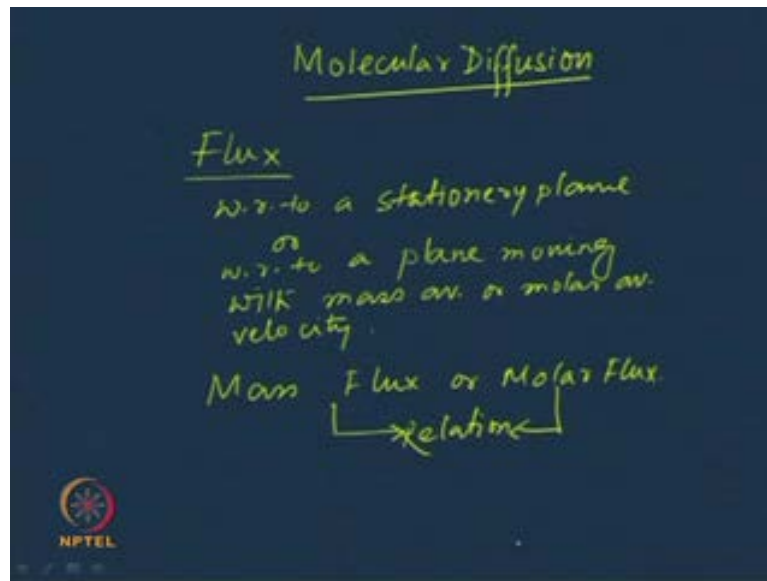


Mass Transfer Operations-I
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Module - 1
Diffusion Mass Transfer
Lecture - 3
Fick's law of Diffusion

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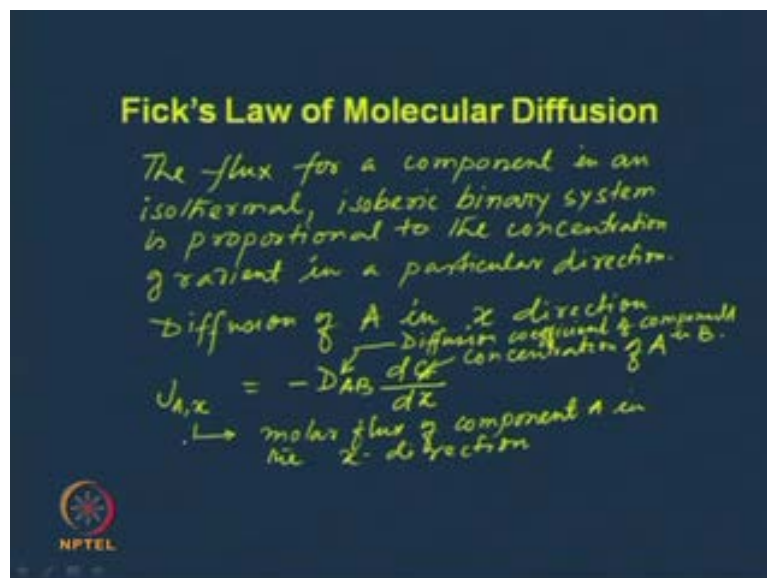


Welcome to the third lecture on mass transfer operation; the third lecture will be on the Fick's law of diffusion under steady state and unsteady state conditions. So before going to the third lecture, let us have a small recap on the last lecture we have; the last lecture was on molecular diffusion. Here, we have seen that the molecular diffusion is much slower compare to the eddy diffusion or turbulent diffusion, and we have seen that the effect of barrier on the molecular diffusion is very important, if we put some stagnant layer on the water surface, it reduces the diffusion by around 600 times. Then we have seen the concentration gradient is very important for the mass transfer for a single phase, and in that case the concentrations are defined in various ways. So, we have seen how the concentration is defined in terms of the mass concentration and in terms of the molar concentration. And we have also seen how to calculate these concentrations for a particular system; we have solved few examples on it.

Then we have seen the molecular velocities or the diffusion velocities is important for the mass transfer or diffusion, we have seen there are two types of velocities - one is mass average velocities, another one is molar average velocities; and how to define that and how to calculate for a particular systems that we have discussed. We have also discussed the fluxes; flux and we have seen that the flux maybe defined with respect to a stationary plane with respect to a stationary plane or with respect to a plane moving with mass average or molar average velocities.

