Mass Transfer Operations - I Prof. Bishnupada Mandal Department of Chemical Engineering Indian Institute of Technology, Guwahati

Diffusion Mass Transfer Lecture – 02 Molecular and Eddy Diffusion, Diffusion Velocities and Fluxes

Welcome to the second lecture on Mass Transfer Operation I. In this lecture we will discuss on Diffusion Mass Transfer, before starting this lecture let us have small recap on the earlier lectures. The last lecture I have introduced to the mass transfer operation concepts.

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The definition of mass transfer, then we have discussed on the classifications of mass transfer based on phases of contacts. And then finally, we discussed the mechanism of mass transfer and the driving force. In this lecture we will start with the molecular diffusion.

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So, the molecular diffusion is defined by the movement of individual molecules through a substance by virtue of their thermal energy. Let us take a beaker and keep some water, if we put a drop of dyes or any ink into a liquid drop then it will try to distribute throughout the solutions. The process by which it takes place without any external effect is known as the molecular diffusion and which is based on their thermal energy.

This can be explained by simplified kinetic theory. Let us 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 molecules, whereupon its velocity changes both in their direction as well as magnitudes.

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The net distance or the average distance the molecules travels between this two collisions is known as the mean free path. You can see that the molecules travels through a very highly zigzag path, as you can see over here the molecules starts over here. And, then it goes in a straight path until it collides, it travels through a straight path and then its after the collisions it changes its direction as well as the velocity. And, it moves to a very highly zigzag position and at finish you could see it reaches over here and the net distance travels d between the start to the finish is the rate of diffusions. So, we define the net distance travel in one direction is given by the rate of diffusion.

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Rate of Molecular Diffusion

- \triangleright Rate of Molecular Diffusion is very slow.
- \triangleright Increase with decreasing pressure (reduces number of collisions).

 \triangleright Increase with increasing temperature (Increases the molecular velocity).

The rate of molecular diffusions is very slow. This we can change this know the rate of diffusion by two ways: one is to reduce the pressure. If we reduce the pressure like if you can consider an example of pressure cooker releasing pressure at a certain time, you can see the it reduces the number of collisions because the number of molecules present in a per unit volume is less.

So, the collisions will be less and its diffusion will be higher. The other way to change the rate of molecular diffusion is to increase the temperature. If we increase the temperature of the system its molecular velocity will increase and hence, it will increase the rate of molecular diffusion.

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Effect of barrier on the molecular diffusions, as you can see if we take a system which where you have a water and kept on a reservoir and it is vacuum above heat. And, if you we can create this system the rate of evaporation of water at 25 degree centigrade if we can keep complete vacuum then the rate is quit high which is around 3.3 kg per second per unit area of water surface. However, if we place a small layer on top of this water surface a may be a thickness of around 0.1 millimeter. Then the rate of diffusion will reduce by a factor of about 600. This shows the barrier has immense importance on the molecular diffusions.

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Let us take another examples: consider a tank of around 1.5 meter diameter and pure water is carefully placed over brine without disturbing the brine. So, at bottom we have a brine solutions of height of about 0.75 meter and top of that we can place a pure water of 0.75 meter height. The salt solution depth is 0.75 meter, pure water depth is 0.75 meter. And, we can see without disturbing it if we can keep it for a longer period; we can calculate the salt concentration at top surface over here, will reach about 85 percent to its final value after 10 years.

And, this concentration will reach about 98 to 99 percent of its final value after 28 years. This signifies that the rate of diffusion is hindered by the effect of the barrier. Now, if we take you know an impeller arrangement and keep the same systems in place and rotate the impeller just about 20 rpm. So, this small revolution of the impeller into the system will lead to the complete uniformity in about 60 seconds. So, this implies that because of the external force the liquid which are over there and mixes well because of the eddy diffusion, which created by the impeller. And, that is why the rate of diffusion by eddy diffusion is much higher compared to the molecular diffusion.

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Now, we have to understand different concentration terms which we use for the calculation in the diffusion mass transfer. One of them is the concentration that can be represented in terms of the mass concentration. So, mass concentration is defined for a component i is rho i is equal to m i by V; m i is the mass of that component and V is the volume of that components. So, m i by V is the mass concentration.

