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

Diffusion Mass Transfer Lecture – 03 Fick's First and Second Law

Welcome to the third lecture on Mass Transfer Operation. Before going to the next lecture let us have small recap on our earlier lecture. In the last lecture we have discussed the molecular diffusion as well as eddy diffusion and the effect of different parameters on the rate of molecular diffusion.

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Recap Molecular Diffusion & Eddy Diffusion
/ Effect of barriers on molecular diffusion
/ Concentrations
/ Diffusion velocities / Fluxes

So, we have discussed molecular diffusion and Eddy diffusion. We have considered the effect of barriers on molecular Diffusion. Then we have discussed the different concentration terms which are used in the discussion of the diffusion mass transfer concentrations. We have discussed the diffusion velocities and we have discussed the fluxes and the relations between the different Fluxes. In this lecture we will discuss Fick's law of molecular diffusion.

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The Fick's who is Adolf Eugen Fick a German physiologist he has given a law for the diffusion of components and Fick's law is divided into two laws. One is Fick's first law and the second one is Fick's second law the Fick's first law defines the diffusion flux of a component A in an isothermal, isoberic binary system is proportional to the concentration gradient in a particular direction.

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So, we can consider a diffusion of component A only in x direction this can be represented by J A which is equal to minus D AB D CA dx here J A x is the molar flux of component A in the x direction. It has units of amount of material diffused per unit area per unit time. So, the amount of material which is diffused may be kg of material diffused or the kilo mole of material diffused per meter square area which is the cross sectional area and per unit time.

C A over here is the concentration terms which is concentration of a and the x is the distance of diffusion D AB over here is the diffusion coefficient or the diffusivity of component A in B. it is called binary diffusion coefficient of component A in B. The unit of diffusion coefficient is length square per time that is meter square per second. The negative term introduced over here is due to the diffusion occurs in decreasing concentrations. And in earlier lectures we have discussed the relation between J A and N A which is shown over here and we will consider this relation and we discuss the relation between the mutual diffusivities of component A and B.

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So, the questions over here is we need to show that for a binary mixture A and B the mutual diffusivities are same that is $D \cap A$ B is equal to $D \cap B$ A; how to solve it? So, we know that the relations between N A and J A. So, N A is equal to J A plus C A by N into N for gas mixture C A by C is equal to y A it is the mole fraction in the gas phase. So, we can write N A is equal to minus D A B D C A dx since J A is equal to minus D A B d C A dx.

So, we can write N A is equal to minus D A B d C A dx plus y A N. Now, if we differentiate this equations we can write $d C A d x$ would be equal to C into $d y a d x$. So, if we substitute d C a d x over here we will obtain minus C D A B d y A d x plus y a N.

> **Relation between Mutual Diffusivity of species A and B** $N_B = -CD_{BA} \frac{dy_B}{dx} + y_B N$ Similarly: Summing up the above two equations: $N_A + N_B$
= -CD_{AB} $\frac{dy_A}{dx} + y_A N - CD_{BA} \frac{dy_B}{dx} + y_B N$ $=-CD_{AB}\frac{dy_A}{dx} - CD_{BA}\frac{dy_B}{dx} + (y_A + y_B)N$ · Since for two component: $N_A + N_B = N$ $y_A + y_B = 1$ $rac{dy_A}{dx} + \frac{dy_B}{dx} = 0$ so, $\frac{dy_A}{dx} = -\frac{dy_B}{dx}$ $N = -CD_{AB} \frac{dy_A}{dx} + CD_{BA} \frac{dy_A}{dx} + 1 \times N$ $\rightarrow \rightarrow$ Hence, $D_{AB} = D_{BA}$ (proved)

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Similarly, for component B we can write N A B is equal to minus C D B A d y B a d x plus y BN. So, if we add this two equations N A and N B together we can get N A plus N B is equal to minus C D A B d y a d x plus y a N minus C D B A d y B d x plus y B N. Now, if we just rearrange these equations we can get minus C D A B d y a d x minus C D B A d y B d x plus y a plus y B into N as for two component mixture N A plus N B is equal to N its a total mole and y A plus y B is equal to one. The total mole fractions would be one for binary systems from here if we just differentiate this equation we will get d y A d x plus d y B d x is equal to 0. And we can write d y A d x would be equal to minus d y B d x. If we substitute this relations in the above relation we can get N A is equal to minus C D A B d y A d x plus C D B A d y A d x plus 1 into N. So, from here we can see that D A B is equal to D B A, that is the mutual diffusivity of component A and component B are same.

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Now, let us consider unsteady state diffusion in this case let us consider at point M which is x y z and point N which is y plus delta x y plus delta y and z plus delta z. Now the change of concentration of a component of the diffusive constituents in a mixture over a time is unsteady state of diffusion.

The balance equations if we write for these is in plus generation is equal to out plus accumulation, the mass flow rate of component a in to this to the point at x y and z. We can write M A into N A x at point x delta y delta x plus N A y at x delta x delta z plus N A z at x delta x delta y where N A x is the flux in the x direction N A x at x is the value of flux at location x and M A is the molecular weight of component A.

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Generation of A by chemical reactions we can write let the rate of reactions is equal to R A which is mole per unit volume into time. Now rate of generation or production would be equal to M A R A into delta x delta y and delta z. R A is the rate of reactions M A is the molecular weight of the component A.