So, depending on that it can be defined as the mass flux or molar flux, mass flux or molar flux, then we have seen the relations between, between the mass average and molar average velocity. And then we had questions and discussion sections at the end.

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Today we will discuss on the Fick's first law, and Fick's law of molecular diffusion says that flux for a component in an isothermal isobaric binary system, binary system is proportional proportional to the concentration gradient in a particular direction. So, if we consider diffusion of A in x direction we can write the flux of A $J_{A,x}$ is equal to minus $D_{AB} \frac{dC_A}{dx}$, where $J_{A,x}$ is the molar flux of component A in the x direction, C_A is the concentration of A, and D_{AB} is the diffusion coefficient diffusion coefficient or diffusivity of component A in B.

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**Relation between Mutual Diffusivity
of species A and B**


$$N_A = J_A + \frac{C_A}{C} N \rightarrow (1)$$

For gas mixtures

$$\frac{C_A}{C} = y_A$$

$$J_A = -D_{AB} \frac{dc_A}{dx} + y_A N = -C D_{AB} \frac{dy_A}{dx} + y_A N \rightarrow (2)$$

Similarly,

$$J_B = -C D_{BA} \frac{dy_B}{dx} + y_B N \rightarrow (3)$$



So, we can relate between flux as per the Fick's law of molecular diffusion, if there are two species A and B; and they are diffusing both the ways in that case we can derive a relation between their mutual diffusivities of component A and B. So, for a binary mixture if we consider the flux N_A we can write is J_A plus $\frac{C_A}{C}$ into N , and for gas mixtures we can write $\frac{C_A}{C}$ is equal to y_A . So, this is equation one and we know that from this we can write N_A is equal to J_A we know, $-D_{AB} \frac{dc_A}{dx}$ plus $y_A N$. So, this we can again write is equal to minus $C D_{AB} \frac{dy_A}{dx}$ plus $y_A N$, this is equation 2. Similarly, we can write N_B is equal to minus $C D_{BA} \frac{dy_B}{dx}$ plus $y_B N$; N is the total flux. So, if we sum between N_A and N_B , so N_A is this and N_B is this, if we sum between N_A and N_B .

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Relation between Mutual Diffusivity of species A and B

$$N_A + N_B = -C D_{AB} \frac{dy_A}{dx} + y_A N - C D_{BA} \frac{dy_B}{dx} + y_B N$$
$$= -C D_{AB} \frac{dy_A}{dx} - C D_{BA} \frac{dy_B}{dx} + (y_A + y_B) N$$

We know

$$N_A + N_B = N$$
$$y_A + y_B = 1 \Rightarrow \frac{dy_A}{dx} + \frac{dy_B}{dx} = 0$$
$$\Rightarrow \frac{dy_A}{dx} = -\frac{dy_B}{dx}$$


So, we can write $N_A + N_B$ is equal to minus $C D_{AB} \frac{dy_A}{dx}$ plus $y_A N$ minus $C D_{BA} \frac{dy_B}{dx}$ plus $y_B N$. So, we can write minus $C D_{AB} \frac{dy_A}{dx}$ minus $C D_{BA} \frac{dy_B}{dx}$ plus $y_A + y_B$ into N . So, this is equation number 4.


We know that $N_A + N_B$ is N , and $y_A + y_B$ is equal to 1. So, from this if we differentiate, so it will be $\frac{dy_A}{dx} + \frac{dy_B}{dx}$ is equal to 0. So, it will lead to $\frac{dy_A}{dx}$ will be equal to minus $\frac{dy_B}{dx}$. Now, if we substitute this $\frac{dy_A}{dx}$ is equal to minus $\frac{dy_B}{dx}$ over here, and then $y_A + y_B$ is equal to 1 over here and $\frac{dy_A}{dx}$ is equal to minus $\frac{dy_B}{dx}$.