The total mass concentration of for a particular mixture can be calculated, if you have n number of components then we can calculate by using this formula rho is equal to summation over i is equal to 1 to n rho i. The sum of all mass fractions we can calculate summation over i is equal to 1 to n W i is equal to summation over i is equal to 1 to n rho i by rho. So, this will give the total mass fractions. So, which will be essentially equal to 1. Mass fraction can calculated w i is equal to rho i divided by summation over i to n rho i which is equal to rho i by rho.

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The other way to represent the concentration is the molar concentration. The molar concentration of component i is defined as C i is equal to p i by RT; p i is the partial pressure of particular component, R is the universal gas constant and T is any temperature. Total molar concentration can be calculated using this equation C is equal to summation over i is equal to 1 to n C i. So, total molar concentration for ideal, if we consider ideal gas mixture, we can represent C is equal to 1 by RT summation over i is equal to 1 to n p i is equal to P t divided by RT. So, we can calculate using this relation.

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The mole fraction of a component i in the liquid phase or solid phase can be calculated x i which is equal to C i by C. And, then mole fractions of component i for gases is defined by y i which is equal to C i by C which is equal to concentration in the gas phase for a particular component divided by the total concentration.

The mole fractions of component i for ideal gas mixture can be represented by y i is equal to p i by p t where, p i is the partial pressure of component i and p t is the total pressure for in the system. So, some of the mole fractions in the liquid phase it will be summation over or in the solid phase is summation over *i* is equal to *i* summation over *i* x i equal to 1 and summation over i y i equal to 1.

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Let us take an example to calculate different concentration terms. The feed gas to an absorber has the following composition at 313 Kelvin and 200 kilo Pascal as given in the figure. So, the composition to an absorber this is the composition which is 90 percent methane, 5 percent ethane, 4 percent normal propene and 1 percent normal butane.

So, we need to calculate the composition of the feed gas in terms of the mass fraction and then total concentration in the feed gas.

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So, to calculate this let us take a basis of 100 kilo mole of feed gas mixture. So, then we can calculate out of 100 kilo mole we have 90 percent methane. So, 90 kilo mole and ethane is 5 kilo mole, propene is 4 kilo mole and butane is 1 kilo mole. So, total 100 kilo mole and we know their molecular weight and then we can calculate the mass of each components. And, then total mass which is calculated over here and then we can calculate mass by total mass, mass of individual components divided by total mass to calculate the mass fractions.

So, for methane it is 0.8, for ethane it is 0.08, for propene it is 0.09, for butane it is 0.03. So, total mole fraction is 1; total molar concentration we can calculate P t by RT. So, P t over here is 200 kilo Pascal as given in the problem and divided by RT. So, it is equal to 200 divided by R is 8.314 into 313 Kelvin. So, it will give around 0.077 kilo mole per meter cube. So, average molecular weight we can calculate the total mass of the component is 1824 and if we divide by 100 it will give because, that is our basis it is 100 kilo mole.

So, we will get 18.24 kg per k mole is the average molecular weight. Then we can calculate the total mass concentration which is rho is equal to C into average molecular weight. So, both we have calculated 0.077 kilo mole per meter cube and 18.24 kg per k mol. So, we will get 1.4 kg per meter cube is the total mass concentration.

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Let us take another examples: A liquid mixture contains 30 weight percent sodium nitrate and 70 weight percent water. The solution temperature is 300 Kelvin and the density of the solution is assumed to be 1050 kg per meter cube. Now, we need to calculate the composition in terms of the mole fraction and the total molar concentration, let us solve this.

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The basis for this let us consider 1 kg of the liquid mixture. So, we can calculate sodium nitrate is 0.3 kg because, it is 30 weight percent and water is 70 weight percent is 0.7 kg.

So, total mixture is 1 kg molecular weight of sodium nitrate is 85 and for water is 18. We can calculate the kilo mole of the each components that can be calculated mass by the molecular weight, we can get kilo mole of the components. The mole fractions can be calculated with the moles for each component divided by total mole which is for sodium nitrate is 0.8, for water is 0.92. So, total mole fractions is 1.

