive constituent in a mixture over a time is unsteady state diffusion and the balance equation can be given as L N generation is equal to out plus accumulation. So, the mass flow rate of the component A can be given this particular equation where  $N_{A,x}$  is the flux in the X direction and this one is the value value of the flux at location some location X and  $M_A$  is the molecular weight of A. So, the generation of A by the chemical reaction. Now, let us the rate of the chemical reaction be  $R_A$  is equal to mole per volume into time and the rate of generation of the product can be given by this particular mathematical representation and mass flow rate of the component A out can be represented by this and the rate of accumulation which can be represented in the data form like where  $\rho_A$  is  $\rho_A$  is the density of component A. Now, suppose we put all the values in the balance equation. In that case, it can become the  $M_A$  into  $N_{A,x} \Delta y \Delta z + N_{A,y} \Delta x \Delta z + N_{A,z} \Delta x \Delta y$  plus  $\Delta x \Delta y \Delta z$  minus  $N_{A,x} \Delta y \Delta z + N_{A,y} \Delta x \Delta z + N_{A,z} \Delta x \Delta y$  plus  $\Delta x \Delta y \Delta z$  minus  $N_{A,y} \Delta x \Delta z + N_{A,z} \Delta x \Delta y$  plus  $\Delta x \Delta y \Delta z$  minus  $N_{A,z} \Delta x \Delta y$  plus  $\Delta x \Delta y \Delta z$  and that is equal to  $M_A R_A \Delta x \Delta y \Delta z$ .

Rate of generation or production

$$M_A R_A \Delta x \Delta y \Delta z$$

Mass flow rate of component A out

$$M_A [N_{A,x}|_{x+\Delta x} \Delta y \Delta z + N_{A,y}|_{x+\Delta x} \Delta x \Delta z + N_{A,z}|_{x+\Delta x} \Delta x \Delta y]$$

Rate of accumulation

$$\Delta x \Delta y \Delta z \frac{\partial \rho_A}{\partial t}$$

Where,

$\rho_A$  is the density of component A



## Unsteady state diffusion

b) Rate of generation or production:

$$M_A R_A \Delta x \Delta y \Delta z$$

c) Mass flow rate of component A out:

$$M_A [N_{A,x}|_{x+\Delta x} \Delta y \Delta z + N_{A,y}|_{x+\Delta x} \Delta x \Delta z + N_{A,z}|_{x+\Delta x} \Delta x \Delta y]$$

d) Rate of accumulation:

$$\Delta x \Delta y \Delta z \frac{\partial \rho_A}{\partial t}$$

Where,

$\rho_A$  is the density of component A

## Unsteady state diffusion

$$M_A [N_{A,x}|_{x+\Delta x} - N_{A,x}|_x] \Delta y \Delta z + (N_{A,y}|_{x+\Delta x} - N_{A,y}|_x) \Delta x \Delta z + (N_{A,z}|_{x+\Delta x} - N_{A,z}|_x) \Delta x \Delta y + \Delta x \Delta y \Delta z \frac{\partial \rho_A}{\partial t} = M_A R_A \Delta x \Delta y \Delta z$$

$$M_A \left( \frac{\partial N_{A,x}}{\partial x} + \dots \right) + \frac{\partial \rho_A}{\partial t} = M_A R_A$$

$$M_A \left( \frac{\partial N_{A,x}}{\partial x} + \dots \right) = M_A R_A$$

Now, if you divide both the side by delta X delta Y delta Z and if you take this delta X tends to 0 delta Y tends to 0 and delta Z tends to 0. So, for we have the component for component A that is  $M_A \frac{\partial N_{A,x}}{\partial x} + \dots + \frac{\partial \rho_A}{\partial t} = M_A R_A$  this can be equation number 5. And if similarly, we can write for the component B and that that can be represented as  $M_B R_B$  or  $M_B \frac{\partial N_{B,x}}{\partial x} + \dots$ . This can be equation 6. Now, the total material balance after adding equation 5 and equation 6 can be represented by  $M_A R_A + M_B R_B$ .

## Unsteady state diffusion

$$M_A R_A + M_B R_B = 0$$

$$\rho = \rho_A + \rho_B = \text{solution density}$$

$$M_A R_A + M_B R_B = 0 \quad \text{--- (7)}$$

$$V_x = \frac{\rho_A v_{Ax} + \rho_B v_{Bx}}{\rho_A + \rho_B}$$

$$\rho V_x = \rho_A v_{Ax} + \rho_B v_{Bx}$$

Now, if we take the  $\rho$  is equal to  $\rho_A$  plus  $\rho_B$  that is the solution density in that case  $M_A R_A$  plus  $M_B R_B$  must be equal to 0. So, if we substitute to this all these things it can become the equation number 7. Since the mass rate of generation, A and B must be equal to 0. So,  $V_x$  is equal to  $\rho_A v_{Ax}$  plus  $\rho_B v_{Bx}$  over  $\rho_A$  plus  $\rho_B$  or  $\rho V_x$  is equal to  $\rho_A v_{Ax}$  plus  $\rho_B v_{Bx}$ . So,  $\rho V_x$  equal to  $M_A C_A v_{Ax}$  plus  $M_B C_B v_{Bx}$  and which is equal to  $M_A N_{Ax}$  plus  $M_B N_{Bx}$  where  $V_x$  is the mass average velocity,  $v_{Ax}$  is the absolute velocity and  $N_{Ax}$  is the molar flux.