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Relation between Mutual Diffusivity of species A and B

$$N = -C D_{AB} \frac{dy_A}{dx} + C D_{BA} \frac{dy_A}{dx} + 1 \times N \quad \rightarrow (5)$$

$$D_{AB} = D_{BA}$$



So, it will give you N is equal to minus $C D_{AB} \frac{dy_A}{dx}$ plus $C D_{BA} \frac{dy_A}{dx}$ plus $1 \times N$. So, this is equation number 5, and in this N will be cancelled out, hence we can write this also we will cancel out and we will have D_{AB} is equal to D_{BA} . So, we conclude that the mutual diffusivities between A and B; that is D_{AB} and D_{BA} are same.

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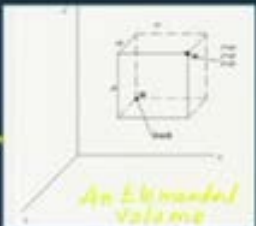
Unsteady State Diffusion

Balance Eqn:
 In + Generation = Out + Accumulation


Mass Flow rate of component A in

$$M_A [N_{A,x}|_{x_1} \Delta y \Delta z + N_{A,y}|_{x_2} \Delta x \Delta z + N_{A,z}|_{x_3} \Delta x \Delta y]$$

$N_{A,x}$ = flux in the x-direction
 $N_{A,y}|_{x_2}$ = value of flux at location x_2
 M_A = molecular wt. of component A.



An Elemental Volume



So, now we will move to unsteady state diffusion; the unsteady diffusion it is defined as the change of the concentration of a particular component in the mixture over the time.

So, that is unsteady state diffusion. We will try to derive the unsteady state diffusion equation, and which is the Fick's second law of diffusion. Let us consider the control volume and elemental volume, and the balance equations are in plus generation is equal to out plus accumulation. So, mass flow rate of component A mass flow rate of component A in at location m we can write M_A into $N_A x$ at x delta y delta z plus $N_A y$ at x delta x delta z plus $N_A z$ at x delta x delta y . So, this is the mass flow rate of component A in at location x . So, $N_A x$ flux in the x direction, and $N_A x$ at x is equal to value of flux at location x , and M_A molecular weight molecular weight of component A. Now, if we do the rate of generation or production of component A by chemical reaction.

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Unsteady State Diffusion

Rate of Generation or Production
 $= M_A R_A \delta x \delta y \delta z \rightarrow (2)$

$R_A = \text{Rate of reaction in } \left(\frac{\text{mol}}{\text{Vol} \times \text{time}}\right)$

Mass rate of flow out
 $M_A \left[N_{Ax} \Big|_{x+\delta x} \delta y \delta z + N_{Ay} \Big|_{x+\delta x} \delta x \delta z + N_{Az} \Big|_{x+\delta x} \delta x \delta y \right] \rightarrow (3)$

Rate of accumulation
 $= \delta x \delta y \delta z \frac{dC_A}{dt} \rightarrow (4)$

NPTEL

We can write rate of generation or production, this will be equal to molecular weight into rate of reaction into the control volume delta x delta y delta z . So, R_A is equal to rate of reaction and its unit will be mole per volume into time, and the rate of mass flow rate out we can write mass rate of flow out. So, let us say out will be... So, at location N , what is the mass flow rate out, that is at distance x plus delta x y plus delta y and z plus delta z . Similarly, the equations remain similar, but at location N . So, for this control volume the mass rate out, we can write M_A into $N_A x$ at x plus delta x delta y delta z plus $N_A y$ x plus delta x will be delta x delta z plus $N_A z$ at x plus delta x will be delta y delta x .

So, this is the mass flow rate out, and then another term is the accumulation. So, rate of accumulation, rate of accumulation we can write will be equal to delta x delta y delta z; this is the volume into d rho A dt. So, now if we just write the equation number equation number 1, so equation number 2, this is 3, and this is 4.