So, average molecular weight we can calculate over here 1 kg divided by total kilo mole, total kilo mole over here is total basis we have considered of the mixture is 1 kg divided by 0.0424 kilo mole. So, it will lead to 23.585 kg per k mole. The total molar concentration is rho by M average which is the density of the solutions is given 1050 kg per meter cube divided by 23.585 kg per k mole. So, the total molar concentration comes out to be 44.52 kilo mole per meter cube.

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Now, we have to understand the different diffusion velocities. The diffusion velocities are of two types: one of them is the mass average velocity. The mass average velocity is defined in terms of the mass concentration. So, if were consider mass average velocity V mass average which is equal to summation over i is equal to 1 to n rho i v i and divided by summation over i is equal to 1 to n rho i.

So, this is we can write summation over i is equal to 1 to n rho i by rho into v i and rho i by rho is equal to w i. So it will be equal to summation over i is equal to 1 to n rho i v i; v i is the absolute velocity of species i with respect to a fixed reference plane and w i is equal to mass fractions of species i.

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The molar average velocity is defined in terms of the molar concentration, as we have discussed before. The V mole average is the molar velocity which is equal to summation over i is equal to 1 to n C i into v i divided by summation over i is equal to 1 to n C i. So, it would be equal to summation over i is equal to 1 to n C i by C into v i. So, C i by C is the mole fractions. So, we can write summation over i is equal to 1 to $n \times i$ v i, where $x \in i$ is the mole fractions of species i.

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Let us take an example: A gas mixture containing hydrogen 15 percent, carbon monoxide 30 percent, carbon dioxide 5 percent and nitrogen 50 percent flows through a tube of 1 inch diameter, at 15 bar total pressure. If the velocity of the respective components are 0.05 meter per second, 0.03 meter per second, 0.02 meter per second and 0.03 meter per second then calculate the mass average and molar average velocities of the mixture.

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Solution of Example 1.3 Rename H₂:1, CO: 2, CO₂:3 and N₂: 4 The volume average velocity $(=$ molar average velocity) given by $V_{\text{mol-avg}} = \frac{1}{c} (C_1 v_1 + C_2 v_2 + C_3 v_3 + C_4 v_4) = y_1 v_1 + y_2 v_2 + y_3 v_3 + y_4 v_4$ Here y_1 is the mole fraction of component i in the gas mixture. Putting the values, we get $V_{\text{mol-avg}} = (0.15)(0.05) + (0.3)(0.03) + (0.05)(0.02) + (0.5)(0.03) = 0.0325 \frac{m}{s}$

Let us solve this. For the simplicity let us rename the component hydrogen 1, carbon monoxide 2, $CO₂$ 3 and nitrogen 4. The volume average velocity which can be related

with equal to the molar average velocity and is given by V mole average would be equal to 1 by total concentration into the concentration of component 1 into the velocity v 1 plus C 2 v 2 and plus C 3 v 3 plus C 4 v 4 which is equal to if we just divide by the total concentration; it will lead to y 1. The mole fractions of that components y 1 v 1 y plus y $2 \text{ v } 2 \text{ plus } \text{ v } 3 \text{ v } 3 \text{ and plus } \text{ v } 4 \text{ v } 4.$

So, y i is the mole fractions of mole fraction of component i in the gas mixture. Putting the values we get V mole average velocities. So, our velocity for each component are given and then their mole fractions are given in the problem. So, 0.15 into 0.05 plus 0.3 into 0.03 plus 0.05 into 0.02 0.5 into 0.03. So, which is equal to 0.0325 meter per second. So, this is molar average velocity.

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The mass average velocity is given by V mass average is equal to 1 by rho into rho 1 v 1 plus rho 2 v 2 plus rho 3 v 3 plus rho 4 v 4; rho i is equal to P i M i divided by RT and rho is equal to PM average divided by RT. So, rho i by rho is equal to P i by P into M i by M average which is equal to y i M i by M average. So, if we just see rho i is the mass density of the ith component, rho is the total mass density of the mixture, M i is the molecular weight of component i and M average is the average molecular weight of the mixture.