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So, the mass flow rate out we can write M A N A x at x plus delta x into delta y delta z. The rate of flow out can be written as M A N A x at x plus delta x delta y delta z plus N A y at x plus delta x into delta x delta z plus N A z at x plus delta x into delta x delta y the

rate of accumulation is delta x delta y delta z into del rho a del t rho a is the density of component A.

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Now, we can write in the balanced equation in plus generation is equal to out plus accumulation. So, if we substitute it would be M A N A x at x delta y delta z plus N A y at x delta x delta z N A z at x delta x delta y plus M A R A delta x delta y delta z. Which would be equal to M A N A x at x plus delta x into delta y delta z plus N A y at x plus delta x into delta x delta z plus N A z at x plus delta x delta x delta y plus delta x delta y delta z into del rho a del t.

Now, from this we can write M A into N A x at x plus delta x minus N A x at x into delta y delta z plus N A y at x plus delta x minus N A y at x into delta x delta z plus N A z at x plus delta x minus N A z at x into delta x delta y plus delta x delta y delta z into del rho a del t which would be equal to M A R A into delta x delta y and into delta z. Now, if we divide both sides by delta x into delta y into delta z and taking the limit delta x tends to 0 delta y tends to 0 and delta z tends to 0.

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We will get for component a M A del N A del x plus del N A y del y plus del N A z del z plus del rho a del t is equal to M A R A. Now for component B it will be M B del B x del x plus del B y del y plus del B z del z plus del rho B del t is equal to M B R B.

Now, if we add these two relations we will get M A R A plus M B R B would be equal to del M A N A plus M B N B at x del x plus del M A N A plus del N B M B N B at y del y plus del M A N A plus M B N B at z del z plus del rho A plus rho B del t.

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Now, del M A N A plus del plus M B N B x del x plus del M A N A plus del M B N B y del y plus del M A N A plus del M B N B. Now, the right hand side terms would be equal to 0 because where rho is equal to rho A plus rho B is equal to the solution density and M A R A plus M B R B would be equal to 0. Since mass rate of generation of A and B must equal 0, that is why if we substitute this in the earlier equations. So, the right hand side term would be equal to 0.

Now, V x we know is equal t rho A V A x plus rho B V B x divide by rho A plus rho B. Where V x is the mass average velocity and small $v A v A x$ is the absolute velocity. Now, if we just rho A plus rho B is the density. Now if we multiply it with the left hand side it will be rho V x is equal to rho A V A x plus rho V V B x. So, now, rho V x would be equal to if we substitute rho a with the molecular weight and the concentration it is M A C A V A x plus M B C B V B x. So, it will be M A N A x plus M B N B x the N A x or N B x is the molar flux of component A and B.

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Now, from the earlier equations we can write del M A N A plus M B N B x del x would be equal to rho del V x del x plus V x del rho del x. Substituting this equation d into the equation c we obtain the following relations. This is the equation of continuity or a mass balance for a total substance. If the solution density is constant from equation e we can write the rho del V x del x plus del V y del y plus del V z del z is equal to 0. And then from there we can write del V x del x plus del V y del y plus del V z del z is equal to 0.

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We know that in terms of mass flux and in the x direction N A x is equal to N x A plus J A x. Now, if we multiply both sides with the molecular weight of the components it is M A N A x is equal to M A N x A plus M A J A x. So, from there we can write M A N A x would be equal to M A C V x into C A by C plus M A J A x. So, if we rearrange M A N A x would be equal to rho a V x plus M A J A x .

And hence if we differentiate this equations it would be M A del N A x del x plus V x del rho a del x plus rho a del V a del x plus M A del J A x del x. Now, if we substitute in place of J A x which is minus D A B del D C A D x. Then this relations would be equal to V x del rho a del x plus rho A del V x del x minus M A D A B del 2 C A del x 2.

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From there we can write the equations for component a M A del N A x del x plus del N A y del y plus del N A z del z plus del rho A del t would be equal to M A R A, this is equation 1. This equation will reduce to this equation V x del rho a del x plus V y del rho a del y plus V z del rho A del z plus rho A into del V x del x plus del V y del y plus del V z del z minus M A D A B del 2 C A del x 2 plus del 2 C A del y 2 plus del 2 C A del x 2 plus del rho A del t which would be equal to M A R A.

Where rho is constant and using equation f and dividing M A in equation g we obtain what is the equation f that is del V x del x plus del V y del y plus del V z del z is equal to 0. So, if we substitute over here this would be equal to 0. And we will obtain V x del C A del x plus V y del C A del y plus V z del C A del z plus del C A del t would be equal to D A B del 2 C A del x 2 plus del 2 C A del y 2 plus del 2 C A del z 2 plus R A.

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In the special case where velocity equals to 0 and there is no chemical reactions from equation h we can write del C A del theta would be equal to D A B del 2 C A del x 2 plus del 2 C A del y 2 plus del 2 C A del z 2, here t is equal to theta. So, this equation is known as the Fick's second law equation and this is frequently applicable to diffusion in solids and to limited situations in fluid.

So thank you for listening this lecture and we will discuss in the next lecture on the different applications of diffusion mass transfer.

Thank you.