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Unsteady State Diffusion

$$\begin{aligned}
 & \text{In} + \text{Generation} = \text{Out} + \text{Accumulation} \\
 & M_A [N_{A,x}|_x \Delta y \Delta z + N_{A,y}|_y \Delta x \Delta z + N_{A,z}|_z \Delta x \Delta y] \\
 & + M_A R_A \Delta x \Delta y \Delta z \\
 & = M_A [N_{A,x}|_{x+\Delta x} \Delta y \Delta z + N_{A,y}|_{y+\Delta y} \Delta x \Delta z + N_{A,z}|_{z+\Delta z} \Delta x \Delta y] \\
 & + \Delta x \Delta y \Delta z \frac{\partial \rho_A}{\partial t} \quad \text{--- (5)} \\
 \Rightarrow & M_A [(N_{A,x}|_{x+\Delta x} - N_{A,x}|_x) \Delta y \Delta z + (N_{A,y}|_{y+\Delta y} - N_{A,y}|_y) \Delta x \Delta z \\
 & + (N_{A,z}|_{z+\Delta z} - N_{A,z}|_z) \Delta x \Delta y] \\
 & + \Delta x \Delta y \Delta z \frac{\partial \rho_A}{\partial t} = M_A R_A \Delta x \Delta y \Delta z \rightarrow
 \end{aligned}$$

If we substitute this 4 equations in the balance equations original balance equation. So we can write the original balance equation was in plus generation is equal to out plus accumulation, now if we substitute it will be M A at N A x at x delta y delta z plus N A y at x delta x delta z plus N A z at x delta x delta y, this is mass flow rate in plus generation is M A R A delta x delta y delta z. So, this is generation and then out will be M A N A x at x plus delta x delta y delta z plus N A y at x plus delta x delta x delta z plus N A z at x plus delta x delta x delta y. So, this is the mass flow rate out plus accumulation; the accumulation term is delta x delta y delta z into del rho A - rho A is the density of component A del t.

So, this is the equation number 5, and if we just rearrange these equation 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, we can write delta x delta z plus N A z at x plus delta x minus N A z at x multiplied by delta x delta y. So, this is first term and then we can write plus delta x delta y del z del rho A del t is equal to M A R A delta x delta y delta z. So, this is equation number 6.

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Unsteady State Diffusion

$\Delta x \rightarrow 0, \Delta y \rightarrow 0, \Delta z \rightarrow 0$
 $\Delta x \Delta y \Delta z$ both sides

For component A

$$M_A \left(\frac{\partial N_{A,x}}{\partial x} + \frac{\partial N_{A,y}}{\partial y} + \frac{\partial N_{A,z}}{\partial z} \right) + \frac{\partial \rho_A}{\partial t} = M_A R_A \quad (7.1)$$

For component B

$$M_B \left(\frac{\partial N_{B,x}}{\partial x} + \frac{\partial N_{B,y}}{\partial y} + \frac{\partial N_{B,z}}{\partial z} \right) + \frac{\partial \rho_B}{\partial t} = M_B R_B \quad (7.2)$$


Now, if we take limit Δx tends to 0, Δy tends to 0 and Δz tends to 0, then divide by $\Delta x \Delta y \Delta z$ both sides of the previous equation 6 both sides, then for component A - component A we can write M_A into $\Delta N_A x \Delta x$ plus $\Delta N_A y \Delta y$ plus $\Delta N_A z \Delta z$ plus $\Delta \rho_A \Delta t$ is equal to $M_A R_A$. So, this is equation number 7.1. So, similarly for component; component B we can write $M_B \Delta N_B x \Delta x$ plus $\Delta N_B y \Delta y$ plus $\Delta N_B z \Delta z$ plus $\Delta \rho_B \Delta t$ is equal to $M_B R_B$. So, this is equation 7.2; so if we at equation 7.1 and 7.2.

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Unsteady State Diffusion

Adding eqns (7.1) & (7.2)

$$\frac{\partial (M_A N_A + M_B N_B)_x}{\partial x} + \frac{\partial (M_A N_A + M_B N_B)_y}{\partial y} + \frac{\partial (M_A N_A + M_B N_B)_z}{\partial z} + \frac{\partial (\rho_A + \rho_B)}{\partial t} = M_A R_A + M_B R_B \quad (7.3)$$

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

$$M_A R_A + M_B R_B = 0$$

$$\frac{\partial (M_A N_A + M_B N_B)_x}{\partial x} + \frac{\partial (M_A N_A + M_B N_B)_y}{\partial y} + \frac{\partial (M_A N_A + M_B N_B)_z}{\partial z} + \frac{\partial \rho}{\partial t} = 0 \quad \rightarrow$$