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Now, M average we can calculate y 1 M 1 plus y 2 M 2 plus y 3 M 3 plus y 4 M 4 using this relation. Now, if we substitute it would be equal to 0.15 into 2 plus 0.3 into 28 plus 0.05 into 44 plus 0.5 into 28; so, it is 24.9. V mass average we can calculate is equal to 1 by M summation over i is equal to 1 to n, here the n is the total number of component which is 4. So, n is equal to 4 y i M i v i.

So, this would be equal to 1 by M average y i M, this would be equal 1 by M average y 1 M 1 v 1 plus y 2 M 2 v 2 plus y 3 M 3 v 3 plus y 4 M 4 v 4. So now, if we substitute it will come around the mass average velocity would be 0.014 meter per second.

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Now, we will discuss the fluxes. The flux of a particular component 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 and flux may be calculated with respect to coordinates fixed in space or coordinates moving with the mass or molar average velocity.

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Fluxes • Mass Flux ❖ Calculated w.r.t coordinates fixed in space or Relative to stationary observer • Mass Flux: $N_{l \text{ mass}} = \rho_l v_l$ • Total Mass Flux: $N_{\text{mass}} = \rho V_{\text{mass_avg}}$ ❖ Calculated w.r.t mass average velocity or relative to an observer moving with the mass average velocity \triangleright Mass Flux: $J_{i-mass} = \int_{i}^{i} (v_i - V_{mass-avg})$

Let us consider mass flux. It is it can be calculated with respect to the coordinate fixed in space or relative to stationary observer. Mass flux is defined by N i mass is equal to rho i v i. So, the total mass flux can be calculated N mass is equal to rho into V mass average.

Now, you can calculate with respect to mass average velocity or relative to an observer moving with the mass average velocity. So, that is defined by mass flux in terms of J i mass is equal to rho i v i minus V mass average velocity.

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The molar flux of component for a particular component can be calculated with respect to the fixed phase or relative to stationary observer. It is calculated as molar flux N i mole is equal to C i v i or total molar flux N mole can be would be equal to C into V molar average velocity. This also can be calculated with respect to the average velocity or relative to an observer moving with the mass average velocity; that is J i mole would be equal to C i v i minus V molar average velocity.

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Now, we need to find out the relation between these two fluxes: one is N another is J, how they are related. The J i mass as you defined is equal to rho i v i minus V mass average. Now, N i mass is equal to rho i v i. So, if we substitute over here rho i v i, it would be N i mass by rho i minus rho i V mass average. If we just rearrange it, we can write N i mass would be equal to J i mass plus rho i V mass average and then we can write it is J i mass plus rho J i mass plus rho i by rho into N mass.

Similarly, in terms of the N i mole we can write J i mole plus C i V mole average which is equal to J i mole plus C i by C N mole. This actually we will use these two relations later in our discussion.

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Let us have some simple questions on the topic which we have covered today. Under what conditions are the mass average velocity and molar average velocity of the component of a mixture are equal. The answer is when the molecular weight of the components are same. If the molecular weight of the components are same, then they will give the both the mass average velocity and molar average velocity of the component of the mixture would be same.

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The next question is: What is the SI unit of molar flux? The molar flux can be, the SI unit of molar flux is kilo mole per meter square second.

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Identify the correct answer to the following; which of the following relation is correct for a gas mixture containing 40 percent carbon dioxide and 60 percent propene at 1 atmosphere and 30 degree centigrade. Option 1 is mass average velocity is greater than molar average velocity, mass average velocity is equal to molar average velocity. And, then third option is mass average velocity is less than molar average velocity. Under, if we look into the composition given in the mixture: one is carbon dioxide another is propene. And, if we look into the molecular weight of both the systems or the mass both for carbon dioxide and propene are 44.

So, since their mass is constant for both the components. So, answer would be V mass average would be equal to V mole average that is mass average velocity would be equal to the molar average velocity.

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Pick up the correct statement: molecular diffusion is caused by? Transfer of molecules from low concertation to high centration region. The second option is thermal energy of the molecules, third option is activation energy of the molecules and the fourth option is potential energy of the molecules. As we have discussed at the beginning the molecular diffusion is basically caused by the thermal motion of the molecules that is with thermal energy of the molecules. So, the correct answer for this is the thermal energy of the molecules.

Thank you very much for listening this lecture. And, in the next lecture we will start with the Fick's law of diffusion.