## Unsteady state diffusion

$$\rho V_x = M_A C_A v_{Ax} + M_B C_B v_{Bx}$$

$$= M_A N_{Ax} + M_B N_{Bx}$$

$$\frac{\partial (M_A N_{Ax} + M_B N_{Bx})}{\partial x} = \frac{\partial V_x}{\partial t} + V_x \frac{\partial \rho}{\partial x} \quad \text{--- (8)}$$

$$\left( \frac{\partial V_x}{\partial t} + \frac{\partial V_x}{\partial y} + \frac{\partial V_x}{\partial z} \right) + V_x \frac{\partial \rho}{\partial x} + V_y \frac{\partial \rho}{\partial y} + V_z \frac{\partial \rho}{\partial z} = 0 \quad \text{--- (9)}$$

So, if we substitute, so, it can become  $M_A N_{Ax}$  plus  $M_B N_{Bx}$  over  $\partial x$  is equal to  $\frac{\partial V_x}{\partial t}$  plus  $V_x \frac{\partial \rho}{\partial x}$ . This is equation number 8. So, if we substitute equation 8 into equation 7, we get  $\frac{\partial V_x}{\partial t}$  plus  $\frac{\partial V_y}{\partial y}$  plus  $\frac{\partial V_z}{\partial z}$  plus  $V_x \frac{\partial \rho}{\partial x}$  plus  $V_y \frac{\partial \rho}{\partial y}$  plus  $V_z \frac{\partial \rho}{\partial z}$  plus  $d \rho / dt = 0$ .

This is equal to 0. This is equation number 9. Now, this is the equation of continuity or the mass balance for total substance. Now, if solution density is constant, then equation 9, we have  $\frac{\partial V_x}{\partial x} + \frac{\partial V_y}{\partial y} + \frac{\partial V_z}{\partial z} = 0$ .

## Unsteady state diffusion

$$\frac{\partial V_x}{\partial x} + \frac{\partial V_y}{\partial y} + \frac{\partial V_z}{\partial z} = 0 \quad (9)$$

$$N_{Ax} = N_x A + j_{Ax}$$

$$M_A N_{Ax} = M_A N_x A + M_A j_{Ax}$$

$$M_A N_{Ax} = M_A \left( v_x \frac{\partial C_A}{\partial x} + v_y \frac{\partial C_A}{\partial y} + v_z \frac{\partial C_A}{\partial z} \right) + M_A D_{AB} \frac{\partial^2 C_A}{\partial x^2}$$

$$\Rightarrow M_A \frac{\partial N_{Ax}}{\partial x} = v_x \frac{\partial \rho A}{\partial x} + \rho A \frac{\partial v_x}{\partial x} + M_A D_{AB} \frac{\partial^2 C_A}{\partial x^2}$$

This is equation number 10. So, we know that in terms of mass flux and in the X direction,  $N_{Ax}$  is equal to  $N_x A + j_{Ax}$ . Now, if we substitute the value of and if we put on all those things, then it becomes  $M_A N_{Ax}$  is equal to  $M_A N_x A + M_A j_{Ax}$  or  $M_A N_{Ax}$  is equal to  $M_A C v_x \frac{\partial C_A}{\partial x} + M_A j_{Ax}$ .

## Unsteady state diffusion

$$v_x \frac{\partial \rho A}{\partial x} + \rho A \left( \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \right) - M_A D_{AB} \left( \frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right) + \frac{\partial \rho A}{\partial t} = M_A R \quad (11)$$

$$\rho = C$$

$$v_x \frac{\partial C_A}{\partial x} + v_y \frac{\partial C_A}{\partial y} + v_z \frac{\partial C_A}{\partial z} + \frac{\partial C_A}{\partial t} = D_{AB} \left( \frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right) + R \quad (12)$$



And this comes out to be  $M_A \frac{\partial N_{Ax}}{\partial x}$  is equal to  $v_x \frac{\partial \rho A}{\partial x} + \rho A \frac{\partial v_x}{\partial x} + M_A \frac{\partial j_{Ax}}{\partial x}$  and this is  $v_x \frac{\partial \rho A}{\partial x} + \rho A \frac{\partial v_x}{\partial x} + M_A \frac{\partial j_{Ax}}{\partial x}$ .

$\frac{\partial C_A}{\partial x} + \frac{\partial C_A}{\partial y} + \frac{\partial C_A}{\partial z} - \frac{M_A D_A V}{\rho_A} \left( \frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right) = M_A r_A$ . Then equation 5 becomes  $\frac{\partial C_A}{\partial t} + \frac{\partial C_A}{\partial x} + \frac{\partial C_A}{\partial y} + \frac{\partial C_A}{\partial z} - \frac{M_A D_A V}{\rho_A} \left( \frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right) = M_A r_A$ . This is the equation number 11. Now when  $\rho$  is constant, so if you use the equation 10 and dividing  $M_A$  in equation 11, this can become  $\frac{\partial C_A}{\partial t} + \frac{\partial C_A}{\partial x} + \frac{\partial C_A}{\partial y} + \frac{\partial C_A}{\partial z} - D_{AB} \left( \frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right) = r_A$ .

### Unsteady state diffusion

$$\frac{\partial C_A}{\partial \theta} = D_{AB} \left( \frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right)$$

Fick's second law



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This can become the equation 12. So, in a special case where the velocity equal to the 0 and no chemicalization occurs, so from equation 12, we get  $\frac{\partial C_A}{\partial \theta} = D_{AB} \left( \frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right)$  and this is the Fick's second law. It is frequently applicable to the diffusion in solid and to limited situation in fluids.

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So dear friends, in this particular segment we discussed about the various mass transfer segments and operation which are useful in the polymer processing and for your convenience we have been listed several references which you can utilize. Thank you very much.