We can write 7.1 and 7.1, we have $\frac{d}{dt} (M_A N_A + M_B N_B)$ at x will be $\frac{d}{dt} (\rho_A + \rho_B)$ at x plus $\frac{d}{dt} (M_A N_A + M_B N_B)$ at y $\frac{d}{dt} y$ plus $\frac{d}{dt} (M_A N_A + M_B N_B)$ at z $\frac{d}{dt} z$ plus $\frac{d}{dt} (\rho_A + \rho_B)$ will be equal to $M_A R_A + M_B R_B$. We know that $\rho_A + \rho_B$ will be equal to ρ a solution density, and $M_A R_A + M_B R_B$ is equal to 0, because the mass rate of generation of A and B, mass B equal to 0. So, in that if we substitute these two in this equation - equation number 7.3, we will have $\frac{d}{dt} (M_A N_A + M_B N_B)$ at x $\frac{d}{dt} x$ plus $\frac{d}{dt} (M_A N_A + M_B N_B)$ at y $\frac{d}{dt} y$ plus $\frac{d}{dt} (M_A N_A + M_B N_B)$ at z $\frac{d}{dt} z$ plus $\frac{d}{dt} (\rho)$ is equal to 0. So, this is equation number 8.

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Unsteady State Diffusion

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

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

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

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

↑ molar flux

$V_x =$ mass average velocity
 $v_{Ax} =$ Absolute velocity of component A

NPTEL

Now, we know that the mass average velocity is $V_x = \frac{\rho_A v_{Ax} + \rho_B v_{Bx}}{\rho_A + \rho_B}$. So, we can write ρ_A and ρ_B , this is equal to ρ , so the mass average velocity V_x will be equal to $\frac{\rho_A v_{Ax} + \rho_B v_{Bx}}{\rho}$, and ρ_A we can write $M_A C_A$ and then v_{Ax} plus $M_B C_B v_{Bx}$ this will be equal to $M_A N_{Ax}$ plus $M_B N_{Bx}$. N_A or N_B ; these are the molar flux, V_x is the mass average velocity, and small v_{Ax} is the absolute velocity of component A, absolute velocity of component A.

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Unsteady State Diffusion

$$\frac{\partial (M_A N_A + M_B N_B)_x}{\partial x} = \rho \frac{\partial V_x}{\partial x} + V_x \frac{\partial \rho}{\partial x} \rightarrow (9)$$

Substitute eqn (9) in eqn (8)

$$\rho \left(\frac{\partial V_x}{\partial x} + \frac{\partial V_y}{\partial y} + \frac{\partial V_z}{\partial z} \right) + \left(V_x \frac{\partial \rho}{\partial x} + V_y \frac{\partial \rho}{\partial y} + V_z \frac{\partial \rho}{\partial z} \right) + \frac{\partial \rho}{\partial t} = 0 \rightarrow (10)$$

Continuity eqn or mass balance for total substance

$$\frac{\partial V_x}{\partial x} + \frac{\partial V_y}{\partial y} + \frac{\partial V_z}{\partial z} = 0 \rightarrow (11)$$


So, then from this we can write $\frac{\partial (M_A N_A + M_B N_B)_x}{\partial x}$ will be equal to $\rho \frac{\partial V_x}{\partial x} + V_x \frac{\partial \rho}{\partial x}$. So, this is equation number 9. Now, if we substitute equation 9 in equation 8, the equation $\rho \frac{\partial V_x}{\partial x} + \rho \frac{\partial V_y}{\partial y} + \rho \frac{\partial V_z}{\partial z} + V_x \frac{\partial \rho}{\partial x} + V_y \frac{\partial \rho}{\partial y} + V_z \frac{\partial \rho}{\partial z} + \frac{\partial \rho}{\partial t}$ is equal to 0, so equation number 10. So, this is the continuity equation, continuity equation or mass balance, balance for total substance. Now, if the solution density ρ is constant if this is constant, so this part will be 0, and this will be 0; in that case, we can write $\frac{\partial V_x}{\partial x} + \frac{\partial V_y}{\partial y} + \frac{\partial V_z}{\partial z} = 0$. So, equation number 11.

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Unsteady State Diffusion

$$N_{A,x} = N x_A + J_{A,x}$$


$$M_A N_{A,x} = M_A N x_A + M_A J_{A,x}$$

$$= M_A C V_x \frac{C_A}{C} + M_A J_{A,x}$$

$$= \rho_A V_x + M_A J_{A,x} \quad \text{---(12)}$$

Taking derivative

$$M_A \frac{\partial N_{A,x}}{\partial x} = V_x \frac{\partial \rho_A}{\partial x} + \rho_A \frac{\partial V_x}{\partial x} + M_A \frac{\partial J_{A,x}}{\partial x}$$

$$= V_x \frac{\partial \rho_A}{\partial x} + \rho_A \frac{\partial V_x}{\partial x} - M_A D_{AB} \frac{\partial^2 C_A}{\partial x^2} \quad \text{---(13)}$$



Now, we know that the flux $N_A x$ is related with total flux into the mole fraction or mass fraction plus $J_A x$. So, if we multiply both sides by molecular weight we can write $M_A N_A x$ will be equal to $M_A N x_A$ plus $M_A J_A x$, from this we can write $M_A C$ into V_x into C_A by C plus $M_A J_A x$. So, this will be equal to $\rho_A V_x$ plus $M_A J_A x$, if we take the derivative of this equation. So, suppose this is equation number twelve, we take derivative, so then we can write $M_A \frac{\partial N_A x}{\partial x}$ will be equal to $V_x \frac{\partial \rho_A}{\partial x}$ plus $\rho_A \frac{\partial V_x}{\partial x}$ plus $M_A \frac{\partial J_A x}{\partial x}$. So, we can write this will be equal to $V_x \frac{\partial \rho_A}{\partial x}$ plus $\rho_A \frac{\partial V_x}{\partial x}$ minus $M_A D_{AB} \frac{\partial^2 C_A}{\partial x^2}$, then if we substitute this equation in equation number 7.1.

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Unsteady State Diffusion

$$V_x \frac{\partial C_A}{\partial x} + V_y \frac{\partial C_A}{\partial y} + V_z \frac{\partial C_A}{\partial z} + \rho \left(\frac{\partial V_x}{\partial x} + \frac{\partial V_y}{\partial y} + \frac{\partial V_z}{\partial z} \right) - M_A D_{AB} \left(\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right) + \frac{\partial C_A}{\partial t} = M_A R_A \quad \rightarrow (14)$$

$\rho = \text{constant}$, divide by $M_A \rho$
eqn. (14)

$$V_x \frac{\partial C_A}{\partial x} + V_y \frac{\partial C_A}{\partial y} + V_z \frac{\partial C_A}{\partial z} + \frac{\partial C_A}{\partial t} - D_{AB} \left(\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right) + R_A = 0 \quad (15)$$


Then we will have the final form $V_x \frac{\partial C_A}{\partial x} + V_y \frac{\partial C_A}{\partial y} + V_z \frac{\partial C_A}{\partial z} + \frac{\partial C_A}{\partial t} - D_{AB} \left(\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right) + R_A = 0$, this is equation number 14.

Now, when ρ is constant constant, and using equation 11, so in this case, if we divide divide by M_A to equation 14, we have $V_x \frac{\partial C_A}{\partial x} + V_y \frac{\partial C_A}{\partial y} + V_z \frac{\partial C_A}{\partial z} + \frac{\partial C_A}{\partial t} - D_{AB} \left(\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right) + R_A = 0$. So, this is equation number 15.

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Unsteady State Diffusion

Special case
velocity = 0
no chemical rxn
eq. (15)

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

This is Fick's 2nd Law of Diffusion (16)

Applicable to Diffusion in solids and limited cases in fluids.

NPTEL

So, if we consider a special case, when velocity is equal to 0 and no chemical reaction. So, in that case the equation 15, we can write $\frac{\partial C_A}{\partial t}$ will be equal to $D_{AB} \left(\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right)$. So, this is equation number 16, and this is Fick's second law of diffusion, this is Fick's second law of diffusion. So, this is mainly applicable for diffusion in solids diffusion in solids, and limited cases, cases in fluids. So, this is end of lecture three of module one, and the next lecture, we will start with steady state molecular diffusion.

Thank you.